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Development of Catalysts for Green Chemistry Transformations

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Abstract

The development of new ligands is crucial to the discovery of effective catalysts for homogeneous reactions. By synthesising ligands with new donor groups and then coordinating these ligands to appropriate metal centres, new complexes may be developed for the catalysis of specific reactions. In this thesis, investigations into the synthesis of a new macrocyclic ligand that contains pyridinium amides as the primary donor groups are reported. Studies of the spectroscopic, structural, and catalytic properties of various transition metal complexes of this new ligand are also reported. Although the first pyridinium amide was synthesised over a century ago, the coordination chemistry of pyridinium amides has only recently been investigated. While some of these complexes have been shown to be effective catalysts for a number of reactions, catalysis by these complexes remains relatively little explored.

The structure of the target macrocyclic pyridinium amide ligand, H₂Lₘ ((5E,18aE)-8,12,12,16-tetramethyl-8,10,14,16-tetrahydro-11H-benzo[e]dipyrido[3,4-b:4’,3’-h][1,4,7,10]tetraazacyclotridecine-11,13(12H)-dione), is related to the structure of tetraamido macrocyclic ligands (TAMLs), porphyrins, and dibenzotetramethyltetraaza[14]annulenes (TMTAAs). Like these ligands, the Lₘ²⁻ ligand is expected to donate strongly to metal centres. While it has been shown that metal complexes of TAML, porphyrin, and TMTAA ligands are effective catalysts for oxidation reactions and for small molecule activation reactions, metal-pyridinium amide complexes have not been investigated as catalysts for these reactions. Consequently, metal complexes of the Lₘ²⁻ ligand were studied in this thesis as potential catalysts for the oxidation of dye substrates by hydrogen peroxide and as potential catalysts for the activation of small molecules (such as dihydrogen, carbon monoxide, and acetylene) to produce organic products.

Upon deprotonation, H₂Lₘ was found to coordinate to a number of transition metals to give complexes that include Fe₃⁺(Lₘ)Cl, Co₃⁺(Lₘ)Br, Ni₃⁺(Lₘ), Pd₃⁺(Lₘ), [Ru₃⁺(Lₘ)₂][BF₄]₂, and Na[[Rh₃⁺(Lₘ)₂]Cl], which were all fully characterised. The data obtained strongly indicates that [Ru₃⁺(Lₘ)₂][BF₄]₂ and Na[[Rh₃⁺(Lₘ)₂]Cl] have direct unsupported metal-metal bonds. A paramagnetic copper complex tentatively formulated as Cu₃⁺(Lₘ)(OH)(H₂O) was also obtained. The complexes Fe₃⁺(Lₘ)Cl and Co₃⁺(Lₘ)Br were paramagnetic, whereas Ni₃⁺(Lₘ), Pd₃⁺(Lₘ), [Ru₃⁺(Lₘ)₂][BF₄]₂, and Na[[Rh₃⁺(Lₘ)₂]Cl] were diamagnetic. The diamagnetic nature of the
latter two complexes could be explained on the basis of simplified orbital diagrams for the metal-metal bonding in these complexes.

An acyclic pyridinium amide ligand, \( \text{H}_2\text{La} \) \((N^1,N^2\text{-bis}(1\text{-methyl-2-}(\text{p-tolylimino})-1,2\text{-dihydropyridin-3-yl})\text{oxalamide})\), was also synthesised and was coordinated to palladium, iron and cobalt. Although the palladium complex, \( \text{Pd}^{\text{II}}(\text{La}) \), was fully characterised, high resolution mass spectrometry suggested that a mixture of iron(III) products and cobalt(III) products was formed in the reaction of \( \text{H}_2\text{La} \) with iron(II) and cobalt(II) salts, respectively. These mixtures were not successfully separated. The high resolution positive ion mass spectra of these products agreed with formulations of \( [(\text{M}^{\text{III}})_{n}(\text{La})_{n+1} + x\text{H}^+]^{(n+x-2)+} \), where \( n = 1 \) to 4 and \( x = 1 \) to 4.

\( \text{Fe}^{\text{III}}(\text{L}_m)\text{Cl} \) and \( \text{Co}^{\text{III}}(\text{L}_m)\text{Br} \) were selected for study as potential catalysts for dye oxidation reactions with hydrogen peroxide because it has been shown that related \( \text{Fe}^{\text{III}}\)-TAML and \( \text{Co}^{\text{III}}\)-TAML complexes are highly effective catalysts for this reaction. Since Orange II dye has been widely used as a substrate in these types of studies, the ability of \( \text{Fe}^{\text{III}}(\text{L}_m)\text{Cl} \) and \( \text{Co}^{\text{III}}(\text{L}_m)\text{Br} \) to behave as oxidation catalysts was determined by monitoring the decolourisation of Orange II dye in the presence of hydrogen peroxide using time-dependent UV-visible absorption spectroscopy. The initial rate of dye oxidation was obtained from these spectra and by varying the reaction conditions, reaction kinetics could be estimated. The typical conditions used in these experiments were: 25 °C, 0.25-10 \( \mu \text{mol} \text{L}^{-1} \) \( \text{Fe}^{\text{III}}(\text{L}_m)\text{Cl} \) or \( \text{Co}^{\text{III}}(\text{L}_m)\text{Br} \), 45 \( \mu \text{mol} \text{L}^{-1} \) Orange II dye, and 0.25-10 mmol L\(^{-1}\) hydrogen peroxide in pH 7.5-10.8 aqueous solutions containing 0.01 mol L\(^{-1}\) carbonate or phosphate buffers. However, even when the ratio of the concentrations of the catalyst to the Orange II dye was relatively high (up to 1:4.5), no significantly acceleration of dye bleaching was observed compared to the blank with no metal compound present. This indicates that \( \text{Fe}^{\text{III}}(\text{L}_m)\text{Cl} \) and \( \text{Co}^{\text{III}}(\text{L}_m)\text{Br} \) are very poor oxidation catalysts under these conditions. In contrast, both of these complexes were found to catalyse the disproportionation of hydrogen peroxide to water and dioxygen.

\( \text{Na}[[\text{Rh}^{\text{II}}(\text{L}_m)]_2\text{Cl}] \) was investigated as a catalyst for the activation of small molecules, because it has been reported that related rhodium(II)-porphyrin and rhodium(II)-TMTAA dimers react in interesting ways with a wide range of small molecules, such as carbon monoxide, dihydrogen, acetylene, alkyl halides, and triarylphosphines. \( \text{Na}[[\text{Rh}^{\text{II}}(\text{L}_m)]_2\text{Cl}] \) and selected derivatives of this compound were found to react stoichiometrically but not catalytically with most of these
molecules. A number of organometallic and coordination complexes were synthesised and characterised through these reactions including Na[[Rh^{II}(L_m)]_2(Cl)(pyridine)], Na[[Rh^{II}(L_m)]_2(Cl)(4-picoline)], [Rh^{III}(L_m)(PPh_3)][PF_6], Na[Rh^{I}(L_m)], Rh^{III}(L_m)Me, Rh^{III}(L_m)Et, Rh^{III}(L_m)Bn, Rh^{III}(L_m)(C(=O)OR), and Rh^{III}(L_m)(CH=CHOR). The OR groups of the latter two complexes depended on the alcohol solvent used for the reaction.

Reactivity studies were investigated to obtain some information about possible reaction pathways for the syntheses of [Rh^{III}(L_m)(PPh_3)]^+, Rh^{III}(L_m)(C(=O)OR), and Rh^{III}(L_m)(CH=CHOR) from the reaction between Na[[Rh^{II}(L_m)]_2Cl] and triphenylphosphine, carbon monoxide, or acetylene, respectively, in alcohol solvents under aerobic conditions. From these studies, it was postulated that coordination of the reagent (triphenylphosphine, carbon monoxide, or acetylene) to Na[[Rh^{II}(L_m)]_2Cl] facilitates heterolytic cleavage of the rhodium-rhodium bond. Of the rhodium(I) and rhodium(III) complexes formed in this process, it is the rhodium(III) species that coordinates the reagent, and in the case of carbon monoxide and acetylene, activates it to undergo further reaction with the alcohol solvent. In a parallel process, the rhodium(I) complex is oxidised under the aerobic conditions to form more of the rhodium(III) complex, which also coordinates reagent. In this way, more of the same ultimate product is formed. This proposed reaction pathway explains the observation that essentially only one product was obtained in very good yield from each of these reactions.
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Chapter 1: Introduction

1.1 Research objectives and thesis outline

The primary goal of the research described in this thesis is to develop new macrocyclic ligands that incorporate novel nitrogen-donor groups into their structures and to investigate the structural, spectroscopic, and catalytic properties of the metal complexes of these ligands. The introductory chapter (Chapter 1) describes the research objectives and methodology, and provides relevant background information. Chapter 2 discusses the synthesis of the new macrocyclic nitrogen-donor ligands and investigates the structures and spectroscopic properties of these compounds. The following chapter (Chapter 3) details the synthesis of metal complexes of the new ligands and their structural and spectroscopic properties are discussed. The ability of these complexes to act as catalysts for the oxidation of substrates by hydrogen peroxide are explored in Chapter 4, while in Chapter 5, investigations into reactions relevant to the catalysis of small molecule activation by the new rhodium-ligand complexes are presented. The research is summarised in the conclusions section (Chapter 6) and future work is also discussed.

1.2 Catalysis and Green Chemistry

Green chemistry is a field of research whose central goal is to reduce and to ultimately eliminate the production and use of hazardous chemicals through the redesign of chemical products and syntheses.\(^1\)\(^2\) The catalysis of chemical reactions is a vital component of this green chemistry approach to chemical synthesis. Because catalysts decrease the activation energy barriers to reactions, lower reaction temperatures are required than for non-catalysed reactions and greater control of product selectivity can be achieved.\(^1\) This reduces both energy expenditure and waste generation, thereby decreasing environmental impact. Many catalysts can achieve a desired chemical transformation in a single step, while the non-catalysed alternative may require multiple reaction steps, further decreasing the amount of waste generated from catalysed chemical reactions.\(^1\)\(^3\)
The development of new ligands is crucial to the discovery of effective catalysts for homogeneous reactions. By synthesising ligands with new donor groups and then coordinating these to appropriate metal centres, new complexes can be developed for the catalysis of specific reactions. In this thesis, pyridinium amides were chosen as the primary donor groups in the ligands synthesised for the target complexes because these groups donate strongly to metal centres through nitrogen-donor atoms. Metal complexes of these ligands have been shown in preliminary studies to catalyse a number of reactions and the study of complexes with these donor groups is still a relatively unexplored area of chemistry.

1.3 Pyridinium amides

Pyridinium amides are compounds formed from the deprotonation of pyridinium amines (Figure 1.1). The structures of pyridinium amides can be viewed in terms of the two limiting resonance forms, A and B. In resonance form A, there is a formal positive charge on the pyridinium nitrogen atom and a formal negative charge on the amide nitrogen atom, whereas in resonance form B, there is no charge separation. Increased contributions from resonance form A are expected to increase the electron donating properties of the amide nitrogen towards metals. In resonance form A, the zwitterionic form is stabilised by the aromatic stabilisation of the pyridinium ring, while resonance form B is stabilised by the absence of charge separation. Although the term “pyridinium amide” technically refers to only the zwitterionic resonance form (A) of these compounds, for convenience, the term “pyridinium amide” is used throughout this thesis to refer to the actual bonding situation for these ligands. Both the zwitterionic resonance form (A) and the imine resonance form (B) contribute to the structures of “pyridinium amides”. Meanwhile, the protonated version of these pyridinium amides (the left hand structures in Figure 1.1) are referred to in this thesis as “pyridinium amines”.
Pyridinium amides are relatively easy to synthesise and a wide variety of substituted derivatives are possible through modification of the substituents on the pyridinium nitrogen atom and on the amide/imine nitrogen atom ($R_1$ and $R_2$ in Figure 1.1, respectively). These modifiable sites enable the development of tunable ligand sets that are useful for altering the catalytic and structural properties of metal-pyridinium amide complexes.

X-ray crystal structures of pyridinium amides are consistent with a predominantly imine-like structure (resonance form $B$) in the solid state, with significant C-N double-bond character and bond localisation about the heterocyclic ring. However, the behaviour of pyridinium amides as strong bases suggests that there is a significant contribution of the amido resonance structure $A$ to their reactivity. Density functional theory (DFT) and natural bond order (NBO) calculations of pyridinium amides also suggest a strong contribution from resonance form $B$.

Structural and computational studies of metal-pyridinium amide complexes show that pyridinium amides donate strongly to metal centres through the nitrogen atom, suggesting that there is a strong contribution from resonance form $A$ to metal-ligand bonding. Measured carbonyl $\nu$(CO) stretching frequencies of $cis$-$[\text{CO}_2\text{Rh(Cl)(L)}]$ complexes suggest that pyridinium amides have similar donating strengths to $N$-heterocyclic carbenes (NHCs). NHCs are very strong $\sigma$-donors and an example of a typical NHC is shown in Figure 1.2. Although they are usually represented as the charge-neutral structure shown on the left hand side of this
figure, NHCs can also be represented as two charge-separated ylid resonance forms (Figure 1.2). Computational studies of the carbonyl $\nu$(CO) stretching frequencies for [IrCp(CO)L] complexes also suggest that pyridinium amides are comparable and probably somewhat greater in donating strength to NHCs.\textsuperscript{4,5,10} Comparison of the Pd-Cl bond lengths of synthesised $[\text{cis-}(L_2)\text{PdCl}_2]$ complexes by X-ray crystallography provides further evidence that pyridinium amides and NHCs have similar electron donating strengths.\textsuperscript{4,5}

\begin{center}
\begin{tikzpicture}
\node at (0,0) (NHC) [shape=circle, draw, align=center] {$\text{R}^+\text{N}^\equiv\text{N}\equiv\text{N}^-\text{R}^-$};
\node at (2,0) (NHC+) [shape=circle, draw, align=center] {$\text{R}^+\text{N}^\equiv\text{N}^+\equiv\text{N}^-\text{R}^-$};
\node at (4,0) (NHC-) [shape=circle, draw, align=center] {$\text{R}^-\text{N}^\equiv\text{N}^-\equiv\text{N}^+\text{R}$};
\draw[->] (NHC) -- (NHC+);
\end{tikzpicture}
\end{center}

\textit{Figure 1.2: Structure and resonance forms of a typical $N$-heterocyclic carbene (NHC)}

### 1.4 Catalysis by metal-pyridinium amide complexes

Although pyridinium amides have been extensively researched for almost a century,\textsuperscript{11} the coordination chemistry of these complexes and their ability to catalyse various reactions has only recently been investigated. While only a handful of papers have been published in this field,\textsuperscript{4-10,12} metal-pyridinium amide complexes have shown promise as catalysts for reactions where strongly donating ligand sets are desirable for enhanced catalytic performances.\textsuperscript{5} A number of metal-pyridinium amide complexes have been investigated as catalysts for cross-coupling, C-H bond activation and C-F bond activation reactions and the results of these experiments are summarised in the sections below.

#### 1.4.1 Catalysis of cross-coupling reactions by palladium(II)-pyridinium amide complexes

A palladium-pyridinium amide complex (Figure 1.3) has been shown to catalyse Suzuki-Miyaura and Heck-Mizoroki cross-coupling reactions.\textsuperscript{7} Suzuki-Miyaura coupling of 4-bromobenzene (1 equivalent) with $p$-tolylboronic acid (1.5 equivalents) in the presence of caesium carbonate (2 equivalents) gave 4-methylbiphenyl in 56% conversion after 6 hours in $N,N$-dimethylformamide (DMF) at 100 °C (Figure 1.3). A catalyst loading of 1 mol% was used.
Heck-Mizoroki coupling of bromobenzene (1 equivalent) with styrene (1.4 equivalents) in the presence of sodium acetate (1.1 equivalents) gave a mixture of trans-1,2-stilbene, cis-1,2-stilbene and α-1,1’-stilbene in a combined yield of 49% after 6 hours at 140 °C in N,N-dimethylacetamide (DMA, Figure 1.3). A catalyst loading of 1 mol% was also used for this reaction. Blanks for both these reactions showed that very little reaction occurs between the substrates in the absence of the palladium-pyridinium amide complex.7

![Figure 1.3: Catalysis of Suzuki-Miyaura and Heck-Mizoroki cross-coupling reactions by a palladium-pyridinium amide complex (inset)](image)

Darkening of the Heck-Mizoroki reaction mixture was attributed to catalyst degradation and subsequent formation of palladium black. However, this was not observed in the Suzuki-Miyaura reaction, suggesting that the catalyst is more robust under these reaction conditions.7 This may be due to catalyst degradation at the higher temperature used for the Heck-Mizoroki reaction than for the Suzuki-Miyaura reaction.
1.4.2 Catalysis of C-F and C-H bond activation reactions by nickel(0)-pyridinium amide complexes

Samuel A. Johnson and his research group at the University of Windsor (in Windsor, Canada) have shown that nickel(0) complexes of the pyridinium amide ligand given in Figure 1.4 catalyse C-F and C-H bond activation reactions.\(^6,8,9\) These nickel(0) complexes were synthesised \textit{in situ} from Ni(COD)\(_2\) (COD = 1,5-cyclooctadiene) and the pyridinium amide ligand.

\[
\text{Ni} \quad \text{(COD)} \quad \text{N} \quad \text{N} \quad \text{Pr}
\]

\textbf{Figure 1.4: A pyridinium amide ligand used by the Johnson research group for \textit{in situ} formation of nickel(0) complexes, which were subsequently used as catalysts for C-F and C-H bond activation reactions}

C-F bond activation of hexa-, penta- and tetrafluorobenzenes was found to occur when one equivalent of the polyfluorobenzene reacts with two equivalents of the pyridinium amide ligand and one equivalent of Ni(COD)\(_2\) in toluene. After 0.5 to 5 hours at room temperature, the C-F bond activated product (Figure 1.5) precipitated out of solution in 70 to 80% yield. C-F bond activation was found to be regioselective and only the isomers shown in Figure 1.5 were synthesised for each polyfluorobenzene reagent used. The isolated nickel(II) complexes were characterised by NMR spectroscopy and X-ray crystallography. This reaction was the first example of regioselective C-F bond activation of tetrafluorobenzenes by a nickel(0) complex. Activation of the strong and relatively inert aromatic C-F bonds in these systems demonstrates that the strongly donating pyridinium amide ligand is important for the oxidative addition of challenging substrates.\(^5\)
Figure 1.5: C-F bond activation of polyfluorobenzenes from a mixture of Ni(COD)$_2$, pyridinium amide (L) and a polyfluorobenzene in toluene

When a slight excess of a vinyl stannane was added to the penta-, tetra- and trifluorobenzene reactions shown in Figure 1.5, catalytic C-H bond activation of the polyfluorobenzenes was found to occur instead of C-F bond activation (Figure 1.6), yielding polyfluoronated monostannananes. After a few hours at 35 to 45 °C, only the monostannylated products were observed in approximately 90% yields, at 3 mol% catalyst loading (based on the amount of pyridinium amide used). For tetra- and trifluorobenzenes, a small amount of distannylated product was observed after longer reaction times (6 to 18 hours). These distannylated products were readily separated from the monostannylated products during reaction isolation. The distannylated products themselves can be synthesised in high yield when 2.5 equivalents of the vinyl stannane are used instead of a slight excess of vinyl stannane. Although the reactions can be carried out in neat polyfluorobenzene, most were conducted in C$_6$D$_6$, to enable reaction monitoring via NMR spectroscopy.\textsuperscript{8}
Figure 1.6: C-H bond stannylation of polyfluorobenzenes with vinyl stannanes, catalysed by Ni(COD)$_2$ and a pyridinium amide

Conversion was found to be highly regioselective, with substitution of the hydrogen atom closest to two fluorine atoms being favoured over substitution of the hydrogen atom closest to only one fluorine atom. No C-F bond activation products were observed and ethylene gas was observed as a by-product by NMR spectroscopy.

Organostannanes are widely used as reagents for the Stille coupling reaction. In this reaction, an organostannane reacts with an organic electrophile (such as an aryl halide) to form a new C-C bond (Figure 1.7). The reaction is catalysed by various palladium(0) complexes. The Stille reaction is tolerant to a wide range of functional groups and most organostannanes are stable to air and moisture. The organostannanes used in the Stille reaction are usually synthesised from expensive precursors involving multiple reaction steps that generate large amounts of toxic waste by-products. Catalytic C-H bond stannylation by nickel-palladium amide complexes therefore provides a convenient and facile route towards the high-yielding synthesis of polyfluoro-substituted organostannanes for the Stille reaction. It may also be possible to catalytically synthesise a variety of organostannanes that are substituted with groups other than fluoride using nickel-palladium amide complexes.
Johnson *et al.* have further shown that by repeating the reaction shown in Figure 1.6 using a different vinyl stannane (H\(_2\)C=CHSnPh\(_3\) instead of H\(_2\)C=CHSnMe\(_3\) or H\(_2\)C=CHSnBu\(_3\)), C-H bond alkylation of pentafluorobenzene can be achieved instead of C-H bond stannylation (Figure 1.8).\(^9\) The reaction was again catalytic and yields of greater than 95% were achieved using 5 mol% catalyst (calculated based on the amount of ligand used). The reaction was much slower than C-H bond stannylation reaction (weeks instead of hours) and \(^1\)H NMR monitoring of the reaction in C\(_6\)D\(_6\) showed that the C-H bond stannylation product given in Figure 1.6 formed as an intermediate product. Using similar conditions, H\(_2\)C=CHSnBu\(_3\) and H\(_2\)C=CHSnBn\(_3\) vinyl stannanes (Bn = benzyl) gave primarily the C-H bond stannylation products and only a small amount of the C-H bond alkylation products. Furthermore, Johnson *et al.* have demonstrated that the isolated C-H bond stannylation product, C\(_6\)F\(_5\)-SnR\(_3\) (R = Ph or Bn), can be converted catalytically into the C-H bond alkylation product, C\(_6\)F\(_5\)-CH\(_2\)CH\(_2\)SnR\(_3\), using ethylene, 10 mol% pyridinium amide and 5 mol% Ni(COD)\(_2\) in C\(_6\)D\(_6\) (Figure 1.9). Interestingly, for both R = Ph and Rh = Bn, C\(_6\)F\(_5\)-CH\(_2\)CH\(_2\)SnR\(_3\) was obtained in high yield, even though C-H bond alkylation using the vinyl stannane H\(_2\)C=CHSnBn\(_3\) via the reaction in Figure 1.8 was found to yield mostly the C\(_6\)F\(_5\)-SnBn\(_3\) C-H stannylation product. As for the C-H bond stannylation products, the C-H bond alkylation products synthesised in these reactions can be used as reagents for the Stille reaction.\(^9\)
Figure 1.8: C-H bond alkylation of pentafluorobenzene with a vinyl stannane, catalysed by Ni(COD)$_2$ and a pyridinium amide

Figure 1.9: Conversion of the isolated C-H bond stannylation product, C$_6$F$_5$-SnR$_3$, to C$_6$F$_5$-CH$_2$CH$_2$SnR$_3$, using catalytic amounts of Ni(COD)$_2$ and a pyridinium amide

1.5 Target ligands

As described in Section 1.1, the primary goal for the research conducted in this thesis is to develop new macrocyclic ligands that incorporate pyridinium amide functional groups into their structures and to investigate the structural, spectroscopic, and catalytic properties of the metal complexes of these ligands. The structures of the target ligands are shown in Figure 1.10. These macrocyclic ligands contain four nitrogen donor atoms. Two of these are pyridinium amide donors, while the other two are (after deprotonation) carboxamide nitrogen donors. All four nitrogen donors are expected to donate strongly to metal centres. Because the term “amide” can refer to either R-NH-C(O)-R’ compounds or to R-N-R’ compounds, the former are referred to as “carboxamides” in this thesis, and the latter are referred to as “amides”.
Macrocyclic target ligands were chosen because they are expected to be more robust than their acyclic analogues. Macrocyclic structures were also selected due to the similarities of the target ligands to tetraamido macrocyclic ligands (TAMLs), porphyrin ligands and dibenzotetramethyltetraaza[14]annulene (TMTAA) ligands (Figure 1.11). These three types of macrocyclic ligands also donate strongly to metal centres through four nitrogen atoms.\textsuperscript{14-16} After deprotonation, TAML ligands bear a 4- charge and donate to metal centres through four amidate nitrogen atoms. Meanwhile, porphyrin and TMTAA ligands both bear a 2- charge and donate to metal centres via four pyrrolic nitrogen atoms, or via two imine and two amide nitrogen atoms, respectively.
Many metal-TAML, metal-porphyrin and metal-TMTAA complexes have interesting catalytic properties. Metal-TAML complexes, particularly iron- and cobalt-TAMLs, are excellent catalysts for the oxidation of substrates by peroxides. They have also been shown to catalyse the small molecule activation of carbon dioxide for the synthesis of cyclic carbonates from epoxides. Metal-porphyrin complexes have been investigated as catalysts for a wide range of reactions. The reactions they successfully catalyse depend on the metal centre used, the substituents on the porphyrin ligand and the presence of any axial ligands. Reactions known to be catalysed by metal-porphyrin complexes include, amongst others, oxidation reactions and the activation of small molecules, such as carbon monoxide, acetylene and dihydrogen. Metal-TMTAA complexes also catalyse a range of reactions, including oxidation reactions and small molecule activation reactions, for example, of carbon monoxide and carbon dioxide.

A vast number of different types of catalytic reactions have been investigated in the literature. Because it was beyond the scope of this research to investigate all of these different types of reactions, the research described in this thesis focuses on two types of catalysis by the new macrocyclic metal-pyridinium amide complexes: the catalysis of oxidation reactions by hydrogen peroxide and the catalysis of small molecule activation. These two types of catalysis are discussed in further detail in Sections 1.6 and 1.7, respectively.

1.6 Catalysis of the oxidation of substrates by hydrogen peroxide

1.6.1 Hydrogen peroxide as a greener alternative oxidant

Oxidation reactions are found in a diverse range of industrial processes and syntheses. Chlorine-based and metal-based oxidants are often used in these systems and can be highly effective oxidants for many chemical transformations. A major drawback of these oxidants is that they often produce organochlorine or metal-based by-products that are highly toxic. The enormous scales at which many of these oxidants are used worldwide means that the disposal of these by-products poses a significant hazard for human health and the environment.
Hydrogen peroxide is an alternative oxidant which does not produce these toxic by-products. Dilute hydrogen peroxide is relatively safe and has low toxicity. However, at high concentrations, hydrogen peroxide is a skin irritant and can decompose explosively when brought into contact with certain compounds, such as transition metals, transition metal salts, bases and some organic compounds (for example, acetals and ethers).\textsuperscript{26} Although the standard reduction potential of hydrogen peroxide suggests that it is a stronger oxidant than common chlorine-based oxidants that are used industrially (Table 1.1), the oxidation of organic substrates by hydrogen peroxide is usually kinetically slow and selectivities are low.\textsuperscript{27} This can be overcome by activating hydrogen peroxide with transition metals complexes to produce new species that react more selectively and with much faster rates than does hydrogen peroxide alone.\textsuperscript{27,28} There are three main methods for the activation of hydrogen peroxide by synthetic transition metal complexes: 1) generation of hydroxyl radicals via the radical decomposition of hydrogen peroxide, in a process generally known as Fenton chemistry (Section 1.6.1.1); 2) generation of metal-peroxy or metal-hydropersoxy species (Section 1.6.1.2); and 3) generation of highly reactive metal-oxo species (Section 1.6.1.3).

Table 1.1: Standard reduction potentials of selected oxidants

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Electrode potential (E₀, V)\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>F\textsubscript{2}</td>
<td>3.00</td>
</tr>
<tr>
<td>HO\textsuperscript{-}</td>
<td>2.80</td>
</tr>
<tr>
<td>O\textsubscript{2} (singlet)</td>
<td>2.42</td>
</tr>
<tr>
<td>O\textsubscript{3}</td>
<td>2.01</td>
</tr>
<tr>
<td>H\textsubscript{2}SO\textsubscript{5}</td>
<td>1.81</td>
</tr>
<tr>
<td>H\textsubscript{2}O\textsubscript{2}</td>
<td>1.76</td>
</tr>
<tr>
<td>KMnO\textsubscript{4}</td>
<td>1.70</td>
</tr>
<tr>
<td>HO\textsubscript{2}\textsuperscript{-}</td>
<td>1.70</td>
</tr>
<tr>
<td>HOCl</td>
<td>1.49</td>
</tr>
<tr>
<td>Cl\textsubscript{2}</td>
<td>1.27</td>
</tr>
<tr>
<td>ClO\textsubscript{2}</td>
<td>1.27</td>
</tr>
<tr>
<td>O\textsubscript{2}</td>
<td>1.20</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Standard reduction potentials are for reactions at 25 °C and 1 atmosphere, calibrated relative to the standard hydrogen electrode potential of 0.00 V.\textsuperscript{27}
1.6.1.1 Fenton chemistry

Fenton chemistry is a process which involves the activation of hydrogen peroxide by iron(II) or iron(III) species in acidic aqueous solutions, to form highly reactive hydroxyl radicals (HO·). Hydroxyl radicals are very powerful oxidants, with a standard reduction potential that is significantly higher than for hydrogen peroxide alone (Table 1.1). A range of iron(II) and iron(III) species can be used as catalysts for the Fenton reaction and the most commonly used Fenton catalyst is iron(II) sulfate.29

Fenton chemistry was discovered in 1894, when Henry Fenton found that acidic aqueous solutions of iron(II) salts oxidised tartaric acid in the presence of hydrogen peroxide.30 A number of mechanisms have been proposed for Fenton chemistry. The most widely accepted of these is the Haber-Weiss classical Fenton chain mechanism (Figure 1.12).29,31 This mechanism was originally proposed in 1934 by Fritz Haber and Joseph Weiss for Fenton reactions that occur in the absence of organic compounds and light. Cycling between the iron(II) and iron(III) oxidation states (reactions 1 and 2, Figure 1.12) produces both hydroxyl (HO·) and hydroperoxyl (HO2·) radicals catalytically from hydrogen peroxide. Both radical species can oxidise substrates, although the hydroperoxyl radical is a weaker oxidant than the hydroxyl radical.29 Superoxide (O2·−) radical anions do not play a key role in the mechanism, because the reaction is performed at acidic pH values that are below the pKₐ value (4.8) of the hydroperoxyl radical.32 This cycling between the iron(II) and iron(III) oxidation states explains why either iron(II) or iron(III) species can be used as Fenton reagents. In practice, a catalytic amount of the iron(II) or iron(III) species is used relative to the amount of hydrogen peroxide, to minimise hydroxyl radical scavenging by iron(II) itself (reaction 4).29

\[
\begin{align*}
\text{Fe}^{II} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{III} + \text{OH}^- + \text{HO}^- & (1) \\
\text{Fe}^{III} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{II} + \text{HO}_2^- + \text{H}^+ & (2) \\
\text{HO}^- + \text{H}_2\text{O}_2 & \rightarrow \text{HO}_2^- + \text{H}_2\text{O} & (3) \\
\text{HO}^- + \text{Fe}^{II} & \rightarrow \text{Fe}^{III} + \text{OH}^- & (4) \\
\text{Fe}^{III} + \text{HO}_2^- & \rightarrow \text{Fe}^{II} + \text{O}_2\text{H}^+ & (5) \\
\text{Fe}^{II} + \text{HO}_2^- + \text{H}^+ & \rightarrow \text{Fe}^{III} + \text{H}_2\text{O}_2 & (6) \\
\text{HO}_2^- + \text{HO}_2 & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 & (7)
\end{align*}
\]

Figure 1.12: The Haber-Weiss mechanism for Fenton chemistry. FeII and FeIII represent all of the iron(II) and iron(III) species in solution, respectively
The optimum pH for Fenton chemistry is just below 3. At higher pH values, formation of Fenton-inactive iron(III) oxyhydrate species becomes dominant. These species precipitate out of solution and do not readily redissolve, significantly decreasing catalyst activity. This limits the possible applications of Fenton chemistry, because many substrates are not tolerant to these acidic conditions. The addition of large amounts of acid are also costly and hazardous. After neutralising the reaction solution, colloidal sludges form which can clog reaction equipment and degrade water quality when released into the environment. Fenton reagents are also sensitive to inactivation via complexation with anions such as phosphates and halides that may be present in solution, further limiting potential applications. Furthermore, hydroxyl radicals have very low substrate selectivities and so substrates other than the target substrate are often oxidised too. Fenton chemistry is therefore rarely used in synthetic applications and is instead used for water treatment and remediation, for example, in decolourising waste streams from the textile and pulp and paper industries; removing phenolic compounds in the effluent streams created from wine distillation; and destroying formaldehyde and herbicides in various waste solutions.

1.6.1.2 Metal-peroxy and metal-hydroperoxy complexes

Some synthetic transition metal complexes react with hydrogen peroxide to form metal-peroxy (M-(η²-O₂)) or metal-hydroperoxy (M-OOH) complexes. These activated forms of hydrogen peroxide are much more active and selective oxidants than hydrogen peroxide alone and many of these complexes are known to catalyse substrate oxidations. Metal-peroxy and metal-hydroperoxy complexes are also much more selective oxidants than the hydroxyl radicals formed in Fenton chemistry. Consequently, unlike complexes that catalyse Fenton chemistry, many metal-peroxy and metal-hydroperoxy complexes can be used as catalysts for the selective synthesis of fine chemicals with hydrogen peroxide. A large number of metal-peroxy and metal-hydroperoxy complexes have been studied as catalysts for substrates oxidations with hydrogen peroxide. Some of the key complexes and the reactions they catalyse are summarised in this section.

The most extensively studied group of transition metal-peroxy complexes are the d⁰ vanadium(V), chromium (VI), molybdenum(VI) and tungsten(VI) peroxometallates. When hydrogen peroxide is added to complexes of these metals that contain suitable ancillary ligands, peroxometallate complexes are usually formed. Some examples of these peroxometallates are
shown in Figure 1.13.\textsuperscript{28,41} Most of these peroxometallate complexes are stable and can be isolated and characterised. These isolated complexes oxidise substrates stoichiometrically and this usually becomes catalytic in the presence of excess hydrogen peroxide and excess substrate (Figure 1.14).\textsuperscript{28} While most peroxometallates contain both metal-oxo and metal-peroxo groups, mechanistic studies indicate that it is the peroxo ligand that usually donates the oxygen atom to the substrate. After oxidising the substrate, the peroxo group becomes an oxo group and the catalyst returns to the resting state. Another equivalent of hydrogen peroxide then adds to the metal-oxo oxygen atom, reforming the peroxometallate active catalyst (Figure 1.14). Addition of hydrogen peroxide to the metal-oxo resting catalyst is believed to form a hydroperoxy intermediate, M(OOH)(OH), which then loses water to form the peroxometallate active catalyst.\textsuperscript{42} Peroxometallates may contain more than one peroxo group (Figure 1.13). Some of these diperoxo complexes are more reactive than analogous monoperoxo complexes, while others are less reactive.\textsuperscript{43} Some titanium(IV), niobium(V) and tantalum(V) $d^0$ peroxometallates can also catalyse substrate oxidations with hydrogen peroxide.\textsuperscript{40}

![Figure 1.13: Examples of $d^0$ metal-peroxy complexes (also known as peroxometallate complexes)](image)

Peroxometallates are effective catalysts for the oxidation of a range of substrates, such as the selective formation of aldehydes from primary alcohols without over-oxidation to carboxylic acids;\textsuperscript{44} oxidation of secondary alcohols to ketones;\textsuperscript{44} epoxidation of alkenes;\textsuperscript{45} oxidation of tertiary amines to tertiary amine oxides;\textsuperscript{46} formation of phenols from substituted benzenes;\textsuperscript{47} and the oxidation of cyclic ketones to lactams.\textsuperscript{48} Most V(V), Mo(VI) and W(VI) peroxometallates complexes have low toxicities and are potential greener alternatives to many catalysts currently used for these transformations.\textsuperscript{49}
Metal-peroxy complexes are also formed from the reaction of hydrogen peroxide with middle- to late-transition metal complexes. The metal centres of these complexes are usually in the $+III$ oxidation state and their formation depends strongly upon the nature of the ancillary ligands surrounding the metal centres. $N$-tetramethylated cyclam (TMC) macrocyclic ligands are the most extensively studied ancillary ligands for these complexes (Figure 1.15). Mn(III), Fe(III), Co(III) and Ni(III) TMC-peroxy complexes can all be synthesised from the reaction of metal(II)-TMC complexes with hydrogen peroxide, in the presence of a suitable base (usually triethylamine or tetaethylammonium hydroxide). Some examples of these complexes are shown in Figure 1.15.$^{50}$ These peroxy complexes have been characterised using X-ray crystallography and various spectroscopic methods. Although it has been demonstrated that $[\text{Ni}^{III}(12\text{-TMC})(O_2)]^+$ can transfer oxygen to $[\text{Mn}^{II}(14\text{-TMC})]^2+$ to form $[\text{Mn}^{III}(14\text{-TMC})(O_2)]^+$, these metal(III)(TMC)-peroxy complexes have not been shown to catalyse oxidation reactions with hydrogen peroxide.$^{50,51}$
Metal-hydroperoxy (M-OOH) complexes are known to form through the reaction of hydrogen peroxide with some late transition metal complexes (Figure 1.16).\textsuperscript{40} This is an acid-base exchange reaction, where the metal centre behaves as a Lewis base towards hydrogen peroxide. On the other hand, the $d^0$ early transition metal-peroxy complexes described earlier are formed through the reaction of the Lewis acidic metal centre with hydrogen peroxide. These two distinct reactions are possible because hydrogen peroxide is amphoteric ($pK_a = 11.6$) and therefore can behave either as an electrophile or as a nucleophile.\textsuperscript{40,43} Most of these late transition metal-hydroperoxy complexes are far less reactive oxidants than the $d^0$ early transition metal-peroxy complexes and their applications are far more limited. Although some of these complexes catalytically transfer oxygen to substrates (for example, in the epoxidation of terminal alkenes with Pt\textsuperscript{II}(diphosphine)(OOH) complexes\textsuperscript{52}), many metal-hydroperoxy complexes are poor oxidation catalysts and they instead tend to catalyse the radical-type (Fenton-like) decomposition of hydrogen peroxide.\textsuperscript{40,50}

\[
M^{II}(L_n)X + H_2O_2 \rightleftharpoons M^{II}(L_n)OOH + HX
\]

\textbf{Figure 1.16: General reaction for the formation of late transition metal-hydroperoxy complexes from the reaction of late transition metal complexes with hydrogen peroxide}
1.6.1.3 Metal-oxo complexes

Synthetic transition metal complexes can also activate hydrogen peroxide via the formation of metal-oxo (M=O) complexes. These metal-oxo complexes are often highly reactive oxidants and are much more reactive than hydrogen peroxide alone. Many mid- to late-transition metal complexes, for example, of manganese, chromium, iron, cobalt, ruthenium, nickel or copper, form metal-oxo complexes in the presence of peroxides. In the presence of excess peroxide and substrate, many of these complexes catalytically oxidise substrates.\textsuperscript{51,53,54} Although some early transition metal complexes (for example, of titanium, vanadium and molybdenum) also form metal-oxo complexes in the presence of peroxides, they usually do not undergo further oxidation reactions and are therefore not catalysts for these reactions. This is due to the highly oxophilic metal centre and the subsequently strong metal-oxygen bond, which prevents oxygen atom transfer to most substrates.\textsuperscript{53} The ancillary ligands play an important role in the formation of effective metal-oxo oxidation catalysts. Suitable ancillary ligands usually donate strongly to metal centres, stabilising the metal in a high oxidation state and polarising the metal-oxo bond. This increases the nucleophilicity of the oxygen atom and therefore increases the reactivity of the metal-oxo complex towards substrate oxidations.\textsuperscript{55} Many of these ancillary ligands are nitrogen or oxygen donors and examples of these complexes are shown in Figure 1.17.\textsuperscript{56-60} Structural modifications to these ancillary ligands are often used to tune the oxidation properties of the metal complexes. Iron-oxo complexes are the most extensively studied of the synthetic metal-oxo complexes, mainly due to the similarities of their structures and reactivities to the active site of many metalloenzymes. They have therefore been widely used as biological mimics to better understand the reactions that occur in certain metalloenzymes.\textsuperscript{61} Metalloenzymes that catalyse reactions with hydrogen peroxide are discussed in more detail in Section 1.6.2.
Figure 1.17: Selected examples of metal-oxo complexes used as oxidation catalysts. Abbreviations: TMC = tetramethyleyclam; TMTACN = 1,4,7-trimethyl-1,4,7-triazacyclononane; N4Py = N,N-bis(2-pyridylmethyl)-N-bis(2-pyridyl)methylamine; "Bu-P2DA = N-(1',1'-bis(2-pyridyl)pentyl)imidodiacetate; terpy = 2,2':6'2"-terpyridine; dcdipy = 6,6'-dichloro-2,2'-bipyridine

A general mechanism for the oxidation of substrates catalysed by metal-oxo complexes is shown in Figure 1.18.\textsuperscript{56,62} The catalytic cycle begins with the coordination of hydrogen peroxide to the vacant coordination site of the resting catalyst. Water is then lost from the coordinated hydrogen peroxide ligand to form the metal-oxo active catalyst, probably via the formation of a metal-peroxo or metal-hydroperoxo species. The active catalyst then oxidises a substrate and returns to the resting catalyst state before beginning the catalytic cycle again with the coordination of another molecule of hydrogen peroxide.\textsuperscript{56,62} More detailed and specific mechanisms are provided for metalloenzyme and iron-TAML systems in Sections 1.6.2 and 1.6.3, respectively.
Figure 1.18: General catalytic cycle for the oxidation of substrates by hydrogen peroxide, catalysed by metal-oxo complexes

Some examples of reactions that have been catalysed by synthetic metal-oxo complexes include: alkene epoxidation; the oxidation of sulfides to sulfoxides and sulfones; alkylaromatic oxidation of cyclohexadiene to benzene; oxidation of alcohols to aldehydes and ketones; hydroxylation of substituted benzenes to substituted phenols; and the oxidation of alkanes to alcohols.\textsuperscript{57-61,63}

While the activation of hydrogen peroxide by synthetic metal complexes via hydroxyl radical (Section 1.6.1.1), metal-peroxy (Section 1.6.1.2), metal-hydroperoxy (Section 1.6.1.2) or metal-oxo (Section 1.6.1.3) species are known to successfully oxidise a variety of substrates, their turnovers, rates and selectivities are much lower than similar reactions that are catalysed by enzymes found in nature. A number of enzymes are known to activate hydrogen peroxide towards the oxidation of substrates and these are discussed in the following section.
1.6.2 Enzymes that catalyse reactions with hydrogen peroxide

Enzymes are proteins found in all living organisms that catalyse a diverse range of biochemical reactions. They are extremely efficient catalysts and are many orders of magnitude more efficient than synthetic analogues. Enzymes are also highly selective and have very high turnover numbers. Long protein chains surround the active site of enzymes, forming a pocket that only fits specific substrates, and which therefore confers a high degree of substrate chemoselectivity, stereoselectivity, and regioselectivity to the catalysed reaction.64

Metalloenzymes are a specific class of enzyme which contain a metal atom at the active site. Metalloenzymes containing vanadium, manganese, iron, cobalt, nickel, copper, zinc, molybdenum or tungsten at the active site are all known. By far the most common metalloenzymes are those with iron at the active site and several classes of these iron-based metalloenzymes are known to activate hydrogen peroxide.65 Three of most extensively studied of these metalloenzymes are summarised in the following sections: cytochrome P₄₅₀ enzymes (Section 1.6.2.1), peroxidase enzymes (Section 1.6.2.2) and catalase enzymes (Section 1.6.2.3).

1.6.2.1 Cytochrome P₄₅₀ enzymes

Cytochrome P₄₅₀ enzymes are a class of metalloenzyme that contain a heme group at the active site. Hemes are iron porphyrin complexes that are found in many metalloenzymes and bioinorganic compounds, such as myoglobin and haemoglobin. The particular type of porphyrin ligand found in cytochrome P₄₅₀ enzymes is known as protoporphyrin IX. Porphyrin ligands are macrocycles which contain four pyrrolic groups that are connected together via unsaturated methine bridges on the α-carbon atoms. In the resting state of cytochrome P₄₅₀, the protoporphyrin IX ligand is bound to iron(III), forming a complex known as ferriprotoporphyrin IX, or heme b (Figure 1.19).64 In the resting state, ferriprotoporphyrin IX is six-coordinate. One of the axial ligands is a water molecule, while the other axial ligand is a protein chain that is bound to the iron centre through the sulfur atom of a cysteinate residue.66 The name cytochrome P₄₅₀ arises from the intense Soret band observed at 450 nm in the UV-visible absorption spectrum of the iron(II)-carbon monoxide adduct of cytochrome P₄₅₀.65
Figure 1.19: Chemical structure of the ferriprotoporphyrin IX heme, found at the active site of cytochrome P450 enzymes. The heme is shown in the resting Fe(III) state.

Cytochrome P450 enzymes primarily catalyse the monooxygenase reaction (Figure 1.20). In this reaction, one of the oxygen atoms of dioxygen is inserted into a substrate (RH) and the second oxygen atom is reduced to water.65,67 A wide range of substrates can be oxidised by cytochrome P450 enzymes and the structure of the protein chain bound to the iron centre controls the selectivity for specific substrates. Over two thousand different cytochrome P450 enzymes have been identified, each with a different protein chain and substrate selectivity.68

Figure 1.20: General scheme for the monooxygenase reaction, catalysed by cytochrome P450 enzymes.

\[ RH + O_2 + 2e^- + 2H^+ \xrightarrow{\text{cytochrome P450}} ROH + H_2O \]

The catalytic cycle for the oxidation of substrates with dioxygen, catalysed by cytochrome P450 enzymes is shown in Figure 1.21.69 In the resting state, the iron centre is in an octahedral low-spin +III oxidation state. As the substrate (RH) enters the pocket created by the protein chains surrounding the active site, the axial water ligand is displaced and the iron centre becomes five-coordinate. This displaces the iron atom out of the porphyrin plane, weakening the interaction between the d-orbitals and the ligand orbitals and decreasing the energy gap between the d-orbital energy levels. This leads to a high-spin iron centre and the iron atom becomes a better
electron acceptor. An electron is then transferred from the reductase domain of the protein chain and the iron centre is reduced to iron(II). In the next step, dioxygen binds to the iron(II) centre, forming a low-spin dioxygen complex which is in resonance with an iron(III)-superoxo complex. A second electron is transferred from the reductase domain in this complex, producing an iron(III)-peroxo species. This complex is now a good Lewis base, and so the peroxo ligand protonates to yield an iron(III)-hydroperoxy complex known as Compound 0. Compound 0 is still a good Lewis base, so a second proton is added, releasing water and forming an iron(IV)-oxo porphyrin radical cation complex known as Compound I. The oxygen atom is then transferred to the substrate and the oxidised substrate (ROH) is released from the protein pocket as it no longer fits this pocket well. A water molecule then binds to the vacant coordination site, reforming the resting catalyst and the cycle begins again.67,69,70

In the presence of hydrogen peroxide, the cytochrome P450 catalytic cycle follows a different route, known as the peroxide shunt pathway (Figure 1.21). In this pathway, the iron(III)-hydroperoxy complex (Compound 0) is formed directly from the iron(III) complex, without reducing the metal centre to iron(II). A proton is formed as the by-product and in the next step, this reacts with the hydroperoxy ligand to form the iron(IV)-oxo porphyrin radical cation complex (Compound I), which then oxidises the substrate.70

Cytochrome P450 enzymes are vital in biological systems for the metabolism of thousands of chemicals and for the synthesis of important molecules, such as hormones and vitamin D. Natural and modified cytochrome P450 enzymes have been used to catalyse reactions, such as alkene epoxidation; saturated C-H bond hydroxylation; oxidative dealkylation; and the oxidation of various heteroatoms.67 They have also been used in other biotechnical applications, for example, in the development of biosensors.67-69
1.6.2.2 Peroxidase enzymes

Peroxidase enzymes make up another class of heme-based metalloenzyme that catalyse reactions with hydrogen peroxide. Like cytochrome P₄₅₀ enzymes, the active site of peroxidase enzymes contains a ferriprotoporphyrin (heme b) complex. However, unlike cytochrome P₄₅₀, the resting catalyst has no axial water ligand and the protein chain is bound to the iron atom via the nitrogen atom of a histidine residue instead of through the sulfur atom of a cysteinate residue.
Horseradish peroxidase is the most extensively studied of the thousands of known peroxidase enzymes and a catalytic cycle has been determined for the oxidation of substrates catalysed by this enzyme (Figure 1.22).\textsuperscript{71,72} The catalytic cycles for other peroxidase enzymes are believed to be similar. In the first step of the catalytic cycle, the resting catalyst is oxidised by hydrogen peroxide to form an iron(IV) porphyrin radical cation (Compound I), producing water as a by-product. Compound I is formally two oxidation equivalents above the enzyme resting state. Like the peroxide shunt pathway of cytochrome P\textsubscript{450} enzymes, Compound I probably forms via an iron(III)-hydroperoxy species (Compound 0). However, unlike cytochrome P\textsubscript{450} enzymes, where Compound I transfers the oxygen atom (and therefore two oxidation equivalents) to the substrate, Compound I of horseradish peroxidase oxidises a substrate (RH) via removal of a proton and transfer of the porphyrin radical electron to the substrate. Therefore, only one oxidation equivalent is transferred to the substrate in this step. The different mechanisms of substrate oxidation for horseradish peroxidase and cytochrome P\textsubscript{450} are controlled by the different protein environments surrounding the active sites. After Compound I of horseradish peroxidase transfers the radical from the porphyrin ligand to the substrate, the complex becomes an iron(IV)-oxo species (known as Compound II), which is formally one oxidation equivalent above the enzyme resting state (Figure 1.22). Compound II can then oxidise a second substrate molecule (RH) via another one electron oxidation and the enzyme returns to the resting state, generating water as a by-product. The overall reaction, which known as oxidative dehydrogenation, is given in Figure 1.23.\textsuperscript{65,71,72}

The organic substrate radicals generated by hydrogen peroxide and peroxidase enzymes are highly reactive and undergo further reactions with other reagents or react with themselves to form oligomers and polymers. Therefore, a mixture of products is usually formed when a specific substrate is oxidised by peroxidase enzymes and the peroxidase enzyme may catalyse further oxidations of these products. In biological systems, peroxidases are important for the formation of some biopolymers, such as polysaccharides.\textsuperscript{72} Natural and modified peroxidase enzymes are used in a range of biotechnological applications, for example, in biosensors, immunoassays and wastewater remediation, although the use of peroxidases in the latter application is limited due to their high cost and sensitivity to inactivation by contaminants in the waste stream. Peroxidase enzymes have also shown promise as selective catalysts for the synthesis of organic compounds, such as the formation of polymers from vinyl-containing monomers via free radical polymerisation; N- and O-dealkylation of aromatic hydrocarbons under mild conditions; asymmetric sulfoxidations of sulfides to sulfoxides; N-oxidation of
nitroso and hydroxylamino functional groups to nitro groups; and C-H bond hydroxylation of aromatic compounds.\textsuperscript{71-75}

\begin{center}
\includegraphics[width=0.8\textwidth]{catalytic_cycle.png}
\end{center}

Figure 1.22: Catalytic cycle for the oxidation of substrates by hydrogen peroxide, catalysed by horseradish peroxidase

\[
\text{H}_2\text{O}_2 + 2\text{RH} \xrightarrow{\text{peroxidase enzyme}} 2\text{H}_2\text{O} + 2\text{R}^* 
\]

Figure 1.23: Overall reaction for the oxidation of substrates by hydrogen peroxide, catalysed by peroxidase enzymes

1.6.2.3 Catalase enzymes

Like cytochrome P\textsubscript{450} and peroxidase enzymes, a ferrirprotoporphyrin IX complex is found at the active site of most catalase enzymes. In these catalase enzymes (which are also known as hydroperoxidase enzymes), the protein chain binds to the axial site of the iron atom through the phenolate oxygen atom of a tyrosine residue. The catalytic cycle for catalase enzymes (Figure 1.24) involves similar intermediates to the catalytic cycles of peroxidase enzymes and the
peroxide shunt pathway of cytochrome P₄₅₀ enzymes. In the first step of this catalytic cycle, hydrogen peroxide coordinates to the vacant axial site of the resting catalyst. The coordinated hydrogen peroxide then loses two hydrogen atoms and one oxygen atom as water, producing Compound I. Instead of transferring oxygen or a radical to an organic substrate, a second molecule of hydrogen peroxide reacts with Compound I via a two-electron oxidation process, producing water and dioxygen. Therefore, for every turnover of the catalytic cycle, two equivalents of hydrogen peroxide disproportionate to two equivalents of water and one equivalent of dioxygen (Figure 1.25). The catalyst then returns to the resting state without forming Compound II.⁶５,⁷⁶

![Catalytic cycle for the disproportionation of hydrogen peroxide, catalysed by catalase enzymes](image)

**Figure 1.24:** Catalytic cycle for the disproportionation of hydrogen peroxide, catalysed by catalase enzymes

2H₂O₂ $\xrightarrow{\text{catalase enzyme}}$ 2H₂O + O₂

**Figure 1.25:** Overall reaction for the disproportionation of hydrogen peroxide, catalysed by catalase enzymes
Catalase enzymes are important in biological systems for protecting cells from being damaged by hydroxyl radicals generated via Fenton-like processes from hydrogen peroxide. Instead of forming hydroxyl radicals, catalase enzymes ensure that excess hydrogen peroxide is converted into dioxygen and water, which are much more benign in biological systems than hydroxyl radicals. This is particularly important if a cell experiences a sudden local increase in hydrogen peroxide concentration, which can occur during certain biological processes. Industrially, catalase enzymes are useful for applications where the efficient removal of hydrogen peroxide is required, for example, to remove the hydrogen peroxide used to sterilise dairy products; for solutions used to clean contact lenses; and in the textile industry, to remove hydrogen peroxide left over from the fabric bleaching process, before the fabric is dyed.

1.6.2.4 Peroxidase-like and catalase-like activities of synthetic catalysts

In the literature, the term “peroxidase-like” catalysts has been used to describe synthetic peroxidase enzyme mimics where the mechanism of substrate oxidation by hydrogen peroxide is believed to occur via the formation of high-valent iron-oxo species. Meanwhile, synthetic iron complexes that are believed to catalyse hydrogen peroxide disproportionation via reactions similar to those of catalase enzymes have been referred to as “catalase-like” catalysts. The detailed mechanisms for these reactions, however, may be quite different from those of peroxidase and catalase enzymes.

1.6.2.5 Designing peroxidase-like synthetic catalysts for substrate oxidations with hydrogen peroxide

Small molecule mimics of peroxidase metalloenzymes that are easy and cheap to synthesise are attractive alternatives to metalloenzymes for the catalytic oxidation of substrates by hydrogen peroxide. While metalloenzymes are extremely efficient and selective oxidation catalysts, they are expensive to isolate and can be inactivated by many contaminants, products and by-products found in industrial reaction media. Their high selectivity can in fact be problematic when a wider substrate scope is required, and the bioengineering of suitable derivatives can be very expensive. These factors have limited the use of peroxidase enzymes in industrial applications. Although the efficiency of oxidation reactions catalysed by synthetic peroxidase mimics are usually significantly lower than analogous reactions catalysed by peroxidase enzymes, synthetic
Peroxidase mimics are often tolerant to a wider range of conditions and substrates. In peroxidase enzymes, substrate selectivity is controlled by the bulky peptide chains surrounding the active site. Synthetic peroxidase mimics do not have these bulky peptide chains and selectivity is instead controlled by modifying the structure of the ligands surrounding the metal centre. The bulky peptide chains of peroxidase enzymes also ensure that the active site catalyses substrate oxidation (peroxidase activity) and not hydrogen peroxide disproportionation (catalase activity). Without these peptide chains, synthetic peroxidase mimics may catalyse peroxidase-like activity, catalase-like activity or even Fenton chemistry. A major goal in designing these catalysts is therefore to maximise peroxidase-like activity and minimise the waste of hydrogen peroxide via catalase-like disproportionation and the production of unselective hydroxyl radicals. Another advantage of the bulky protein chains of peroxidase enzymes is that they protect the active site from oxidative degradation. The absence of these protective protein chains provides a further challenge in designing robust synthetic peroxidase mimics, which can be overcome by designing ligands that are resistant to oxidation by the active form of the catalyst. While some of these synthetic oxidation catalysts were discussed in Sections 1.6.1.2 and 1.6.1.3, by far the most effective small molecule peroxidase mimics are the iron-TAML (TAML = tetraamido macrocyclic ligands) complexes. These robust complexes have high peroxidase-like activities and minimal catalase-like activities and do not form hydroxyl radicals via Fenton-like chemistry. Metal-TAMLS and the catalytic properties of these compounds are discussed in the following section.

1.6.3 Metal-TAML complexes as oxidation catalysts

TAMLs were originally developed by Terrence J. Collins at Carnegie Mellon University. The chemical structure of a typical TAML ligand is shown in Figure 1.26. This particular ligand is known as H₄B*. These macrocyclic ligands have four carboxamide groups which, when deprotonated, donate strongly to metal centres through the nitrogen atoms. The four strongly electron-donating amidates stabilise metal centres in high oxidation states. For example, TAML complexes of Cr(V), Mn(V), Fe(IV), Fe(V), Co(III) and Ni(III) have been synthesised and characterised.
Metal-TAMLs (particularly Fe-TAMLs) efficiently catalyse the oxidation of a wide range of substrates by hydrogen peroxide. There are many sites on the macrocyclic ligand that can be modified to allow tuning of the catalyst properties for specific applications and this has resulted in the development of a large suite of metal-TAML oxidation catalysts. An added advantage of Fe-TAMLs is that most of these complexes contain only the low-toxicity elements iron, carbon, hydrogen, nitrogen and oxygen, reducing the risk of forming toxic catalyst degradation products.\(^{17}\)

1.6.3.1 Development of TAML ligands

The first TAML ligand was developed in the late 1980s and was named H\(_4\)MAC* (Figure 1.27).\(^{81}\) The structures of TAML ligands were inspired by T. J. Collins’ polyaromatic chelating (PAC) ligands.\(^{85}\) PAC ligands are acyclic ligands which donate strongly to metal centres through two amidate nitrogen atoms and two alkoxide oxygen atoms (for example, H\(_4\)HMPA-DMP, Figure 1.27). Although PAC ligands were found to stabilise metal centres in high oxidation states, their susceptibility to self-oxidation and hydrolysis restricted their use as oxidation catalysts. This was attributed in part to their tendency towards intramolecular isomerisation, forming non-planar complexes which were much more susceptible to self-oxidation and hydrolysis than the planar isomers.\(^{85-88}\) Macrocyclic versions of these ligands were therefore targeted, because this would reduce the likelihood of non-planar complex formation. To form a macrocycle, the two alkoxide oxygen atoms were replaced with two secondary carboxamide nitrogen atoms, forming the tetraamidate macrocycle. Earlier work by Dale Margerum and his research group had shown that acyclic polyamidate ligands were also effective for stabilising metal centres in high oxidation states, such as Cu(III) and Ni(III),\(^{89,90}\) suggesting that tetraamidate macrocyclic ligands would also stabilise high oxidation state metal centres. Metal
complexes of the first TAML ligand, $\text{H}_4\text{MAC}^*$, were found to be hydrolytically sensitive and of limited use as oxidation catalysts (Figure 1.27).\textsuperscript{55}

Figure 1.27: Evolution of TAML ligands. Many TAMLs have been derivatised with functional groups on the aromatic ring (X substituents) and the aliphatic “arms” (R substituents), enabling tuning of catalytic properties. The names below the TAML ligands correspond to TAMLs where $R = H$ and $X = H$. 
Since the development of H₄MAC*, an iterative design cycle has been applied to synthesise more oxidatively robust TAML ligands. In this iterative design cycle, the metal-TAML complex is exposed to an oxidant until the ligand undergoes oxidative decay. The degradation products are then characterised and the most oxidatively vulnerable site of the ligand is identified. A new ligand is then designed which removes this vulnerability and should therefore be more oxidatively resistant, and the cycle is repeated again. Using a similar iterative process, more hydrolytically stable complexes can also be developed by exposing the active metal-TAML complex to acids until hydrolysis occurs. Through these processes, steadily more oxidatively and hydrolytically robust TAML ligands have been developed, and some of the major ligand families are shown in Figure 1.27. Substitution of functional groups on the aromatic ring (X, Figure 1.27) and on the “arms” (R, Figure 1.27) of these ligands can be used to tune the oxidation properties of the metal-TAML complexes for a variety of applications.¹⁷,⁵⁵,⁹¹,⁹² Research is still ongoing to discover metal-TAMLs with even better oxidative and hydrolytic resistances.

1.6.3.2 Iron-TAMLs as catalysts for the oxidation of dye substrates by hydrogen peroxide

The catalytic cycles, mechanisms and kinetics for the Fe-TAML-catalysed oxidation of substrates by hydrogen peroxide have been elucidated in a number of studies.¹⁴,⁶²,⁹²-¹⁰³ Organic dyes are often used as substrates in these studies, because they degrade to colourless products and this can be monitored by UV-visible spectroscopy. The structures of several of these dye substrates are shown in Figure 1.28.⁹³ Fe-TAMLs efficiently catalyse the oxidation of these dyes by hydrogen peroxide under mildly basic conditions in buffered aqueous solutions, with high reaction turnover numbers. However, in acidic solutions Fe-TAMLs become inactivated via acid-induced demetallation, although for some of the more recently-developed catalysts, demetallation is slow under mildly acidic conditions.¹⁴

Figure 1.28: Chemical structures of Orange II, Safranine O and Pinacyanol chloride dyes, used in dye oxidation studies with metal-TAMLs
X-ray crystallographic studies demonstrate that Fe-TAMLs are five-coordinate in the solid state, with an axial water or chloride ligand. The four nitrogen atoms are highly planar and the iron(III) atom sits slightly out of the plane, on the side towards the axial ligand. In mildly basic aqueous solutions, EPR studies show that the Fe(III) centre becomes six-coordinate, forming the resting catalyst (Figure 1.29). Furthermore, gas-phase DFT studies demonstrate that six-coordinate Fe-TAML complexes are more energetically favoured than five-coordinate species in aqueous solutions. The resting catalyst has either two axial water ligands or an axial water ligand and an axial hydroxide ligand, depending on the pH of the solution and the pKₐ of the catalyst. The postulated catalytic cycle for the oxidation of substrates with Fe-TAMLs and hydrogen peroxide is shown in Figure 1.29, for the case where both axial ligands are water molecules. In the first step of the catalytic cycle, one of the water ligands is displaced by hydrogen peroxide. A proton is then lost from the coordinated hydrogen peroxide to form a Fe(III)-hydroperoxy complex. It is then postulated that the O-O bond is cleaved to form a strongly oxidising Fe(V)-oxo active catalyst. The active catalyst then oxidises a substrate and returns to the resting catalyst state before undergoing the next cycle with another molecule of hydrogen peroxide. At pH values above the pKₐ of the bis(aquo) resting catalyst, the catalytic cycle is analogous to Figure 1.29, except that one of the axial water ligands is a hydroxide ligand instead of a water ligand. If the pH of the aqueous solution is significantly higher than the pKₐ of hydrogen peroxide (pKₐ = 11.6), most of the hydrogen peroxide exists as the hydroperoxide (HOO⁻) anion, and the catalytic cycle can be redrawn with [Fe^{III}(TAML)(OH)(OOH)]⁻ forming directly from [Fe^{III}(TAML)(H₂O)(OH)]²⁻.

Fe(V)-oxo TAML complexes have not been identified spectroscopically in aqueous solutions, although Fe(IV)-oxo species have been identified. However, Fe(V)-oxo TAML species have been spectroscopically identified at -60 °C in non-aqueous solutions, using m-chloroperbenzoic acid as the oxidant. Fe(V)-oxo species are still believed to be the active oxidants in aqueous solutions with hydrogen peroxide, but presumably have not been observed due to the rapid comproportionation of Fe(V)-oxo species with Fe(III) species to form Fe(IV)-oxo species. Although the Fe(IV)-oxo species also oxidises substrates, the Fe(V)-oxo species is a far more powerful oxidant. Spectroscopic evidence suggests that, unlike the Fe-porphyrin systems of cytochrome P₄₅₀, peroxidase and catalase enzymes, Fe(IV)-oxo ligand radical cation species are not formed in the catalytic cycle. The formation of hydroxyl radicals via Fenton-like processes also has not been observed in Fe-TAML systems. In the absence of substrates, the active Fe-
TAML catalyst can disproportionate hydrogen peroxide to water and dioxygen via catalase-like activity. Although a small amount of catalase-like activity also occurs in the presence of an oxidisable substrate, this is minor compared to the peroxidase-like activity (substrate oxidation). This behaviour is similar to that of peroxidase enzymes, indicating that Fe-TAMLs are indeed effective small molecule mimics of these enzymes.\textsuperscript{62,80}

\textbf{Figure 1.29: Proposed catalytic cycle for the oxidation of substrates with hydrogen peroxide, catalysed by Fe-TAMLs}

The optimum pH for Fe-TAML-catalysed substrate oxidations by hydrogen peroxide is usually between 9.5 and 10.5, and some of the later generations of Fe-TAMLs become optimal at about pH 9. The exact value depends on the TAML ligand structure and slight variations have been observed when the same Fe-TAML complex has been used to oxidise different
For most green chemistry applications, it is desirable for the optimum pH to be as close to neutral as possible, to minimise the amount of base that has to be added to the solution, particularly if the waste from these applications is to be released into the environment.\textsuperscript{105}

Recent studies have shown that cobalt(III)-TAMLs are also highly effective catalysts for the oxidation of dye substrates by hydrogen peroxide and the mechanism of substrate oxidation is currently under investigation.\textsuperscript{106} These complexes are discussed in further detail in Chapter 3.

1.6.3.3 Applications of metal-TAMLs

A diverse range of substrates can be oxidised by peroxides in the presence of metal-TAML (mostly Fe-TAML) complexes. Various potential applications for metal-TAML catalysed substrate oxidations have been investigated and reported in the literature. These studies have demonstrated that metal-TAMLs are effective for: the bleaching of wood pulp in the manufacture of white paper;\textsuperscript{107} the destruction of bacterial spores of anthrax surrogates;\textsuperscript{108} as sensors for detecting the presence of traces of hydrogen peroxide in aqueous solutions;\textsuperscript{109} oxidative degradation of insecticides and pesticides;\textsuperscript{110,111} oxidising sulfur-containing chemicals in diesel;\textsuperscript{112} destroying estrogens and other endocrine-disrupting chemicals in wastewater;\textsuperscript{113} the safe destruction of trinitrotoluene and trinitrobenzene explosives;\textsuperscript{114} decolourisation of effluent streams from various industrial processes;\textsuperscript{102,115} and activation of the C-H bond of cyclohexane to form cyclohexanol and cyclohexanone.\textsuperscript{116}

1.7 Small molecule activation

Small molecules such as CO\textsubscript{2}, CO, NO, N\textsubscript{2}O, N\textsubscript{2}, H\textsubscript{2}, CH\textsubscript{4}, H\textsubscript{2}O and O\textsubscript{2} are cheap and abundant chemicals that are either found in the natural environment, or else are produced on a large scale as by-products from industrial processes. They are useful as cheap feedstocks and reagents for chemical syntheses, but their generally high thermodynamic stability means that these reactions usually require activation by catalysts.\textsuperscript{117} Their use as reagents provides a greener approach to
chemical syntheses than many of the petrochemical-derived reagents currently used in industrial processes.\textsuperscript{1,3}

The activation of small molecules is a vast field of research, so this section will focus on the activation of carbon monoxide, acetylene, dihydrogen and carbon dioxide. Only these fields are discussed here because these small molecules were investigated as reagents for reactions catalysed by the new rhodium-pyridinium amide complexes that are described in Chapter 5. The following sections discuss some of the more relevant aspects of the activation of these molecules, with an emphasis on industrially-relevant reactions that are catalysed by homogeneous catalysts.

1.7.1 Activation of carbon monoxide

Carbon monoxide is a chemical used in a large number of industrial processes. It is used mainly as a feedstock for the synthesis of fuels and petrochemicals and is produced on a very large scale worldwide, usually from either the reforming of methane and water; the partial oxidation of methane; or as a mixture with dihydrogen, known as syngas, that is produced from coal and water.\textsuperscript{117} Hydroformylations and carbonylations are two major classes of industrial carbon monoxide activation reactions that are catalysed by homogeneous catalysts. In hydroformylation reactions, aldehydes are synthesised from the reaction of alkenes with carbon monoxide and dihydrogen, whereas carbonylations involve the insertion of carbon monoxide into a variety of organic substrates.\textsuperscript{118}

1.7.1.1 Hydroformylation reactions

The catalytic hydroformylation of alkenes to aldehydes is a widely used industrial process. Worldwide, over 12 million tons of aldehydes are produced annually via hydroformylation reactions. Of all the industrial reactions that are catalysed by organometallic complexes, hydroformylation is second only to the polymerisation of alkenes and dienes in terms of product value and production volume.\textsuperscript{119} The aldehydes produced from this process are used to synthesise a wide range of products industrially, such as alcohols, amines, carboxylic acids, diols, acetals and ethers.\textsuperscript{120}
The first generation of homogeneous hydroformylation catalysts were developed in the 1940s and were based on cobalt carbonyl hydride complexes. Harsh reaction conditions were required to stabilise the cobalt carbonyl hydride resting catalyst and to attain good reaction rates. Thus, pressures of 200 to 350 bar and temperatures of 150 to 180 °C were typically used to suppress catalyst decomposition into carbon monoxide and inactive cobalt complexes. Product selectivities were also reasonably low with these first generation catalysts, because both linear and branched aldehydes were produced.\textsuperscript{120,121} A catalytic cycle has been determined for this reaction (Figure 1.30). Dicobaltoctacarbonyl, \( \text{Co}_2(\text{CO})_8 \), is typically used as the precatalyst. In the presence of dihydrogen gas, the cobalt(I) carbonyl hydride complex, \( \text{Co}^1\text{H}(\text{CO})_4 \), forms. The catalytic cycle begins with loss of one of the carbonyl ligands, forming the resting catalyst, \( \text{Co}^1\text{H}(\text{CO})_3 \). The alkene then coordinates to the coordinatively-unsaturated (16 valence electron) \( \text{Co}^1\text{H}(\text{CO})_3 \) complex to form a coordinatively-saturated cobalt(I) \( \pi \)-bound alkene complex. The alkene then formally inserts into the cobalt-hydride bond, producing a 16 valence electron \( n \)-alkylcobalt(I) complex. In the next step, carbon monoxide coordinates to the \( n \)-alkylcobalt(I) complex metal centre and a coordinatively-saturated cobalt(I) complex is formed. Migratory insertion of this carbonyl ligand into the cobalt-carbon bond of the \( n \)-alkyl ligand forms a 16 valence electron acylcobalt(I) complex and dihydrogen then oxidatively adds to this complex, producing an acyldihydridocobalt(III) species. In the final step, reductive elimination of this complex yields the aldehyde and the cobalt(I) carbonyl hydride resting catalyst is reformed.\textsuperscript{119}

In the formal alkene insertion step of the above catalytic cycle (Figure 1.30), an \( n \)-alkylcobalt(I) complex usually forms via the reaction of the cobalt centre with the terminal alkene carbon atom. However, the second carbon atom of some of the \( \pi \)-bound alkene ligands will react with the cobalt centre instead of the terminal carbon atom reacting with the cobalt centre. In this reaction, isoaldehydes are formed instead of \( n \)-aldehydes, which lowers the overall reaction selectivity.\textsuperscript{119} Improvements were made to these catalysts in the 1960s by replacing some of the carbonyl ligands with phosphine or arsine ligands. The steric bulk of the phosphine ligands hindered isoaldehyde formation and significantly improved product selectivity towards \( n \)-aldehyde formation. Lower pressures (50 to 100 bar) were required to stabilise these catalysts than were required for the cobalt(I) carbonyl hydride catalysts. Although the phosphine-containing cobalt(I) catalysts were more thermodynamically-stable than the cobalt(I) carbonyl hydride catalysts, their catalytic activities were lower and higher reaction temperatures were required (around 180 to 200 °C).\textsuperscript{119,120}
In the 1970s, a second generation of hydroformylation catalysts were developed that were based on rhodium(I) phosphine carbonyl hydride complexes, such as $\text{Rh}^1\text{H(CO)}(\text{PPh}_3)_3$. Reaction pressures of 7 to 25 bar were used with these catalysts, which was significantly lower than the reaction pressures required for the first generation cobalt catalysts. These rhodium catalysts were found to be around 1,000 times greater in catalytic activity than the cobalt catalysts. They were also much more selective towards $n$-aldehyde formation and catalyst lifetimes were significantly higher. The catalytic cycle for these rhodium catalysts (Figure 1.31) is similar to the catalytic cycle for the cobalt(I) carbonyl hydride catalysts (Figure 1.30), except that the $\text{Rh}^1\text{H(CO)}(\text{PPh}_3)_3$ resting catalyst is formed from the loss of triphenylphosphine from the $\text{Rh}^1\text{H(CO)}(\text{PPh}_3)_3$ precatalyst, instead of from the loss of a carbonyl ligand.\textsuperscript{119}
Figure 1.31: Catalytic cycle for the hydroformylation of alkenes with carbon monoxide and dihydrogen, catalysed by rhodium(I) carbonyl phosphine hydride complexes

Since the initial development of simple rhodium(I) carbonyl hydride phosphine complexes, many other phosphine ligands have been designed for these hydroformylation catalyst systems. This has enabled the tuning of the reaction properties, the substrate scope, and the selectivities for linear versus branched aldehydes. Several important developments in hydroformylation catalysts include: the synthesis of chiral diphosphines for enantioselective hydroformylations;\textsuperscript{117,119} the development of water-soluble phosphine ligands for biphasic hydroformylations, so that the product is easier to isolate;\textsuperscript{120} and the discovery that phosphite and diphosphite ligands can be used instead of phosphine ligands, leading to significant increases in catalyst stabilities and activities for some substrates.\textsuperscript{119,122} Further improvements to hydroformylation catalysts continue to be made.
Carbonylation reactions are another major class of industrial reactions where carbon monoxide is catalytically activated to synthesise organic products. In these carbonylation reactions, a transition metal complex catalyses the addition of carbon monoxide to an organic substrate. A wide variety organic substrates can be used, and many different classes of organic compounds are synthesised commercially via carbonylation reactions, such as the formation of methanol from dihydrogen; carboxylic acids and esters from alkenes; carboxylic acids and aldehydes from alcohols; acetic anhydride from methyl acetate; acid halides from alkyl halides; and amides from amines.\textsuperscript{120,121,123}

The synthesis of acetic acid from methanol is the largest-scale use of a metal-catalysed carbonylation reaction found in industry. Over 8 million tons of acetic acid are synthesised annually via this process.\textsuperscript{117} Most of the acetic acid produced worldwide is synthesised using either the Monsanto process, which is based on rhodium catalysts, or the Cativa process, which is based on iridium catalysts. The acetic acid produced from these processes is mainly used to synthesise cellulose acetate and polyvinyl acetate.\textsuperscript{119}

The Monsanto process was developed in the 1960s and the first production plant to use this technology began operating in 1970. The catalytic cycle for the Monsanto process (Figure 1.32) begins with reduction of the RhI\textsubscript{3} precatalyst by water and carbon monoxide, forming the [Rh\textsuperscript{I}(I)\textsubscript{2}(CO)\textsubscript{2}]\textsuperscript{-} resting catalyst. Iodomethane is produced in a second cycle of the Monsanto process, via the reaction of methanol with hydroiodic acid. Oxidative addition of iodomethane to the coordinatively unsaturated (16 valence electron) [Rh\textsuperscript{I}(I)\textsubscript{2}(CO)\textsubscript{2}]\textsuperscript{-} complex produces a coordinatively saturated [Rh\textsuperscript{III}(I)\textsubscript{3}(CO)\textsubscript{2}(CH\textsubscript{3})]\textsuperscript{-} complex. Migratory insertion of one of the carbonyl ligands into the Rh-C bond of the methyl ligand forms the 16 valence electron rhodium(III) acetyl complex, [Rh\textsuperscript{III}(I)\textsubscript{3}(CO)(COCH\textsubscript{3})]\textsuperscript{3-}. In the next step, carbon monoxide coordinates to the vacant coordination site of this acetyl complex, forming a coordinatively saturated [Rh\textsuperscript{III}(I)\textsubscript{3}(CO)\textsubscript{2}(COCH\textsubscript{3})]\textsuperscript{-} complex. Reductive elimination of acetyl iodide from this complex regenerates the resting catalyst. The acetyl iodide is then hydrolysed to acetic acid by the water molecule that was produced as a by-product from the reaction of methanol with hydroiodic acid, reforming hydroiodic acid as a by-product.\textsuperscript{117,119}
One disadvantage of the Monsanto process is that the [Rh(I)₂(CO)₂]⁻ resting catalyst also catalyses the water-gas shift reaction (Figure 1.33). This reaction wastes carbon monoxide by converting water and carbon monoxide into dihydrogen and carbon dioxide instead of converting carbon monoxide and methanol into acetic acid. This side reaction therefore decreases the selectivity of the Monsanto process with respect to carbon monoxide. A catalytic cycle for the [Rh(I)₂(CO)₂]⁻-catalysed water-gas shift reaction is shown in Figure 1.34. In this catalytic cycle, the [Rh(I)₂(CO)₂]⁻ resting catalyst first reacts with hydroiodic acid, forming [Rh(III)₄(CO)₂]⁻ and dihydrogen. This rhodium(III) complex then converts water and carbon monoxide into hydroiodic acid and carbon dioxide, and the resting catalyst is regenerated. The hydroiodic acid by-product is then used as a reagent in the next turnover of the catalytic cycle. The [Rh(III)₄(CO)₂]⁻ complex also decomposes to RhI₃ and this precipitates...
out of solution under the lower carbon monoxide pressures used at the end of the reaction. Consequently, this removes rhodium from the system and increases the amount of catalyst that has to be added to the reaction. This problem can be mitigated by using a high water content in the Monsanto reaction to drive \([\text{Rh}^{III}(I)_4(\text{CO})_2]^-\) back to \([\text{Rh}^I(II)(\text{CO})_2]^+\) and therefore to maintain catalyst stability and activity. A high water content also ensures that methanol is converted to acetic acid at a rate that is fast enough for the process to be economically viable. However, separation of this water from the acetic acid product is an expensive and energy-intensive process, adding significantly to running costs.\(^{117,119,120}\)

\[
\text{CO} + \text{H}_2\text{O} \xrightarrow{\text{catalyst}} \text{H}_2 + \text{CO}_2
\]

**Figure 1.33:** The water-gas shift reaction

![Diagram of water-gas shift reaction](image)

**Figure 1.34:** Catalytic cycle for the water-gas shift reaction, catalysed by the resting catalyst of the Monsanto process

In 1996, a significant improvement was made to the Monsanto process by replacing the rhodium catalyst with iridium catalysts. The new process, known as the Cativa process, has a much higher selectivity for acetic acid (over 99%) than the Monsanto process (around 95%) and the rate of conversion of methanol to acetic acid is significantly faster. It is now the process of choice for the production of acetic acid from methanol and many plants that use the Monsanto process are gradually being converted to the Cativa process, because the reactor designs for both processes are similar.\(^{117,119,121}\)
The catalytic cycle for the Cativa process (Figure 1.35) is similar to the catalytic cycle of the Monsanto process, but differs in a few respects. In the Cativa process, a promotor is added to the reaction mixture. These promoters are usually metal iodides (such as ZnI₂, CdI₂, HgI₂, GaI₃ or InI₃) or carbonyl-iodo complexes of tungsten, rhenium, ruthenium, osmium or platinum. Promotors accelerate the reaction by abstracting iodide from the \([\text{Ir}^{\text{III}}(\text{I})_3(\text{CO})_2(\text{CH}_3)]^\text{-}\) intermediate, which is involved in the rate determining step of the catalytic cycle (Figure 1.35).

Interestingly, in the absence of these promotors, the rhodium catalysts of the Monsanto process have superior performance over the iridium catalysts used in the Cativa process. Promotors can also be used in the Monsanto process, but they are far less effective at accelerating the rate of acetic acid formation. Promotors shift the equilibria of the iridium complexes, so that the \([\text{Ir}^{\text{III}}(\text{I})_3(\text{CO})(\text{CH}_3)]^\text{-}\) complex loses an iodide ligand by complexation with the promotor and the iodide ligand is replaced by a carbonyl ligand, forming an \([\text{Ir}^{\text{III}}(\text{I})_2(\text{CO})_3(\text{CH}_3)]^\text{-}\) complex. This occurs instead of migratory insertion of carbon monoxide into the Ir-C bond of \([\text{Ir}^{\text{III}}(\text{I})_3(\text{CO})_2(\text{CH}_3)]^\text{-}\) to form \([\text{Ir}^{\text{III}}(\text{I})_3(\text{CO})(\text{COCH}_3)]^\text{-}\) (which occurs for the analogous rhodium complexes in the Monsanto process). The subsequent migratory insertion of a carbonyl ligand into the Ir-C bond of the methyl ligand of \([\text{Ir}^{\text{III}}(\text{I})_2(\text{CO})_3(\text{CH}_3)]^\text{-}\) is 800 times faster than migratory insertion of a carbonyl ligand into the Ir-C bond of the methyl ligand of \([\text{Ir}^{\text{III}}(\text{I})_3(\text{CO})_2(\text{CH}_3)]^\text{-}\).

In the absence of promotors, the latter slower reaction is favoured and this step is rate-determining. Therefore, the addition of promotors to the Cativa reaction significantly increases the rate of reaction. After migratory insertion, a neutral \([\text{Ir}^{\text{III}}(\text{I})_2(\text{CO})_2(\text{COCH}_3)]\) complex is formed and the resting catalyst is regenerated after loss of the acetyl ligand by reaction with the iodide anion coordinated to the promotor. As in the Monsanto process, the acetyl iodide produced from this step is hydrolysed to acetic acid.

The addition of promotors to the Cativa reaction also suppresses formation of \([\text{Ir}^{\text{III}}(\text{I})_4(\text{CO})_2]\), which would otherwise catalyse the water-gas shift reaction (Figure 1.34) and would decompose the catalyst, thereby decreasing the product yield. As described above, the \([\text{Rh}^{\text{III}}(\text{I})_4(\text{CO})_2]\) complex is known to form in the Monsanto process, which can be partially suppressed by adding a large amount of water to the reaction. Thus, less water has to be added to the Cativa reaction than to the Monsanto reaction, which decreases the energy demands in separating water from the acetic acid product. Product isolation steps are also reduced because less propionic acid is formed as a by-product in the Cativa process than in the Monsanto process. Furthermore, the iridium catalysts are cheaper than the rhodium catalysts and higher catalyst concentrations can be used in the Cativa process than in the Monsanto process, thereby increasing plant
It has been estimated that the costs involved in the Cativa process are about 30% lower than for the Monsanto process.\textsuperscript{117} Another metal-catalysed carbonylation reaction of industrial significance is the synthesis of acetic anhydride from methyl acetate and carbon monoxide (Figure 1.36). Although this process is catalysed by the same rhodium complexes that are used in the Monsanto process, the reaction conditions are somewhat different. Thus, water is not used or generated in the reaction system and methyl iodide is instead generated from the reaction of methyl acetate with hydroiodic acid.\textsuperscript{119}
Figure 1.36: General reaction for the synthesis of acetic anhydride from the carbonylation of methyl acetate, catalysed by rhodium complexes

Many other organic reagents can be carbonylated in the presence of homogeneous catalysts and some of these reactions are used on small scales industrially. Some of the more relevant processes are discussed in the remainder of this section.

The carbonylation of alkenes in the presence of nucleophiles leads to a variety of products. With water as the nucleophile, alkenes can be converted into carboxylic acids, in a reaction known as hydroxycarbonylation (Figure 1.37). This reaction is currently used to synthesise propionic acid from ethylene on a large industrial scale, using metal carbonyl catalysts.\textsuperscript{120} The use of methanol instead of water leads to the formation of esters via the alkoxyacarbonylation (hydroesterification) reaction. These reactions are often catalysed by nickel or palladium complexes. The hydroformylation reaction (Figure 1.30 and Figure 1.31) can also be considered as a type of carbonylation reaction, where the nucleophile in this case is dihydrogen. Some other important carbonylation reactions of alkenes include the formation of amides from amines, and the synthesis of acid anhydrides from carboxylic acids (Figure 1.37). The catalysts for these systems are usually transition metal complexes of iron, cobalt, nickel, molybdenum, ruthenium, rhodium, palladium, tungsten, iridium or platinum. Similar reactions to those shown in Figure 1.37 can be used to synthesise mono- or di-functionalised products from dienes.\textsuperscript{120,121,124}

\[ \text{R} = \text{C} + \text{CO} + \text{H}_2\text{O} \xrightarrow{\text{catalyst}} \text{R-CH}_2\text{-CH}_2\text{-C(O)OH} \]

\[ \text{R} = \text{C} + \text{CO} + \text{R}_1\text{OH} \xrightarrow{\text{catalyst}} \text{R-CH}_2\text{-CH}_2\text{-C(O)OR}_1 \]

\[ \text{R} = \text{C} + \text{CO} + \text{HNR}_1\text{R}_2 \xrightarrow{\text{catalyst}} \text{R-CH}_2\text{-CH}_2\text{-C(O)NR}_1\text{R}_2 \]

\[ \text{R} = \text{C} + \text{CO} + \text{R}_1\text{C(O)OH} \xrightarrow{\text{catalyst}} \text{R-CH}_2\text{-CH}_2\text{-C(O)-O-C(O)R}_1 \]

Figure 1.37: Catalytic carbonylation of alkenes, in the presence of various nucleophiles
Alkynes can also be catalytically carbonylated in the presence of various nucleophiles to synthesise organic products. For example, methyl acrylate is produced industrially from the carbonylation of acetylene with methanol, in the presence of a nickel tetracarbonyl catalyst. A catalytic cycle for this process is shown in Figure 1.38. This catalytic cycle begins with oxidative addition of an appropriate acid (HX) to the nickel(0) tetracarbonyl precatalyst, which generates the resting catalyst, Ni^{II}(CO)_{2}(X)(H). Insertion of acetylene into the Ni-H bond of this complex produces Ni^{II}(CO)_{2}(X)(CH=CH_{2}) and this is followed by insertion of carbon monoxide into the Ni-C bond to form the complex, Ni^{II}(CO)_{2}(X)(C(O)CH=CH_{2}). The Ni-C bond of Ni^{II}(CO)_{2}(X)(C(O)CH=CH_{2}) is then cleaved by methanol, yielding methyl acrylate and regenerating the resting catalyst. A similar process was once used to synthesise acrylic acid industrially via the carbonylation of acetylene in the presence of water, catalysed by nickel tetracarbonyl. This reaction has now been superseded by other synthetic methods. Carbonylation of longer-chain alkynes leads to either branched or linear products (Figure 1.39) and the product selectivity of these reactions can be controlled through the use of different catalysts.\textsuperscript{120,121}

Figure 1.38: Catalytic cycle for the carbonylation of acetylene and methanol to methyl acrylate, catalysed by nickel tetracarbonyl
The catalytic carbonylation of substituted aromatic compounds is a facile route towards the synthesis of many substituted aromatic compounds. Carbonylation of aromatic compounds with appropriate leaving groups (such as halides, organophosphates, sulfonates or sulfonyl chlorides) in the presence of a suitable nucleophile (and usually a base), leads to the formation of aromatic compounds substituted with carbonyl-containing functional groups. Some examples are shown in Figure 1.40. The catalysts used in these reactions are typically based on cobalt, nickel or palladium, although other transition metal complexes have also been used.120,124 A related reaction is the commercial synthesis of ibuprofen by the Hoechst-Celanese company, where an alcohol is carbonylated to a carboxylic acid using palladium chloride and triphenylphosphine as the catalyst system, in the presence of hydrochloric acid (Figure 1.41).124
Figure 1.41: Final step of the Hoescht-Celanese process for the synthesis of ibuprofen

Oxidative carbonylations are yet another important class of carbonylation reactions. These reactions are used commercially to synthesise dialkyl carbonates and dialkyl oxalates from alcohols and carbon monoxide in the presence of dioxygen (Figure 1.42). Palladium or copper complexes are commonly used as catalysts for these reactions. Different catalysts can be used to selectively synthesise either the dialkyl carbonate or the dialkyl oxalate, with only a small amount of the undesired product. Other substrates can also be oxidatively carbonylated in the presence of a suitable catalyst. For example, ethylene can be oxidatively carbonylated to acrylic acid and 3-acetoxypropanoic acid, which is then followed by thermal decomposition of 3-acetoxypropanoic acid to acrylic acid and acetic acid (Figure 1.43).\(^{120}\)

\[4 \text{ROH} + 3 \text{CO} + \text{O}_2 \xrightarrow{\text{catalyst}} \text{RO}_2\text{C} \quad \text{RO}_2\text{C} \quad + \quad 2\text{H}_2\text{O}\]

Figure 1.42: Oxidative carbonylation of alcohols to dialkyl carbonates and dialkyl oxalates

\[3\text{H}_2\text{C} = \text{CH}_2 + 2\text{CO} + 2\text{O}_2 \xrightarrow{\text{catalyst}} \text{COOH} + \text{O} \quad \text{COO}\text{CH} \quad \text{COOH} \quad \xrightarrow{\text{heat}} \quad \text{COOH} + \text{CH}_{2}\text{O}\]

Figure 1.43: Oxidative carbonylation of ethylene to acrylic acid and acetic acid
1.7.1.3 Other reactions used to catalytically activate carbon monoxide

The activation of carbon monoxide via Fischer-Tropsch synthesis is used industrially to convert syngas (a mixture of carbon monoxide and dihydrogen gases formed from coal and water) into higher hydrocarbons and oxygen-containing compounds. Today, it is mainly used to synthesise methanol from syngas over heterogeneous iron or cobalt catalysts. Reaction conditions can be altered so that alkanes, alkenes or long-chain alcohols are synthesised instead (Figure 1.44). Although only heterogeneous catalysts have been used commercially in these processes, some homogeneous catalyst systems (for example, based on Ni(CO)_4 and potassium methylate) also catalyse this reaction.\(^{119,121}\)

\[
\begin{align*}
n \text{CO} + (2n + 1) \text{H}_2 & \xrightarrow{\text{heterogeneous catalyst}} C_{n+2} \text{H}_{2n+2} + n \text{H}_2\text{O} \quad \text{alkanes} \\
n \text{CO} + 2n \text{H}_2 & \xrightarrow{\text{heterogeneous catalyst}} C_n\text{H}_{2n} + n \text{H}_2\text{O} \quad \text{alkenes} \\
n \text{CO} + 2n \text{H}_2 & \xrightarrow{\text{heterogeneous catalyst}} C_{n+1}\text{H}_{2n+1}\text{OH} + (n-1) \text{H}_2\text{O} \quad \text{alcohols}
\end{align*}
\]

**Figure 1.44: Fischer-Tropsch synthesis of alkanes, alkenes and alcohols from carbon monoxide and dihydrogen over heterogeneous catalysts**

Catalysis of the water-gas shift reaction (Figure 1.33) is used industrially as a convenient method for synthesising dihydrogen gas and carbon dioxide from water and carbon monoxide. This process is frequently used as a second stage of the steam-reforming process. In the steam-reforming process, carbon monoxide and dihydrogen gas are synthesised from water and methane at high temperature (usually 700 to 1100 °C) over heterogeneous catalysts. The carbon monoxide produced from this reaction can then be converted in a separate step to carbon dioxide and more dihydrogen by using complexes that catalyse the water-gas shift reaction. Steam reforming and the water-gas shift reaction are the two main methods used for synthesising dihydrogen gas industrially. Although homogeneous catalysts (mainly carbonyl or phosphine
complexes of iron, ruthenium, rhodium or platinum) effectively catalyse the water-gas shift reaction, heterogeneous catalysts such as chromium(III) oxides and copper/zinc oxides are used industrially. The catalytic cycle for the water-gas shift reaction, catalysed by homogeneous metal carbonyl complexes (such as Fe(CO)₅) is shown in Figure 1.45. In the first step of this catalytic cycle, nucleophilic attack of the LnM(CO) resting catalyst by hydroxide (or water) forms a metal-hydroxycarbonyl complex. This complex is unstable and the hydroxycarbonyl ligand decarbonylates via β-hydrogen elimination, releasing carbon dioxide and forming a hydridometal complex. The hydridometal complex then reacts with water to produce a dihydridometal complex, oxidising the metal centre by two units and generating hydroxide as a by-product. This dihydridometal complex then reductively eliminates dihydrogen and the subsequent coordination of carbon monoxide regenerates the resting catalyst.¹¹⁸-¹²⁰,¹²³

![Catalytic cycle for the water-gas shift reaction, catalysed by homogeneous metal-carbonyl complexes](image)

**Figure 1.45: Catalytic cycle for the water-gas shift reaction, catalysed by homogeneous metal-carbonyl complexes**

### 1.7.2 Activation of acetylene

Although acetylene is a reactive molecule that undergoes a number of organic reactions, the relatively high stability of acetylene at room temperature and pressure means that many reactions with acetylene need to be catalysed to achieve reasonable conversion rates and selectivities.¹²⁰ While many industrial syntheses that use acetylene as a reagent are not catalysed, this section focuses on selected homogeneously-catalysed reactions with acetylene. These
reactions can be divided into two main types: those where the acetylene triple bond is retained, and those where the triple bond is transformed into other functional groups. One class of the latter reaction, the carbonylation of alkynes, has already been discussed in Section 1.7.1.2.

1.7.2.1 Catalysed reactions with acetylene where the triple bond is retained

Retention of the acetylene triple bond is useful for synthesising longer chain alkynes from smaller alkyne precursors, which can then be functionalised further. One example of this reaction is the synthesis of butynediol from the reaction of acetylene with formaldehyde (Figure 1.46). Although this reaction can be catalysed homogeneously by copper acetylide, heterogeneous copper catalysts on support materials are normally used for this reaction. The butynediol product can then be hydrogenated into butenediol and butanediol. The latter product is used for the commercial synthesis of tetrahydrofuran.\textsuperscript{118,120} The addition of secondary amines to these ethynylation reactions yields propargylamines instead of butynediol (Figure 1.47). In contrast to the synthesis of butynediol, the catalysis of this reaction by copper acetylide gives superior yields to heterogeneous copper catalyst systems.\textsuperscript{120}

\[
\begin{align*}
\text{HC} &= \text{CH} + 2 \text{HCHO} \xrightarrow{\text{CuC_2}} \text{HO-CHCH}_2\text{OH} \\
\text{HC} &= \text{CH} + \text{HCHO} + \text{HNR_2} \xrightarrow{\text{CuC_2}} \text{HO-CHCH}_2\text{NR_2} + \text{H}_2\text{O}
\end{align*}
\]

Figure 1.46: Copper acetylide-catalysed synthesis of butynediol from acetylene and formaldehyde

Figure 1.47: Copper acetylide-catalysed synthesis of propargylamines from acetylene, formaldehyde and a secondary amine

The Sonogashira coupling reaction is another catalytic method used to activate alkynes to give products where the triple bond is retained. In this reaction, a terminal alkyne reacts with an aryl or vinyl halide (or triflate) in the presence of catalytic amounts of a palladium complex and copper iodide, to form a longer-chain alkyne (Figure 1.48). A base is also added to react with the acid that is produced as a by-product in this reaction.\textsuperscript{119,120}
The triple bond of acetylene is also retained in the acetylene dimerisation reaction (Figure 1.49). In this reaction, copper(I) chloride catalyses the dimerisation of acetylene to vinylacetylene. Hydrochloric acid is then added to the reaction mixture and the same complex catalyses the formation of chloroprene from vinylacetylene. This process was once used industrially to synthesise chloroprene, which was then polymerised to form neoprene rubber.118

Various vinyl-containing products can be synthesised by catalytically activating acetylene. These include, amongst others, the synthesis of vinyl esters, vinyl ethers, acetaldehyde, acrylonitrile and vinyl silanes. Vinyl esters can be synthesised from the reaction of acetylene with carboxylic acids, catalysed by ruthenium complexes such as Ru₄(CO)₁₆ (Figure 1.50), while vinyl ethers are formed via the catalytic reaction of acetylene with alcohols (Figure 1.51). The latter reaction is usually catalysed by platinum complexes such as Na₂PtCl₆, and these complexes often catalyse further reaction of the vinyl ether with another alcohol molecule to form acetals (Figure 1.51). Acetaldehyde can be synthesised using a reaction similar to the acetal synthesis reaction. In this reaction, mercury(II) salts catalyse the synthesis of an enol from acetylene and water, in the presence of sulfuric acid (Figure 1.52) and the enol then isomerises to acetaldehyde.119 This reaction is also catalysed by rhodium complexes.123 Although this process was once used to synthesise acetaldehyde industrially, it has now been superseded by the Wacker process, which converts ethylene to acetaldehyde using tetrachloropalladium(II) as the catalyst.118 The use of hydrogen cyanide instead of water leads to the formation of
acrylonitrile, which does not rearrange or react further to form other products (Figure 1.53). This hydrocyanation reaction is catalysed by copper(II) chloride in aqueous solutions and was once used for synthesising acrylonitrile commercially.\textsuperscript{118,119} A further example of the synthesis of vinyl-containing products from acetylene is the hydrosilylation of acetylene with silanes, which yields vinyl silanes (Figure 1.54). These reactions are catalysed by rhodium or platinum complexes.\textsuperscript{123}

\[ \text{HC} \equiv \text{CH} + \text{R}_3\text{SiH} \xrightarrow{\text{catalyst}} \text{HC} \equiv \text{SiR}_3 \]

\textbf{Figure 1.50: Synthesis of vinyl esters from acetylene and carboxylic acids, catalysed by Ru}_4\text{(CO)}_{16}\]

\[ \text{HC} \equiv \text{CH} + \text{R'OH} \xrightarrow{\text{Na}_2\text{PtCl}_6, 175^\circ\text{C}} \text{R'O} \xrightarrow{\text{Na}_2\text{PtCl}_6, 175^\circ\text{C}} \text{OR} \]

\textbf{Figure 1.51: Synthesis of acetics from acetylene and an alcohol via vinyl ether intermediates, catalysed by platinum complexes}

\[ \text{HC} \equiv \text{CH} + \text{H}_2\text{O} \xrightarrow{\text{H}_2\text{SO}_4, \text{Hg}^{2+}} \text{CHO} \]

\textbf{Figure 1.52: Synthesis of acetaldehyde from acetylene and water, via an enol intermediate, catalysed by mercury(II) salts in sulfuric acid}

\[ \text{HC} \equiv \text{CH} + \text{HCN} \xrightarrow{\text{CuCl}_2, \text{H}_2\text{O}} \text{HC} \equiv \text{CN} \]

\textbf{Figure 1.53: Synthesis of acrylonitrile from acetylene and hydrogen cyanide, catalysed by copper(II) chloride in aqueous solutions}

\[ \text{HC} \equiv \text{CH} + \text{R}_3\text{SiH} \xrightarrow{\text{catalyst}} \text{SiR}_3 \]

\textbf{Figure 1.54: Synthesis of vinyl silanes from acetylene and a silane, catalysed by rhodium or platinum complexes}
Acetylene can also be chlorinated to produce 1,1,2,2-tetrachloroethane (Figure 1.55), which was once widely used as a solvent and as a precursor to trichloroethylene. Today, 1,1,2,2-tetrachloroethane is produced on a much smaller commercial scale, due to its high toxicity. Anhydrous iron(III) chloride is used to catalyse this reaction and the reaction is carried out in the absence of air or light to prevent the explosive reaction of acetylene with chlorine gas.\textsuperscript{118}

\[
\text{HC}≡\text{CH} + 2\text{Cl}_2 \xrightarrow{\text{FeCl}_3} \text{Cl}_2\text{HC}−\text{CHCl}_2
\]

\textbf{Figure 1.55: Chlorination of acetylene to form 1,1,2,2-tetrachloroethane, catalysed by FeCl}_\textsubscript{3}

The catalysis of acetylene cyclooligomerisation reactions by homogeneous transition metal complexes is a useful method for synthesising various cyclic products. An example of this reaction is the cyclotrimerisation of acetylene to benzene using nickel-based catalysts under mild conditions. Although the cyclotrimerisation of acetylene to benzene also occurs under non-catalysed conditions, harsh reaction conditions are required (typically 300 to 400 °C) and yields are low.\textsuperscript{118} If monosubstituted alkynes are used, trisubstituted benzenes can be synthesised using iron, cobalt, nickel or rhodium-based catalysts (Figure 1.56). This reaction is important industrially because trisubstituted benzenes are formed in a single step under mild conditions, circumventing the use of otherwise laborious and often wasteful synthetic procedures. This reaction is tolerant to many functional groups. The addition of other substrates to the reaction mixture is used to synthesise heterocycles. For example, catalytic cotrimerisation of acetylene with acetonitrile yields 2-methylpyridine (Figure 1.57). Substituted alkynes and nitriles can be used to synthesise various substituted pyridines using this method. Cyclotetramerisation of acetylene can also be catalysed by some nickel complexes and this method is used commercially to synthesise cyclooctatetraene from acetylene (Figure 1.58) and tetrasubstituted cyclooctatetraenes from monosubstituted alkynes.\textsuperscript{118,120,121} Disubstituted alkynes often undergo alkyne metathesis reactions instead of cyclooligomerisation reactions in the presence of certain transition metal complexes, retaining the triple bond in the products (Figure 1.59). If non-terminal dialkynes are used instead, cycloalkynes can be synthesised through ring closing metathesis. The catalytic ring opening metathesis of these cycloalkyne products leads to alkyne polymers (Figure 1.60), where the triple bond is also retained.\textsuperscript{119,120}
Figure 1.56: Synthesis of trisubstituted benzenes by catalytic cyclotrimerisation of monosubstituted alkynes

\[
3 \text{R} = \text{H} \quad \xrightarrow{\text{catalyst}} \quad \text{R} = \text{R} \quad \text{R}
\]

Figure 1.57: Synthesis of 2-methylpyridine by catalytic cotrimerisation of acetylene with acetonitrile

\[
2 \text{HC} = \text{CH} + \text{C} = \text{N} \quad \xrightarrow{\text{catalyst}} \quad \text{N}
\]

Figure 1.58: Catalytic cyclotetramerisation of acetylene to cyclooctatetraene

\[
4 \text{HC} = \text{CH} \quad \xrightarrow{\text{catalyst}} \quad \text{O}
\]

Figure 1.59: General scheme for catalysed alkyne metathesis reactions

\[
\text{R}_1 = \text{R}_2 + \text{R}_3 = \text{R}_4 \quad \xrightarrow{\text{catalyst}} \quad \text{R}_1 = \text{R}_3 + \text{R}_2 = \text{R}_4
\]

Figure 1.60: Catalytic ring closing metathesis of alkynes to form cyclic alkynes, and subsequent catalytic ring opening metathesis polymerisation to form alkyne polymers
1.7.3 Activation of dihydrogen

Dihydrogen is a relatively unreactive molecule under ambient conditions and most reactions with this molecule require catalytic activation to achieve appreciable rates of product formation. This is primarily due to the reasonably high strength of the H-H bond (H-H bond dissociation energy = 103 kcal mol\(^{-1}\)), the nonpolar nature of the bond so that the molecule is unlikely to be attacked by nucleophiles or electrophiles, and the orientation of the frontier molecular orbitals of dihydrogen, which restrict direct concerted reactions between non-metals and dihydrogen, consequently leading to high activation energy barriers for these reactions. Because many bonds between hydrogen and non-metals are weaker than H-H bonds, there is often no thermodynamic driving force for cleaving the H-H bond and even when reactions are thermodynamically favourable, the reaction rate is usually very slow. In contrast, many metal centres react readily with dihydrogen because the symmetry of the metal frontier orbitals match the symmetry of the dihydrogen frontier orbitals, allowing a direct low activation energy barrier reaction between dihydrogen and the metal. Donation of electron density from the filled dihydrogen HOMO orbital to the empty LUMO \(d_{z^2}\) orbital of the metal, and back-donation of the filled \(d_{xz}\) (or \(d_{yz}\)) HOMO metal orbital to the empty LUMO dihydrogen orbital are often strong enough to cleave the H-H bond (Figure 1.61). The metal complexes produced from this process may then donate hydrogen to a substrate and the process is often catalytic in the presence of excess dihydrogen.\(^{117}\)

![Figure 1.61: Molecular orbitals involved in bonding interactions between metal centres (M) and dihydrogen](image)

Dihydrogen can be activated by either heterogeneous or homogenous catalysts. Heterogeneous catalysts are more common in industrial applications than homogeneous catalysts and some notable applications of these catalysts include: the synthesis of ammonia from dinitrogen and dihydrogen over solid iron or ruthenium catalysts via the Haber-Bosch process; hydrocracking
of heavy hydrocarbons to lighter hydrocarbons through catalytic C-C bond cleavage with dihydrogen over heterogeneous platinum, palladium, MoS₂ or WS₂ catalysts; Fischer-Tropsch synthesis of aliphatic compounds from syngas (Section 1.7.1.3); and the removal of sulfides from fuels through the hydrodesulfurisation reaction with dihydrogen, catalysed by alumina-supported metal sulfides. The latter process can be used to remove sulfur from a range of functional groups. For example, alkanes can be synthesised from alkyl thiols via this reaction, producing hydrogen sulfide as a by-product.⁷⁹,⁸⁰ Although homogenous catalysts have been developed for these reactions, heterogeneous catalysts are generally more effective and economically viable. While homogeneous catalysts are less common than heterogeneous catalysts in industrial reactions involving dihydrogen activation, they are usually much more effective than heterogeneous catalysts when selective transformations with dihydrogen are required.⁷⁸,⁷⁹ Examples of these reactions are discussed in this section.

Although the alkene hydroformylation reaction (Section 1.7.1.1) is the largest-scale homogeneously-catalysed dihydrogen activation reaction used in industry, the alkene hydrogenation reaction is also carried out on a large industrial scale. A variety of homogeneous catalysts can be used to catalyse alkene hydrogenation and the most common catalyst is a Rh(1)(Cl)(PPh₃)₃ complex, known as Wilkinson’s catalyst. A major advantage of Wilkinson’s catalyst is that hydrogenations are usually conducted at room temperatures and pressures, simplifying the design of reactors for these processes. Functional group tolerance is also reasonably high and alkenes with carboxylic acid, ester, nitrile, amide, alcohol, chloro, hydroxyl, or even nitro functional groups can be hydrogenated to alkanes without hydrogenating these functional groups. These catalyst systems also tolerate most sulfur-containing compounds, which tend to poison heterogeneous hydrogenation catalysts. However, aldehyde, ketone, and acid chloride functional groups are decarbonylated by Wilkinson’s catalyst. Generally, the Rh(1)(Cl)(PPh₃)₃-catalysed hydrogenation reaction is slower with more heavily substituted double bonds, and trans- alkenes are slower than cis- alkenes. Alcohols, acetone, THF, or benzene are the most common solvents used in these systems. Chlorinated solvents are generally avoided because hydrogen can be exchanged for chlorine in the catalytic cycle in the presence of these solvents.⁷⁹,⁸⁰ A catalytic cycle has been determined for alkene hydrogenations, catalysed by Wilkinson’s catalyst (Figure 1.62). In the first step, a triphenylphosphine ligand dissociates from the Rh(Cl)(PPh₃)₃ precatalyst. Oxidative addition of dihydrogen to the coordinatively unsaturated 14 valence electron Rh(1)(Cl)(PPh₃)₂ resting catalyst then yields a 16 valence electron Rh(Ⅲ)(Cl)(H)₂(PPh₃)₂ complex. Coordination of the alkene to this species then yields a coordinatively saturated π-bound Rh(Ⅲ)(Cl)(H)₂(PPh₃)₂(alkene) complex, and in the next step, the
alkene inserts into the cis-Rh-H bond, producing a 16 valence electron rhodium(III) cis-alkyl-hydrido complex. Reductive elimination of the coordinated alkyl group with the remaining hydride ligand yields the corresponding alkane and the catalyst returns to the resting state. In polar solvents, the vacant coordinate sites on the species shown Figure 1.62 are believed to be occupied by weakly coordinated solvent molecules.\textsuperscript{119}

![Catalytic cycle for the hydrogenation of alkenes with dihydrogen, catalysed by Wilkinson's catalyst](image)

**Figure 1.62: Catalytic cycle for the hydrogenation of alkenes with dihydrogen, catalysed by Wilkinson’s catalyst**

Since the development of the original triphenylphosphine-based Wilkinson’s catalyst (Rh\textsuperscript{3}(Cl)(PPh\textsubscript{3})\textsubscript{3}), many different phosphine ligands have been designed for these complexes. Generally, phosphines with moderate basicities have the greatest catalytic activities. Asymmetric hydrogenations can also be achieved by employing chiral bisphosphine ligands and
these are used industrially to synthesise many pharmaceuticals and fine chemicals where only one enantiomeric form is desired. Many other transition metal complexes also catalyse alkene hydrogenations, particularly those based on late transition metals (for example, Ru(H)(Cl)(PPh₃)₃ and [Co(H)(CN)₅]³⁻). Some early transition metal complexes and lanthanoid complexes (such as [La(H)(η⁵-C₅Me₅)₂]₂) can also catalyse these reactions. A few of these complexes are air-stable and some can even be used for hydrogenations in aqueous solutions. Additionally, some of these catalysts are tolerant to certain carbonyl-containing functional groups. Unsaturated compounds other than alkenes can also be catalytically hydrogenated using transition metal complexes (for example, alkynes and arenes) and a few catalyst systems are known to selectively hydrogenate trienes and dienes to monoalkenes. Furthermore, homogeneous hydrogenation catalysts have been used to hydrogenate C=O bonds (for example, of ketones to secondary alcohols; carboxylic acids to primary alcohols; and lactones to diols) and C=N bonds (for example, imines, enamines and oximes can be hydrogenated to amines).

Certain transition metal catalysts can also activate dihydrogen towards homologation reactions. In these reactions, a range of oxygen-containing molecules can be extended in chain length by one CH₂ unit by reacting with dihydrogen and carbon monoxide (usually from syngas), producing water as a by-product. Alcohols, aldehydes, carboxylic acids and esters can all be extended by one CH₂ group and further homologation of the products can also occur (Figure 1.63). Although these reactions are commercially useful, they remain at pilot-plant scales, due to the high reaction pressures and long reaction times that are required, and the low selectivities of these reactions for products of a specific chain length. Catalysts for these systems are usually cobalt, iron, ruthenium or rhodium complexes and promotors such as iodine or phosphines are often added. Homologations can be considered as a type of hydrocarbonylation reaction and are therefore related to the carbonylation reactions discussed in Section 1.7.1.2.
Amidocarbonylation reactions are another class of reaction where dihydrogen and carbon monoxide are activated by transition metal catalysts to form useful organic products. In these reactions, an $N$-acyl amino acid is synthesised from an amide, an alkene, dihydrogen and carbon monoxide (Figure 1.64). No waste by-products are produced in this reaction. Cobalt carbonyl-based complexes are commonly used to catalyse this reaction and a range of different substituents on the amide and the alkene reagents can be used. The use of allyl alcohols or oxiranes instead of alkenes produces $N$-acyl amino acids with higher and lower degrees of substitution, respectively. This process is used commercially to selectively synthesise a number of $N$-acyl amino acids from simple precursors, circumventing the use of otherwise laborious synthetic routes to these products. $N$-acyl amino acids are useful as surfactants, as polyamido acid chelating agents, and as intermediates for sweeteners, such as aspartame. The amidocarbonylation reaction is a greener alternative to the Strecker reaction, where amino acids are synthesised from aldehydes or ketones using highly toxic hydrogen cyanide and ammonia.  

![Figure 1.63: Examples of homologation reactions, catalysed by transition metal complexes](image-url)

Amidocarbonylation reactions are another class of reaction where dihydrogen and carbon monoxide are activated by transition metal catalysts to form useful organic products. In these reactions, an $N$-acyl amino acid is synthesised from an amide, an alkene, dihydrogen and carbon monoxide (Figure 1.64). No waste by-products are produced in this reaction. Cobalt carbonyl-based complexes are commonly used to catalyse this reaction and a range of different substituents on the amide and the alkene reagents can be used. The use of allyl alcohols or oxiranes instead of alkenes produces $N$-acyl amino acids with higher and lower degrees of substitution, respectively. This process is used commercially to selectively synthesise a number of $N$-acyl amino acids from simple precursors, circumventing the use of otherwise laborious synthetic routes to these products. $N$-acyl amino acids are useful as surfactants, as polyamido acid chelating agents, and as intermediates for sweeteners, such as aspartame. The amidocarbonylation reaction is a greener alternative to the Strecker reaction, where amino acids are synthesised from aldehydes or ketones using highly toxic hydrogen cyanide and ammonia.  

![Figure 1.64: Synthesis of $N$-acyl amino acids via the amidocarbonylation reaction](image-url)
1.7.4 Activation of carbon dioxide

Carbon dioxide is an excellent raw material for the synthesis of many organic products, because it is abundant, cheap, and relatively easy to store, handle, and transport. However, carbon dioxide has a high thermodynamic stability and reactions of this molecule with organic substrates usually have high activation energy barriers, limiting its use as a reagent in chemical reactions. This can be overcome by activating carbon dioxide with suitable transition metal complexes to synthesise various organic products. Although some of these reactions are catalysed by heterogeneous catalysts, most commercial catalyst systems are based on homogeneous complexes. Some examples of these reactions that are of industrial relevance are given in this section.

Cyclic carbonates are often synthesised commercially from the reaction of epoxides with carbon dioxide. These cyclic carbonates are often used as monomers for polymerisation reactions, or as reactants for the synthesis of hydroxyesters and hydroxyamines.\(^{117}\) Coordinatively unsaturated nickel(0) complexes (often nickel phosphines) are commonly used as catalysts for these reactions, although organic compounds such as amines, ammonium salts, halides, phosphines and carbonates are also known to catalyse these reactions. A catalytic cycle for this process, catalysed by nickel(0) complexes, is shown in Figure 1.65. The catalytic cycle begins with oxidative addition of an epoxide to the nickel centre of the resting catalyst, forming a nickel(II) oxametallacyclobutane complex. Carbon dioxide then inserts into the nickel-oxygen bond, and reductive elimination of the cyclic carbonate from this species regenerates the resting catalyst. Other transition metal catalysts, such as ZnEt\(_2\), catalyse the formation of polycarbonates instead of cyclic carbonates (Figure 1.66). This method is used for synthesising a number of polycarbonates commercially as an alternative to methods that use highly toxic phosgene gas.\(^{121}\)
Carbon dioxide can also be activated by transition metal complexes to synthesise cyclic products from dienes. An important example of this type of reaction is the synthesis of δ-lactones from 1,3-dienes and carbon dioxide, catalysed by coordinatively unsaturated palladium(0) phosphine complexes. Trialkylphosphines are particularly useful as ligands for these complexes. A catalytic cycle for the conversion of butadiene to a δ-lactone is shown in Figure 1.67. Precatalysts such as Pd(acac)\(_2\) are used in these reactions (acac = acetylacetonate). In the presence of trialkylphosphines, the acetylacetonate ligands dissociate and are replaced by two trialkylphosphine ligands, forming the Pd(PR\(_3\))\(_2\) resting catalyst. Butadiene then coordinates to the coordinatively unsaturated resting catalyst, forming a Pd(PR\(_3\))\(_2\)(diene) complex, where the diene is bound to the metal centre through two palladium-alkene π-bonds. Oxidative coupling of a second butadiene molecule forms a bis(allyl) palladium complex and one of the phosphine ligands dissociates. Insertion of carbon dioxide into the terminal end of one of the palladium-allyl bonds produces a palladium complex where the organic ligand is bound to the metal centre through one allyl group and one carboxylate oxygen atom. Reductive elimination and
isomerisation then forms the δ-lactone, and the catalyst returns to the resting state. This is a type of telomerisation reaction because a 1,3-diene is dimerised with the simultaneous addition of a nucleophile (in this case, carbon dioxide). Nitriles or cyclic carbonates are typically used as solvents for this reaction and the reaction also works in the absence of an added solvent. Various δ-lactones are synthesised commercially on small scales under mild conditions using this method (typically, at 80 °C and 40 bar), and can be further functionalised or ring-opened to form commercially useful derivatives. 120,121

Figure 1.67: Catalytic cycle for the telomerisation of 1,3-dienes and carbon dioxide to form δ-lactones, catalysed by palladium(0) phosphine complexes. L = neutral donor ligand, such as acetylacetonate (acac)
In a reaction similar to the telomerisation of 1,3-dienes, pyrones can be synthesised catalytically via the reaction of alkynes with carbon dioxide, in the presence of nickel or rhodium complexes. Ni(COD)$_2$ is often used as a precatalyst and the resting catalyst is formed after addition of a trialkylphosphine to the system (Figure 1.68). The postulated catalytic cycle for this process (Figure 1.68) is similar to the telomerisation of 1,3-dienes (Figure 1.67). After formation of the resting catalyst, the alkyne coordinates to the coordinatively unsaturated nickel centre, forming a $\pi$-bound nickel(0) alkyne complex. Oxidative coupling of carbon dioxide to this species yields an oxanickela-cyclopentene complex. A second alkyne molecule then inserts into the nickel-carbon bond to form a seven-membered cyclic nickel complex, which then reductively eliminates the pyrone and the catalyst returns to the resting state. THF or acetonitrile are used as solvents for this reaction under mild conditions (typically, 20 to 100 °C and about 10 bar) and these solvent molecules weakly coordinate to the metal centre. The reaction tolerates alkoxy and carboxyl functional groups on the alkynes, and either monosubstituted or disubstituted alkynes can be used. Basic phosphines with small cone angles are the most effective in these systems. One to two equivalents of the phosphine ligand are normally used relative to the metal centre and the catalytic activity decreases significantly if larger excesses of the phosphine are used, due to the formation of coordinatively saturated nickel complexes that are catalytically inactive. This method is currently used to synthesise pyrones on small industrial scales.$^{120,121}$ If diynes are used instead of monoalkynes, polypyrones can be synthesised (Figure 1.69). These polymers have high thermal stabilities but are at present not commercially viable.$^{121}$

Homogenous complexes can also catalyse the reaction of carbon dioxide with dihydrogen to give formic acid. If methanol is added to this reaction, methyl formate is synthesised, and if dimethylamine is used instead of methanol, dimethylformamide is produced (Figure 1.70). Although complexes based on nickel, ruthenium, rhodium, palladium or iridium are known to catalyse these reactions, they have not been commercialised yet because the current industrial methods used to synthesise these chemicals are much cheaper. With improved catalyst systems, this greener approach to formic acid, methyl formate and dimethylformamide production may eventually replace the current hazardous and polluting technologies.$^{120,121}$
Figure 1.68: Catalytic cycle for the synthesis of pyrones from alkynes and carbon dioxide, catalysed by nickel(0) complexes. L = neutral donor ligand such as 1,5-cyclooctadiene (COD)

Figure 1.69: Synthesis of polypyrones from diynes and carbon dioxide, catalysed by nickel complexes

\[
\begin{align*}
n \text{HC} &= \text{C} - \text{R} - \text{C} \equiv \text{CH} + n \text{CO}_2 \xrightarrow{\text{nickel catalyst}} \left[ \begin{array}{c} \text{O} \\ \text{R} \end{array} \right]_n 
\end{align*}
\]
Although the catalytic activation of carbon dioxide by transition metal complexes is currently used in only a handful of industrial syntheses, carbon dioxide has enormous potential as a cheap and renewable feedstock for the synthesis of a vast range of chemical products that are currently produced from fossil fuel-derived feedstocks. For example, heterogeneous catalysts are being developed for the hydrogenation of carbon dioxide to methanol as a greener alternative to the current commercial synthesis of methanol from carbon monoxide and dihydrogen (syngas). While this reaction has been successfully established in several pilot plants, it is currently not economically competitive with the production of methanol from syngas.\textsuperscript{117} Catalysts are also being developed for the production of aldehydes from carbon dioxide and dihydrogen, which are currently synthesised via the hydroformylation of carbon monoxide with alkenes (Section 1.7.1.1).\textsuperscript{119} Both the hydrogenation of carbon monoxide to methanol and the synthesis of aldehydes via the hydroformylation reaction are carried out on very large scales worldwide. Replacing fossil fuel-derived carbon monoxide with carbon dioxide from renewable sources therefore provides a greener approach to the synthesis of these commodity chemicals. The development of improved catalyst systems is crucial to this movement.\textsuperscript{117}


2 Chapter 2: Synthesis of New Ligands with Pyridinium Amide Functionalities

2.1 Introduction

2.1.1 Structural and spectroscopic properties of pyridinium amides

As discussed in Section 1.3, two different resonance forms contribute to the structures of pyridinium amides: a zwitterionic (or charge-separated) form and a neutral imine form. In the solid state, the imine form usually predominates, whereas in solution, either form (or even both) may predominate. Several studies have investigated the resonance form that various pyridinium amides adopt in solution under a variety of conditions.\textsuperscript{125-127} It has generally been found that electron-withdrawing substituents on the pyridinium amide (at position R\textsubscript{2} in Figure 1.1) and higher polarity solvents increase the contribution of the zwitterionic form.\textsuperscript{125} These effects are summarised in the following sections.

2.1.1.1 Effect of substituents on the spectroscopic properties of pyridinium amides

Giorgio Pagani of the University of Milano-Bicocca (Italy) and his research group have used NMR spectroscopy to investigate the relative contribution of the neutral imine resonance form to the structure of deprotonated pyridinium amides in solution.\textsuperscript{125} Para-substituted pyridinium amides of the general structure shown Figure 2.1 were used in these studies. In the fully zwitterionic resonance form (A, Figure 2.1), the proton and carbon atoms at positions 2 and 3 of monosubstituted pyridinium amides (where R\textsubscript{2} = H) are expected to be equivalent by NMR spectroscopy because of the relatively unhindered rotation about the N-C1 bond. In contrast, for the imine resonance form (B), the double bond character of the C=N imine bond hinders rotation of the pyridyl ring and positions 2 and 3 become inequivalent because one proton faces the essentially parallel \textit{cis} phenyl ring, whereas the other proton does not. The proton facing the \textit{cis} phenyl ring (proton 2 in Figure 2.1) experiences a shielding effect and therefore shifts upfield relative to the other proton. The magnitude of the difference in chemical shifts between positions 2 and 3 by either \textsuperscript{1}H or \textsuperscript{13}C NMR spectroscopy can therefore be used to determine the relative contribution of resonance form B in a series of related compounds. Using this method for the
series shown in Figure 2.1, the relative contribution of zwitterionic resonance structure A has been found to increase with more electron-withdrawing substituents. For example, for the compounds substituted with an electron-withdrawing nitro or p-tolylsulfonate group at position R1, no difference between the chemical shifts of positions 2 and 3 were observed at room temperature in DMSO-\textit{d}6 and CDCl3, suggesting that zwitterionic resonance form A predominates in these compounds. However, for the pyridinium amide substituted with a proton at the R1 position, a large difference between positions 2 and 3 were observed by 1H and 13C NMR spectroscopy at room temperature in DMSO-\textit{d}6 and CDCl3, suggesting that there is a strong contribution from imine resonance form B to the structure of this compound in solution.\textsuperscript{125}

![Zwitterionic form and Imine form](image)

**Figure 2.1: Pyridinium amides investigated by Pagani \textit{et al.}, showing the two limiting resonance forms of these compounds and an atom numbering scheme**

Variable temperature NMR studies of the R1/R2 = H/H pyridinium amide in DMSO-\textit{d}6 (Figure 2.1) demonstrated that as the temperature increases, the difference in 1H NMR chemical shifts between positions 2 and 3 decreased until they became equivalent at about 313 K. Although Pagani \textit{et al.} attributed this effect to the zwitterionic resonance form (A) becoming dominant above 313 K, this could also be due to an increase in the rate of rotation about the C=N bond of imine resonance form (B) as the temperature increases. For the mono nitro-substituted pyridinium amide, which was predominantly in zwitterionic resonance form A at room temperature, separation of 1H NMR signals 2 and 3 was observed at about 180 K upon cooling an 8:1 CD2Cl2/CDCl3 solution of this compound. Pagani \textit{et al.} inferred that this was due to
resonance form B becoming dominant below 180 K for this compound, but again did not take into account the fact that the rate of rotation about the C=N bond of resonance form B is expected to increase with increasing temperature.\textsuperscript{125}

The aforementioned NMR studies were used as a qualitative method for determining the relative contributions of resonance forms A and B to the structures of pyridinium amides in solution. A more quantitative method was developed by determining the π-electron density on the pyridinium nitrogen atom, using \(^{15}\text{N}\) NMR spectroscopy. Comparison of the \(^{15}\text{N}\) NMR chemical shifts of the pyridinium amides to the \(^{15}\text{N}\) NMR chemical shifts of compounds that represent the limiting resonance forms A (using 1-methylpyridinium triflate) and B (using 1-methylpyridin-4(1H)-imine) was used to determine the approximate location of the pyridinium amides on a continuum between the fully zwitterionic and fully imine resonance forms. The empirical formula \(\Delta\delta^{15}\text{N} = -366\Delta q^{\pi}\text{N}\) was then used to determine the relative π-electron density (\(\Delta q^{\pi}\text{N}\), in electrons) on the pyridinium nitrogen atom by calculating the difference in the \(^{15}\text{N}\) NMR chemical shifts (\(\Delta\delta^{15}\text{N}\)) between the pyridinium amide and a reference compound in the series of related pyridinium amide compounds. Both the \(^{15}\text{N}\) NMR chemical shift and the relative π-electron density increased as the substituents \(R_{1}/R_{2}\) became more electron-withdrawing. This indicated that more positive charge resides on the pyridinium nitrogen atom of pyridinium amides that contain more electron-withdrawing substituents, again confirming that the contribution from resonance form A increases with more electron-withdrawing substituents. In contrast, the \(^{15}\text{N}\) NMR signals of the amide nitrogen atom shifted upfield with more electron-withdrawing substituents due to an increase in charge separation. This was attributed to increasing stabilisation of the negative charge on the amide nitrogen atom with increasing electron-withdrawing capacity of the substituents. It was concluded that this negative charge is relatively localised and is not significantly delocalised onto the aromatic ring.\textsuperscript{125} Pagani et al.\textsuperscript{125} also synthesised a pyridinium amide that was substituted with 2,4-dinitrobenzene instead of a methyl group on the pyridinium nitrogen atom of the \(R_{1}/R_{2} = p\)-tolylsulfonate/H substituted pyridinium amide. This modification further increased the electron withdrawing nature of the pyridinium amide, and zwitterionic resonance form A was found to be even more dominant than for the other pyridinium amides that were studied.
NMR and UV-visible spectroscopic studies of pyridinium amides have shown that the relative contribution of zwitterionic resonance form \( A \) (Figure 2.1) increases with increasing solvent polarity. For example, Pagani et al. used the \(^1\)H, \(^{13}\)C and \(^{15}\)N NMR spectroscopic methods that were described above in Section 2.1.1.1 to demonstrate that the zwitterionic resonance form becomes more dominant when the same pyridinium amide is dissolved in higher polarity deuterio-solvents. Pagani et al. also demonstrated that UV-visible absorption spectroscopy can be used to determine the effect that solvents have on the structures that pyridinium amides adopt in solution. Thus, the wavelength at \( \lambda_{\text{max}} \) of the UV-visible absorption bands of the pyridinium amides shown in Figure 2.1 shifted considerably with changes in solvent polarity (Table 2.1). This effect has been termed solvatochromism. For the nitro- and bis(nitro)-substituted pyridinium amides, electronic transitions were observed in the visible region, whereas for the \( p \)-tolylsulfonate-substituted pyridinium amides, these transitions were observed in the UV region. UV-visible absorption spectra were not recorded for the unsubstituted \((R_1/R_2 = H/H)\) pyridinium amide.

The solvent polarities given in Table 2.1 were reported as Reichardt solvent polarity scale \((E_T)\) values, which places solvents in a somewhat different polarity order to the commonly used dielectric constant values. The Reichardt scale is an empirical solvent polarity scale that is derived from the measured UV-visible absorption spectra of the solvatochromic dye, pyridinium N-phenolate betaine, and is given here in units of kcal mol\(^{-1}\). Pagani et al. have postulated that Reichardt solvent polarity values represent solvent polarities in pyridinium amide systems better than dielectric constant values. A clear trend of decreasing wavelength at \( \lambda_{\text{max}} \) with increasing solvent polarity was observed for the \( R_1/R_2 = SO_2\text{-}p\text{-}tol/H \) compound (Table 2.1), while for the \( R_1/R_2 = NO_2/H \) and \( R_1/R_2 = NO_2/NO_2 \) compounds, the wavelength at \( \lambda_{\text{max}} \) was longest in solvents with intermediate \( E_T \) values. Based on the common interpretation for solvatochromic interactions, Pagani et al. inferred from these results that the molecular dipole moment of the ground state generally increases with respect to the molecular dipole moment of the excited state as the solvent polarity increases. Because the difference between the ground and excited state dipole moments is expected to be larger in zwitterionic resonance form \( A \) than in imine resonance form \( B \), these results suggested that (in agreement with the NMR studies) the zwitterionic character of the pyridinium amide ground state generally increased with increasing solvent polarity. Pagani et al. noted, however, that these solvatochromic results must be treated cautiously because conclusions are in principle valid only if the same resonance
form (A or B) is maintained when the solvent is changed, and this was not always the case in these studies.\textsuperscript{125}

**Table 2.1: Effect of solvent polarity on the wavelength at $\lambda_{\text{max}}$ observed in the UV-visible absorption spectra of various pyridinium amides**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$E_T$ \textsuperscript{b}</th>
<th>$\text{NO}_2$/H</th>
<th>$\text{NO}_2$/NO$_2$</th>
<th>SO$_2$-p-tol/H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>55.4</td>
<td>408 \textsuperscript{c}</td>
<td>427</td>
<td>299</td>
</tr>
<tr>
<td>Acetonitrile</td>
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<td>432</td>
<td>449</td>
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</tr>
<tr>
<td>DMSO</td>
<td>45.1</td>
<td>457</td>
<td>466</td>
<td>307</td>
</tr>
<tr>
<td>N-N-dimethylformamide</td>
<td>43.2</td>
<td>448</td>
<td>460</td>
<td>307</td>
</tr>
<tr>
<td>Acetone</td>
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<td>432</td>
<td>447</td>
<td>d</td>
</tr>
<tr>
<td>Chloroform</td>
<td>39.1</td>
<td>412</td>
<td>429</td>
<td>310</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Substituents on the phenyl ring of the pyridinium amides shown in Figure 2.1. Values have not been recorded for $R_1/R_2 = \text{H/H}$.  
\textsuperscript{b} Reichardt solvent polarity scale value (in kcal mol\textsuperscript{-1}). Larger values indicate more polar solvents.  
\textsuperscript{c} A pellet of sodium hydroxide was added to the cuvette to prevent protonation of the pyridinium amide in methanol.  
\textsuperscript{d} Peak obscured by solvent absorption band.\textsuperscript{125}

Hassimi Traore \textit{et al.} (University of Wisconsin-Whitewater, USA), have investigated solvatochromism in an ortho-substituted pyridinium amide of the structure shown in Figure 2.2.\textsuperscript{127} This compound was soluble in both water and $n$-hexane, and a considerable shift in absorption maxima was observed between the UV-visible spectra recorded in these two solvents. In both solvents, two absorption maxima were observed between 200 and 600 nm. The shorter wavelength peak maximum shifted from 251 nm in $n$-hexane to 231 nm in water, while the longer wavelength peak maximum shifted from 370 nm in $n$-hexane to 312 nm in water. These results suggested that the ground electronic state becomes more strongly stabilised relative to the excited electronic state as the solvent polarity increases. However, Traore \textit{et al.}\textsuperscript{127} attributed the shorter $\lambda_{\text{max}}$ wavelengths in water to protonation of the pyridinium amide to form a pyridinium amine, rather than to an increase in the contribution of the zwitterionic resonance form in water. This was based on the observation that the UV-visible absorption spectrum of the pyridinium amine in water remained virtually unchanged after addition of excess hydroiodic acid. It was also postulated that negligible protonation of the pyridinium amide occurs in $n$-
hexane. Thus, the pyridinium amide protonated when it was added to water, but did not protonate when it was added to n-hexane. The UV-visible spectra were not recorded in water in the presence of a base, nor were they recorded in polar aprotic solvents, and so conclusions were not made on the effect that solvent polarity has upon the dominant resonance form that the non-protonated pyridinium amide adopts in solution.\textsuperscript{127}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{structure.png}
\caption{Structure of a pyridinium amide used by Traore et al. for solvatochromic studies}
\end{figure}

Fluorescence spectra of the pyridinium amide shown in Figure 2.2 were also recorded by Traore et al. in n-hexane and water.\textsuperscript{127} In n-hexane, an excitation wavelength of 360 nm was selected. Compared to the 360 nm Raman transition and the second-order diffraction from the fluorimeter grating at 720 nm, the intensity of the fluorescence emission from the pyridinium amide in n-hexane was very low and was difficult to distinguish from the noise of the spectrum. On the other hand, the intensity of the fluorescence emission from the pyridinium amine in water (using an excitation wavelength of 300 nm) was very strong relative to the Raman transition and the emission maximum occurred at about 360 nm. These differences have again been attributed to protonation of the pyridinium amide in water to form a pyridinium amine.\textsuperscript{127}

2.1.1.3 Spectroscopic properties of compounds structurally related to pyridinium amides

Albrecht and Wright et al.\textsuperscript{131} (University College Dublin, Ireland and the University of Auckland, New Zealand, respectively) have observed solvatochromic effects in ruthenium complexes of pyridinium amidate ligands, whose structures are shown in Figure 2.3. Pyridinium amidates are structurally related to pyridinium amides and have an acyl group bound to the amine nitrogen atom. The particular pyridinium amidate ligand shown in Figure 2.3 is bound to an N-heterocyclic carbene (NHC). Three resonance forms contribute to the structure of pyridinium amidates and these are shown in Figure 2.3.\textsuperscript{131}
Figure 2.3: Ruthenium-pyridinium amidate complexes used in solvatochromic studies by Albrecht and Wright *et al.*, showing the three resonance forms of the pyridinium amidate ligand

Proton NMR spectroscopy has been used to determine the relative contribution of resonance forms A-C to the structure of the R = Me ruthenium-pyridinium amidate complex in different deuterio-solvents (Figure 2.3). When the solvent was changed from CD$_2$Cl$_2$ to DMSO-$d_6$, most of the ligand $^1$H NMR chemical shifts remained essentially unchanged, except for those at positions 1a, 1b, 2a and 2b (Figure 2.4). In both deuterio-solvents, protons 1a and 1b were equivalent. Protons 2a and 2b were also found to be equivalent. However, the difference in chemical shift between protons 1 and 2 was significantly larger in DMSO-$d_6$ (0.33 ppm) than in CD$_2$Cl$_2$ (0.19 ppm) and the chemical shift difference in methanol-$d_4$ was similar to that observed in DMSO-$d_6$. The difference in chemical shift is expected to increase with increasing contribution of zwitterionic resonance form A (Figure 2.3) because protons 2a and 2b are closer to the positively-charged pyridinium nitrogen atom and are therefore more deshielded. Therefore, like the pyridinium amides studied by Pagani *et al.*, the contribution of resonance form A was found to increase with increasing solvent polarity for the ruthenium-pyridinium amidate complexes. Strong amide stretching frequencies at 1606 cm$^{-1}$ (dichloromethane) and 1605 cm$^{-1}$ (methanol) suggested that the carbonyl unit does not change significantly with changes in solvent polarity and it was therefore concluded that the contribution from resonance structure C in solution is minor. It has been speculated that this may be due to the ionic character of the Ru-N bond of resonance form A disfavouring the migration of negative charge onto the oxygen atom.
UV-visible absorption spectroscopy also suggested that the contribution of resonance structure A to the structure of the R = Me ruthenium-pyridinium amidate complex (Figure 2.3) in solution increases with increasing solvent polarity. UV-visible absorption spectra of this complex were measured in mixtures of methanol and dichloromethane. Strong solvent-dependent absorptions were observed below 240 nm and a very broad and weak non-solvent dependent absorption band was observed with a peak maximum at 275 nm. The wavelength at $\lambda_{\text{max}}$ for the solvent-dependent absorptions could not be determined because it occurred below the solvent cut-off wavelength, where the solvent itself begins to absorb strongly. The change in peak wavelength with changing solvent polarity was instead determined by measuring the wavelength at a constant molar absorptivity value (arbitrarily set to 1,000 L mol$^{-1}$ cm$^{-1}$). In 100% methanol, the wavelength at this molar absorptivity ($\lambda_{\varepsilon 1000}$) was 208 nm. As the percentage of dichloromethane in the methanol solution increased, a non-linear change in wavelength was observed. With only 1% dichloromethane, $\lambda_{\varepsilon 1000}$ increased to 221 nm and as the relative amount of dichloromethane in methanol increased further, the change in $\lambda_{\varepsilon 1000}$ was more gradual, reaching a wavelength of 235 nm in 100% dichloromethane. Between about 10% and 100% dichloromethane, the plot of $\lambda_{\varepsilon 1000}$ wavelength versus percent dichloromethane in methanol was approximately linear.\textsuperscript{131} It was therefore concluded that a small decrease in solvent polarity results in a large increase in the relative contribution from resonance form B to the structure of the complex in solution, again confirming that the structure of the pyridinium amidate ligand is to some extent solvent-dependent.\textsuperscript{131}

Cyclic voltammetry (CV) experiments provided further confirmation that resonance form A is more favoured in higher polarity solvents. CV studies in dichloromethane and methanol showed irreversible oxidations that were presumably metal-centred. In dichloromethane, these
oxidations occurred at +0.91 and +0.90 V (versus a saturated calomel electrode, SCE) for R = Me and R = iPr, respectively, whereas in methanol, oxidations were observed at +0.79 and +0.75 V (versus SCE). These changes were substantial when compared to the corresponding values for the Fc*/Fc couple of ferrocene in dichloromethane (+0.46 V) and methanol (+0.52 V) and so could not be attributed to solvent effects alone. This was expected, because an increase in contribution of resonance form A in more polar solvents increases electron donation from the ligand to the metal centre and therefore makes the complex easier to oxidise.\(^{131}\)

X-ray crystallography of the R = iPr ruthenium-pyridinium amidate complex revealed that the carbon-carbon bonds between 1a and 2a and between 1b and 2b are significantly shorter than the other two carbon-carbon bonds of the pyridyl ring, suggesting that resonance form B predominates in the solid state. Analysis of the X-ray crystal structure suggested that the nitrogen atom is sp\(^2\)-hybridised, which also indicated that there is a strong contribution from resonance structure B in the solid state. The presence of a sp\(^2\)-hybridised nitrogen atom was inferred from the planar angle between the pyridinium ring centroid, the pyridinium nitrogen atom and the pyridinium methyl group carbon atom (179°), and also from the sum of the angles around the pyridinium nitrogen atom (360°).

### 2.1.2 Design of the new pyridinium amide ligands

The primary goal of the research described in this thesis is to develop new macrocyclic ligands that incorporate pyridinium amide functional groups into their structures and to investigate the structural, spectroscopic, and catalytic properties of the metal complexes of these ligands. Macrocyclic structures were chosen for the target ligands because these are expected to be more robust than acyclic analogues in catalytic reactions. Metal complexes of these ligands are studied as catalysts for a range of reactions in Chapters 4 and 5. Macrocyclic structures were also selected for the target ligands because of their structural similarities to TAML, porphyrin, and TMTAA ligands (see Section 1.5 for structures of these ligands), and because various metal complexes of TAML, porphyrin, and TMTAA ligands are effective catalysts for a wide variety of reactions. Macrocyclic ligands containing pyridinium amide functional groups are unknown in the literature and the structural and spectroscopic properties of these ligands may differ from known acyclic pyridinium amide ligands. The properties of the newly synthesised macrocyclic ligands have been investigated and the results are reported in this chapter.
2.2 Synthesis of the new pyridinium amide ligands

2.2.1 Synthetic route towards the target macrocyclic ligand

The initial route that was used to synthesise the target macrocyclic ligand is shown in Figure 2.5. In the first step, 3-amino-2-chloropyridine was successfully N-methylated with methyl triflate in dichloromethane to obtain 3-amino-2-chloro-1-methylpyridinium triflate (A) in 92% yield after purification. The subsequent reaction of A with oxalyl chloride and triethylamine in THF was used to synthesise 3,3’-(oxalylbis(azanediyi))bis(2-chloro-1-methylpyridin-1-ium) triflate (B) in 81% yield following purification. Although, for convenience, B is drawn with a *cis* oxalamide group in Figure 2.5, the X-ray crystal structure that was obtained of B (Figure 2.6) confirms that this group is transoidal, as expected. Full experimental procedures for these reactions and characterising data for the new compounds are given in Section 2.5.

![Diagram of synthetic route](image)

**Figure 2.5: Initial synthetic route towards the new pyridinium amine macrocycle (C). Deprotonation of this macrocyclic ligand would give the macrocyclic pyridinium amide**
Analysis of the X-ray crystal structure of B (Figure 2.6) reveals that the molecule has a centre of inversion that lies at the centre of the C(1)-C(1’) bond. Thus, the symmetry related atoms on each half of the molecule are labelled C(1)/C(1’), N(1)/N(1’), O(1)/O(1’), and so forth in Figure 2.6. As expected, the oxalamide bond is transoidal, presumably to minimise steric repulsions between the two O(1) atoms. The angle between the plane through C(1)-N(1)-O(1) and the plane through C(1’)-N(1’)-O(1’) is 0.00°, indicating that the oxalamide group is planar. An intramolecular hydrogen bond may exist between O(1’) and H(1), which helps to hold the oxalamide bond in a transoidal geometry. Although the distance between N(1) and O(1’) in the X-ray crystal structure of B (2.697 Å) is considerably shorter than the typical nitrogen-oxygen distances found for N-H···O type hydrogen bonds (2.81-3.04 Å), the small N(1)-H(1)···O(1’) angle (106.5°) suggests that this hydrogen bond is not strong. Furthermore, some conservative sources have set an angular cut-off of >110° for hydrogen bonds, although other sources state a cut-off of >90° for hydrogen bonds. The pyridinium rings of B are twisted away from the oxalamide unit (angle between the plane through N(1)-C(1)-O(1) relative to the plane through the pyridinium ring = 47.11°), presumably to minimise steric repulsions between O(1) and H(3), and between Cl(1) and H(1).

Figure 2.6: Numbering scheme for the atoms in the X-ray crystal structure of 3,3’-(oxalylbis(azanediyl))bis(2-chloro-1-methylpyridin-1-ium) triflate (B). The two triflate counteranions have been omitted for clarity.

For the oxalamide unit of B, the C(1)-C(1’) bond length (1.538(2) Å) is close to the C-C bond lengths of RO(O)C-C(O)OR dialkyl oxalate compounds (1.538 ± 0.007 Å). Meanwhile, the C(1)=O(1) bond length of B (1.2154(16) Å) is somewhat shorter than the typical C=O bond length of secondary amides (1.231 ± 0.012 Å), and the C(1)-N(1) bond length of B (1.3617(16) Å).
Å) is somewhat longer than the typical C-N bond length of secondary amides (1.334 ± 0.011 Å). A full list of bond lengths and bond angles for the X-ray crystal structure of B are given in Appendix A.

Although A and B were successfully synthesised (Figure 2.5), problems were encountered in the ring-closing step used to synthesise target macrocycle C from B through treatment with 1,2-phenylenediamine. A base was added to react with the hydrochloric acid by-product produced from B and 1,2-phenylenediamine. In the absence of a base, the hydrochloric acid by-product would otherwise react with 1,2-phenylenediamine or the mono-substituted intermediate to the macrocycle (Ca, Figure 2.7), preventing complete conversion of B to C. Although a variety of bases (NaHCO₃, Na₂CO₃, NEt₃, DBU, K’BuO and NaH) were used in this reaction, NMR spectroscopy indicated that, despite the use of high dilution and stringently dry conditions, a large number of major products were synthesised in each reaction. While mass spectrometry suggested that one of these products was in fact the desired macrocycle, the yield was very low and purification from the large number of by-products was difficult. Reactions using sub-stoichiometric, stoichiometric, small excesses and large excesses of base were attempted, and the reaction temperatures, the order of substrate addition, and the stoichiometric ratio of B to 1,2-phenylenediamine were also changed. However, a large number of major products were still obtained in each reaction. Because mass spectrometry suggested that some of the by-products formed in these reactions are oligomers and polymers, reactions were attempted at very high dilution. Slow addition of the reagents (in various orders of addition) was also carried out in some of these reactions to obtain high relative dilutions. The relative number and amount of by-products decreased only slightly with these reaction modifications. THF was used as the solvent for all of the aforementioned reactions and similar results were obtained for reactions in acetonitrile. Attempts to purify the macrocycle by recrystallisations, extractions and column chromatography were unsuccessful. High temperature solventless reactions with nitrogen gas purging through the flask were also attempted to drive off the hydrochloric acid by-product, but these experiments resulted in loss of 1,2-phenylenediamine by sublimation and decomposition of the reactants.

Further reactions were attempted in the absence of an added base. Using this method, the desired macrocycle (C) was obtained as an approximately 1:2 mixture of C with a mono-substituted product, Ca (Figure 2.7), along with small amounts of unreacted B and 1,2-phenylenediamine. The monosubstituted product in this case acts as an internal base for the hydrochloric acid by-
product. By varying reaction time, temperature, solvent (THF or acetonitrile), order of reagent addition, dilution, and reagent stoichiometry, the maximum amount of macrocycle C obtained was 25\% (by $^1$H NMR spectroscopy, relative to C$_A$ and unreacted reagents). A small amount (about 10\%) of each reagent was left unreacted, even after prolonged reaction times. The best conditions that were found for this reaction are shown in Figure 2.7. Many attempts were made to separate the macrocycle from the acyclic by-product and the unreacted reagents, using normal-phase silica, reverse-phase silica, neutral alumina, and basic alumina columns with various eluent mixtures, and also by various recrystallisations and extractions. Although some of these purification methods removed the unreacted reagents, the macrocycle and the acyclic by-product were not successfully separated. The addition of a base to the product mixture, either in situ to the completed reaction, or to the isolated product mixture (either crude or partially purified) again resulted in the formation of a large number of by-products. This suggested that the presence of a base is detrimental to macrocycle formation and that the macrocycle itself may even decompose in the presence of a base. Similar problems were encountered when the TAML ligand, H$_4$B$_1$ (Figure 1.27) was ring-closed with 1,2-phenylenediamine.$^{135}$

![Figure 2.7: Best conditions found for the synthesis of macrocycle C in the absence of an external base: 1,2-phenylenediamine was added slowly dropwise over an hour to a dilute refluxing solution of B in acetonitrile, followed by refluxing the solution overnight (14 hours)](attachment:figure27.png)

The reason for the low macrocycle yields obtained in the presence of a base could be because base-induced decomposition is more energetically-favoured than the ring-closing reaction. The transoidal nature of the oxalamide bond in B and the close proximity of the N-methyl protons to the phenyl ring protons in C may increase the energy barrier to this ring-closing reaction. To test this, an acyclic analogue of macrocycle C was synthesised by reaction of one equivalent of B with two equivalents of p-toluidine, in the presence of DBU (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene). After 1 hour in refluxing acetonitrile, the desired product, D (Figure 2.8) was obtained in high yield (by $^1$H NMR spectroscopy). Although D is drawn with a cis oxalamide bond in Figure 2.8 (for comparison to the structure of C), this bond is expected
to prefer a transoidal arrangement. It is noteworthy that the oxalamide bond of B does not have to undergo internal rotation to form product D, unlike in the formation of macrocycle C from B. Also, unlike the phenyl ring in C, the phenyl rings of the p-toluidine substituents can rotate so that they minimise steric repulsions between the N-methyl protons and the phenyl protons. The ready formation of D in high yield suggests that steric strain in macrocycle C may indeed be hindering its formation from B in the presence of a base.

![Figure 2.8: Synthesis of an acyclic analogue of macrocycle C by reaction of p-toluidine with B, in the presence of DBU](image)

2.2.2 Modifications to the original synthetic route

Because the ring-closing of B with 1,2-phenylenediamine to form macrocycle C and the purification of this product was of limited success, both the synthetic route and the structure of the target macrocycle were modified. The N-methyl groups of the new target macrocycle, H (Figure 2.9) are para to the phenyl N-H groups in order to minimise steric repulsions between the N-methyl protons and the phenyl protons. The synthetic route (Figure 2.9), was also changed so that the macrocycle was synthesised from the opposite end to the route used to synthesise macrocycle C (Figure 2.5). The ring-closing step in the synthesis of H was designed so that the carboxamide bonds were formed in the final step, via the addition of oxalyl chloride. This is because this process is expected to occur rapidly and steric pressures would be relatively small.
In the first step of the synthetic route to macrocycle H, N-methylation of 4-chloro-3-nitropyridine with methyl triflate in dichloromethane was used to obtain 4-chloro-1-methyl-3-nitropyridinium triflate (E) in 90% yield after purification. In the next step, F was synthesised in 90% yield (after purification) by refluxing two equivalents of E with one equivalent of 1,2-phenylenediamine and two equivalents triethylamine in 1,4-dioxane. The nitro groups on F were then reduced to amino groups using dihydrogen (1 atmosphere) and a catalytic amount of 10% palladium on charcoal in ethanol, giving G in 88% yield after purification. Although G can be obtained directly by reaction of 3-amino-4-chloro-1-methylpyridinium triflate with 1,2-phenylenediamine, this reaction was very slow in refluxing 1,4-dioxane (weeks), presumably due to the more electron-rich nature of the pyridinium ring in this compound than in E.

In the final step of the synthetic route (Figure 2.9), macrocycle H was obtained in moderate yield by the reaction of G with a slight excess of oxalyl chloride and a slight excess of sodium hydride at room temperature in acetonitrile. In the crude product, the $^1$H NMR signals of macrocycle H were sharp and the only significant by-product (about 20 to 30% relative to H by integration) was observed as a set of broad signals shifted very slightly (less than 0.05 ppm) from the $^1$H NMR signals of H. Mass spectrometry of this product mixture suggested that this by-product is a [2+2] macrocycle. Repeating the reaction under very dilute conditions and
adding the oxalyl chloride slowly over several hours decreased the relative amount of the [2+2] macrocycle only slightly. Many purification attempts were made to separate the [2+2] macrocycle from the [1+1] macrocycle (H), but these were unsuccessful. These included normal-phase silica, reverse-phase silica, neutral alumina, and basic alumina columns with various eluents, including columns with small amounts of acids or bases added to the eluent; recrystallisations; exchange of the anions for PF$_6^-$, BF$_4^-$ and BPh$_4^-$ on anion exchange columns, and also by addition of a large excess of the sodium salt of these anions to a solution of the crude macrocycle, followed by purification using columns and recrystallisations; and size exclusion chromatography on Sephadex LH-20, using various eluents. In each case, little or no separation of H from the [2+2] macrocycle was achieved. Purifications were also attempted by deprotonating the crude macrocycle (either in situ in the reaction by adding excess base, or by the addition of a base to the crude isolated product), followed by purification of the deprotonated product by column chromatography or recrystallisations. However, in these experiments, the deprotonated product partially reprotonated in the presence of adventitious water. Modifications to the reaction conditions used to synthesise the macrocycle were also attempted by varying reaction temperatures, reaction times, the order of reagent addition, reagent stoichiometries, dilution, and the bases and solvents used (acetonitrile or THF). Although product yields varied in these reactions, a significant amount of [2+2] macrocycle still formed in each reaction.

Because purification of macrocycle H was unsuccessful, the target macrocycle was again modified. The new target pyridinium amine macrocycle, I, is shown in Figure 2.10. This new macrocycle required dimethylmalonyl dichloride to be used in the ring-closing step instead of oxalyl chloride. While the structure of macrocycle H is similar to the structure of the H$_4$B$^J$ TAML ligand, macrocycle I is similar to the structure the H$_4$B$^*$ TAML ligand (Figure 1.27). The reaction conditions used to synthesise I were varied and the highest product yield was obtained using the procedure given in Section 2.5.9. In this method, G was deprotonated with a moderate excess of NaH in dry acetonitrile at room temperature and the excess sodium hydride was then removed by air-free filtration. The filtrate was then heated to 70 °C and a slight excess of dimethylmalonyl dichloride in dry acetonitrile was added slowly dropwise over 2 hours. The solution was stirred for a further 2 hours at 70 °C, and then at room temperature overnight. After removal of the solvent, the macrocycle was isolated by deprotonating the two pyridinium amine N-H protons with aqueous sodium carbonate and extracting the neutral deprotonated pyridinium amide macrocycle, H$_2$L$_m$, into dichloromethane (Figure 2.11). The extracted H$_2$L$_m$ macrocycle was dried thoroughly under vacuum and was then further purified by column chromatography on basic alumina, obtaining H$_2$L$_m$ in 20% yield (based on the amount of G used). Unlike
macrocycle $\text{H}$, the $\text{H}_2\text{L}_m$ macrocycle is stable in the bisdeprotonated (neutral overall) form and is not readily reprotonated by adventitious water. Two limiting resonance forms can be drawn for $\text{H}_2\text{L}_m$: a charge-separated form, where both pyridinium amide groups are zwitterionic, and a neutral bis(imine) form (Figure 2.11). Unlike simple pyridinium amide compounds published in the literature that have only one pyridinium amide group, intermediate resonance forms of $\text{H}_2\text{L}_m$ can also be drawn, where one pyridinium amide is in the charge-separated form and the other is in the imine form. Because macrocycle $\text{H}_2\text{L}_m$ was successfully synthesised and purified, its structural and spectroscopic characteristics were studied further (see later in this chapter). The ligand was also metallated using various metal salts and the products formed are described in Chapter 3.

Figure 2.10: Synthesis of pyridinium amine macrocycle $\text{I}$ from $\text{G}$ and dimethylmalonyldichloride, in the presence of sodium hydride

Figure 2.11: Deprotonation of pyridinium amine macrocycle $\text{I}$ with sodium carbonate, to form pyridinium amide macrocycle $\text{H}_2\text{L}_m$. Two limiting resonance forms of $\text{H}_2\text{L}_m$ are shown here
2.3 Structures and spectroscopic properties of the new pyridinium amide ligands

2.3.1 Acyclic ligand, D

The procedure used to synthesise acyclic ligand D that was given in Figure 2.8 was modified to obtain a higher product yield. In this modified procedure, four equivalents of p-toluidine were used instead of two equivalents and an external base was not added to the reaction (see Section 2.5.4 for detailed procedure). The extra two equivalents of p-toluidine acted as an internal base for the hydrochloric acid by-product formed in this reaction. A convenient purification method was found by deprotonating D with moderate excess of DBU in situ at the end of the reaction, forming the acyclic pyridinium amide ligand, H2La (Figure 2.12). The H2La ligand precipitated out of acetonitrile, and was collected by filtration and washed with acetonitrile, which removed the p-toluidine hydrochloride and other by-products.

Figure 2.12: Synthesis of H2La from B and p-toluidine, followed by deprotonation with a moderate excess of DBU. The two limiting resonance forms of H2La are shown here

The solubility of H2La was very low in most solvents and was too low to obtain UV-visible absorption and 1H NMR spectra. In the case of the 1H NMR spectrum, even when a very large number of scans were collected, suitable spectra could not be obtained. However, the solubility was high enough that mass spectrometry could be obtained in methanol and this confirmed product formation. For routine experiments, the purity of H2La was gauged by adding a moderate excess of acid (usually trifluoroacetic acid) to a suspension of H2La in DMSO-d6. The H2La ligand protonated to form D (or H4La2+), with trifluoroacetate counteranions, which was much more soluble than H2La. As expected, the 1H NMR signals of D obtained by this method
were the same as the $^1$H NMR signals of crude D, obtained using the method given in Figure 2.8. No by-products were observed in the $^1$H NMR spectrum of product D obtained by the acid-addition method, suggesting that H$_2$L$_m$ is indeed obtained in high purity using the method outlined in Figure 2.12. The solubility of H$_2$L$_m$ was also high enough in certain solvents that it could be metallated with various metal salts in the presence of a base. These experiments are discussed in Chapter 3.

### 2.3.2 Macroyclic ligand, H$_2$L$_m$

Macroyclic ligand H$_2$L$_m$ was obtained in high purity using the procedure described in Sections 2.2.2 and 2.5.9. This procedure illustrates that the protonated macrocycle (I or H$_4$L$_m$$^{2+}$), is readily deprotonated by sodium carbonate to form H$_2$L$_m$. Other bases can also be used to deprotonate H$_4$L$_m$$^{2+}$ and similar product yields and purities were obtained when sodium hydroxide was used instead of sodium carbonate. This suggests that H$_2$L$_m$ is not hydrolysed by sodium hydroxide under these conditions, even at a concentration of 1 mol L$^{-1}$. Attempts to purify H$_4$L$_m$$^{2+}$ without the deliberate addition of a base resulted in partial deprotonation to H$_2$L$_m$, most likely by the adventitious water present during these purification attempts.

#### 2.3.2.1 Comparison of ligand H$_2$L$_m$ to protonated ligand H$_4$L$_m$$^{2+}$

NMR spectroscopy of H$_4$L$_m$$^{2+}$ was obtained by addition of a moderate excess of trifluoroacetic acid to a solution of purified H$_2$L$_m$ in DMSO-$d_6$ (detailed procedure given in 2.5.10). As expected, the $^1$H and $^{13}$C NMR chemical shifts of this product are identical to the chemical shifts of the crude H$_4$L$_m$$^{2+}$ product, before it was deprotonated and extracted into dichloromethane.

Table 2.2 and Figure 2.13 show that significant downfield shifts occurred for most $^1$H and $^{13}$C NMR signals upon protonation of H$_2$L$_m$ to H$_4$L$_m$$^{2+}$, as expected. In the $^1$H NMR spectra, downfield shifts of up to 0.74 ppm were observed upon protonation. Generally, greater downfield shifts were observed for the phenyl and pyridinium group protons, and a smaller downfield shift was observed for the N-methyl protons. The smallest downfield shift occurred for the geminal-C-methyl protons, which is probably because they are more remote from the pyridinium group. Interestingly, one of the two pyridinium group C-H protons that is ortho to
Table 2.2: $^1$H and $^{13}$C NMR chemical shifts of H$_2$L$_m$ and H$_4$L$_m^{2+}$ in DMSO-$d_6$

<table>
<thead>
<tr>
<th>Position $^a$</th>
<th>H$_2$L$_m$ $^1$H (ppm)</th>
<th>H$_4$L$_m^{2+}$ $^1$H (ppm)</th>
<th>H$_2$L$_m$ $^{13}$C (ppm)</th>
<th>H$_4$L$_m^{2+}$ $^{13}$C (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.01-7.03 (m)</td>
<td>7.50-7.53 (m)</td>
<td>122.0</td>
<td>127.2</td>
</tr>
<tr>
<td>2</td>
<td>7.47-7.49 (m)</td>
<td>7.84-7.88 (m)</td>
<td>117.4</td>
<td>125.1</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>-</td>
<td>136.7</td>
<td>130.8</td>
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<tr>
<td>4</td>
<td>-</td>
<td>-</td>
<td>146.0</td>
<td>150.4</td>
</tr>
<tr>
<td>5</td>
<td>7.09 (d)</td>
<td>7.60 (d)</td>
<td>102.2</td>
<td>106.9</td>
</tr>
<tr>
<td>6</td>
<td>7.64 (dd)</td>
<td>8.38 (dd)</td>
<td>136.4</td>
<td>143.0</td>
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<tr>
<td>7</td>
<td>3.78 (s)</td>
<td>4.10 (s)</td>
<td>44.3</td>
<td>45.3</td>
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<tr>
<td>8</td>
<td>8.73 (d)</td>
<td>8.65 (d)</td>
<td>127.9</td>
<td>142.6</td>
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<tr>
<td>9</td>
<td>-</td>
<td>-</td>
<td>132.4</td>
<td>122.0</td>
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<tr>
<td>10</td>
<td>-</td>
<td>-</td>
<td>175.1</td>
<td>172.3</td>
</tr>
<tr>
<td>11</td>
<td>-</td>
<td>-</td>
<td>53.3</td>
<td>50.9</td>
</tr>
<tr>
<td>12</td>
<td>1.45 (s)</td>
<td>1.56 (s)</td>
<td>26.0</td>
<td>23.3</td>
</tr>
<tr>
<td>13</td>
<td>-</td>
<td>9.96 (br s)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>14</td>
<td>11.25 (s)</td>
<td>8.98 (br s)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CF$_3$C(O)O$^-$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>158.5 (q)</td>
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<tr>
<td>CF$_3$C(O)O$^-$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>161.9</td>
</tr>
</tbody>
</table>

$^a$ Numbered positions are shown in Figure 2.13. Coupling constants are given in Sections 2.5.9 and 2.5.10. Abbreviations: s = singlet, d = doublet, dd = doublet of doublets, q = quartet, m = multiplet, br s = broad singlet.

Figure 2.13: Numbered positions of carbon and proton atoms on H$_4$L$_m^{2+}$ and the analogous H$_2$L$_m$ structure, used in the above table. Because the molecule is symmetric about a vertical mirror plane, only one half of the molecule is numbered here.
the N-methyl group (position 8, Figure 2.13) shifted slightly upfield upon protonation, whereas the other ortho proton (position 6) showed the greatest downfield shift of all the protons in the molecule upon protonation. This was unexpected, because significant downfield shifts are expected for the pyridinium C-H protons closest to the N-methyl nitrogen atom, due to the large increase in positive charge density on this nitrogen atom upon protonation. In the deprotonated \( \text{H}_2\text{L}_m \) form, this nitrogen atom has only a partial positive charge, because two resonance forms (a charge separated species and a neutral imine species, Figure 2.11) contribute to its structure in solution. Although further studies described below in Section 2.3.2.2 suggest that the charge-separated (zwitterionic) resonance form may dominate in polar solvents such as DMSO-\( d_6 \), this still does not explain why one ortho proton shifts significantly downfield, while the other shifts slightly upfield upon protonation. A possible reason for the slight upfield shift of the \( H_8 \) atom may be due to a change in the ring conformation on protonation, which brings \( H_8 \) into a position where it is no longer deshielded by the adjacent carboxamide carbonyl group. The only other proton that shifts upfield upon protonation (by 2.27 ppm) is the carboxamide NH proton (\( H_{14} \)). This might be because protonation of the imine nitrogen atoms at \( N_{13} \) prevents any hydrogen bonding between the \( N_{13} \) nitrogen atoms and the \( H_{14} \) carboxamide protons. Removal of the hydrogen bonding interactions is expected to result in an upfield chemical shift for the \( H_{14} \) protons.

Large downfield shifts were also observed for the \(^{13}\text{C} \) NMR signals of the pyridinium, phenyl, and N-methyl C-H carbon atoms upon protonation (Table 2.2). The largest downfield shift occurred for the \( C_8 \) position, even though an upfield shift was observed for the \( H_8 \) position in the \(^1\text{H} \) NMR spectra. All of the \(^{13}\text{C} \) NMR signals for the groups at the “tail” end of the macrocycle (positions \( C_9 \) to \( C_{12} \)) actually shifted upfield upon protonation, but this was not observed for the corresponding protons in the \(^1\text{H} \) NMR spectra.

UV-visible absorption spectra of \( \text{H}_2\text{L}_m \) and \( \text{H}_4\text{L}_m^{2+} \) were obtained in methanol. The UV-visible absorption spectrum of \( \text{H}_2\text{L}_m \) was first recorded in methanol, then a small excess of trifluoroacetic acid was added and the UV-visible absorption spectrum of \( \text{H}_4\text{L}_m^{2+} \) was recorded. The spectrum was later rerun with a larger excess of trifluoroacetic acid, to confirm that \( \text{H}_2\text{L}_m \) had completely protonated to \( \text{H}_4\text{L}_m^{2+} \). Two intense peaks were observed in the UV region of \( \text{H}_2\text{L}_m \) in methanol, at 321.5 and 368.5 nm (Figure 2.14). The high molar absorptivities of these peaks (26,200 and 25,100 L mol\(^{-1}\) cm\(^{-1}\), respectively) suggests that these transitions are strongly allowed. A shoulder at about 212 nm (33,900 L mol\(^{-1}\) cm\(^{-1}\)) for \( \text{H}_2\text{L}_m \) suggests that there may
be a third transition in the UV region that is partially obscured by the strong absorption of the solvent in this region. The tail end of the longer wavelength peak extended well into the visible region and this explains why $H_2L_m$ is strongly yellow coloured in methanol. Expansion of the baseline revealed that there were no further absorption maxima between 500 and 900 nm.

![Figure 2.14: UV-visible absorption spectra of $H_2L_m$ (solid line) and $H_4L_m^{2+}$ (dashed line) in methanol](image)

Upon protonation, the absorption maxima undergo a considerable shift to shorter wavelengths (Figure 2.14), indicating that the energy of these transitions increases significantly after protonation. Only one clear peak maximum was observed for $H_4L_m^{2+}$ in methanol, at a wavelength of 319 nm. The molar absorptivity at $\lambda_{\text{max}}$ was slightly higher for this peak (30,900 L mol$^{-1}$ cm$^{-1}$) than for the peaks observed in the UV-visible spectrum of $H_2L_m$. A shoulder on the 319 nm peak was observed at about 308 nm (21,200 L mol$^{-1}$ cm$^{-1}$), suggesting that $H_4L_m^{2+}$ still has at least two electronic transitions in the UV region. As for $H_2L_m$, there may also be a third transition in the UV region of $H_4L_m^{2+}$ in methanol, because a peak maximum was observed at 201 nm, which has also shifted to shorter wavelengths compared to the 212 nm shoulder observed for $H_2L_m$ in methanol. However, this peak was very close to the solvent cut-off wavelength of about 200 nm (where methanol begins to absorb strongly), so it was difficult to distinguish whether this was a true peak or a spectrum artefact. The absorbance of $H_4L_m^{2+}$ was
negligible in the visible region and this explains why the solution became colourless upon protonation.

Very few studies on the electronic properties of pyridinium amides have been published in the literature. Although published studies\(^\text{125,127}\) have investigated the effects of solvent polarity on the UV-visible absorption spectra of pyridinium amides (summarised in Section 2.1.1.2), the spectra of pyridinium amides and protonated pyridinium amides (that is, pyridinium amines) have not been compared in the same solvent. Pagani \textit{et al.}\(^\text{125}\) showed that the wavelength at \(\lambda_{\text{max}}\) varied substantially for different pyridinium amides in methanol (299 nm to 427 nm, see Table 2.1), but did not report molar absorptivity values for these compounds. For some of these pyridinium amides, \(\lambda_{\text{max}}\) occurred at short visible wavelengths, and so, like \(\text{H}_2\text{L}_n\), these compounds were yellow in solution. Traore \textit{et al.}\(^\text{127}\) have studied a simple pyridinium amide, \(N,1\text{-dimethylpyridin-2(1H)-imine}\) (see Figure 2.2 for structure). It was concluded that \(N,1\text{-dimethylpyridin-2(1H)-imine}\) protonated when it was added to water to form a pyridinium amine. Two peak maxima were observed in the UV-visible absorption spectrum of this compound in water, at 231 and 312 nm. Although the wavelength at \(\lambda_{\text{max}}\) for the longer wavelength peak of the protonated \(N,1\text{-dimethylpyridin-2(1H)-imine}\) compound in water is similar to the longer wavelength peak of \(\text{H}_4\text{L}_m^{2+}\) (319 nm) in methanol, the molar absorptivity is considerably higher for the 319 nm \(\text{H}_4\text{L}_m^{2+}\) peak (30,900 L mol\(^{-1}\) cm\(^{-1}\)) than it is for the \(N,1\text{-dimethylpyridin-2(1H)-imine}\) 312 nm peak (about 8,000 L mol\(^{-1}\) cm\(^{-1}\)). In contrast, the 231 nm peak of protonated \(N,1\text{-dimethylpyridin-2(1H)-imine}\) in water is significantly higher in molar absorptivity (about 28,000 L mol\(^{-1}\) cm\(^{-1}\)) than the protonated \(N,1\text{-dimethylpyridin-2(1H)-imine}\) 312 nm peak, and is much closer to the molar absorptivity of the peak observed at 201 nm for \(\text{H}_4\text{L}_m^{2+}\) in methanol (35,900 L mol\(^{-1}\) cm\(^{-1}\)). Like \(\text{H}_4\text{L}_m^{2+}\), the absorbance of protonated \(N,1\text{-dimethylpyridin-2(1H)-imine}\) in the visible region is negligible, and so both pyridinium amine compounds are colourless in solution.

Unlike when \(N,1\text{-dimethylpyridin-2(1H)-imine}\) was added to water, Traore \textit{et al.}\(^\text{127}\) inferred from spectroscopic data that \(N,1\text{-dimethylpyridin-2(1H)-imine}\) does not protonate when it is dissolved in \(n\)-hexane under ambient conditions. In \(n\)-hexane, the UV-visible absorption transitions of \(N,1\text{-dimethylpyridin-2(1H)-imine}\) were observed at 251 nm (\(\varepsilon\) value of approximately 15,000 L mol\(^{-1}\) cm\(^{-1}\)) and 370 nm (\(\varepsilon\) value of approximately 4,000 L mol\(^{-1}\) cm\(^{-1}\)). The longer wavelength absorption extended well into the visible region and thus, like \(\text{H}_2\text{L}_n\), \(N,1\text{-dimethylpyridin-2(1H)-imine}\) is yellow in solutions where the pyridinium amide moiety
does not protonate. The molar absorptivities of the electronic transitions of $\text{H}_2\text{L}_m$ in methanol (321.5 nm, 26,200 L mol$^{-1}$ cm$^{-1}$; 368.5 nm, 25,100 L mol$^{-1}$ cm$^{-1}$) are significantly higher than for $N,1$-dimethylpyridin-2(1H)-imine in $n$-hexane.

Traore $et$ $al.$\textsuperscript{127} ascribed the shorter $\lambda_{\text{max}}$ wavelengths of $N,1$-dimethylpyridin-2(1H)-imine in water than in $n$-hexane to solvent interactions and to the protonation of $N,1$-dimethylpyridin-2(1H)-imine in water but not in $n$-hexane. Like other pyridinium amides, a strong effect of solvent polarity on the wavelength at $\lambda_{\text{max}}$ is expected for the $N,1$-dimethylpyridin-2(1H)-imine pyridinium amide.\textsuperscript{127} Because Traore $et$ $al.$ only compared the UV-visible absorption spectra of the protonated $N,1$-dimethylpyridin-2(1H)-imine pyridinium amine in water to the $N,1$-dimethylpyridin-2(1H)-imine pyridinium amide in $n$-hexane, the observed changes in $\lambda_{\text{max}}$ are due to both the solvent effect and the change from the deprotonated (pyridinium amide) to the protonated (pyridinium amine) structure, and it is difficult to deconvolute these two separate effects from the reported data. If Traore $et$ $al.$ recorded spectra in, for example, basic water, then some more direct comparisons could be made. Nevertheless, the general observation of a shift to shorter wavelengths upon protonation of $N,1$-dimethylpyridin-2(1H)-imine can tentatively be said to agree with the direction of the wavelength shift observed upon protonating $\text{H}_2\text{L}_m$ to give $\text{H}_4\text{L}_m^{2+}$.  

2.3.2.2 Effect of solvent polarity on the spectroscopic properties of $\text{H}_2\text{L}_m$

Studies have shown that the properties of pyridinium amides and, in one case, a ruthenium-pyridinium amidate complex, are solvent-dependent and that the zwitterionic resonance form becomes more dominant over the imine resonance form as the solvent polarity increases. These results are summarised in Section 2.1.1.\textsuperscript{125,127,131}

The effect of solvent polarity on the $^1\text{H}$ NMR spectrum of $\text{H}_2\text{L}_m$ was studied. The chemical shift of the protons in positions H$_6$ and H$_5$ of $\text{H}_2\text{L}_m$ (Figure 2.13) and the difference in chemical shift between these two protons in a variety of deutero-solvents are given in Table 2.3. As the solvent polarity (as measured by the dielectric constants for the corresponding proteo-solvents\textsuperscript{136}) increased, proton H$_6$ shifted downfield and the difference in chemical shift between protons H$_6$ and H$_5$ became larger. These results suggest that, like other pyridinium amides, the contribution of the zwitterionic resonance form to the structure of $\text{H}_2\text{L}_m$ in solution increases with increasing
solvent polarity. This is because a greater contribution from the zwitterionic resonance structure increases the positive charge on the pyridinium nitrogen atom, causing proton H₆ to become more deshielded and increasing the difference in chemical shift between protons H₆ and H₅. Although the chemical shift of H₆ increased steadily with increasing solvent polarity, for unknown reasons, the difference between protons H₆ and H₅ was slightly lower in methanol-\(d₄\) (0.41 ppm) than in acetone-\(d₆\) (0.46 ppm). This was not due to partial protonation of H₂Lₘ in the protic methanol-\(d₄\) solvent, because the H₂Lₘ \(^1\)H NMR signals did not shift after the addition of a large excess of sodium hydroxide. Also, partial protonation of H₂Lₘ is expected to increase the difference in chemical shift between H₆ and H₅, rather than decrease it, as illustrated by the larger H₆-H₅ difference for H₄Lₘ\(^{2+}\) (0.78 ppm) than for H₂Lₘ (0.55 ppm) in DMSO-\(d₆\) (Table 2.2). Changes in \(^1\)C and \(^1\)N NMR chemical shifts with solvent polarity were not studied due to the low solubility of H₂Lₘ in all of the deuto-solvents used in Table 2.3, except DMSO-\(d₆\).

### Table 2.3: Chemical shifts of protons H₅ and H₆ of H₂Lₘ in various deuto-solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dielectric constant</th>
<th>(E_T)</th>
<th>H₅</th>
<th>H₆</th>
<th>Difference, H₆-H₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMSO-(d₆)</td>
<td>47.2</td>
<td>45.1</td>
<td>7.09</td>
<td>7.64</td>
<td>0.55</td>
</tr>
<tr>
<td>Methanol-(d₄)</td>
<td>33.0</td>
<td>55.4</td>
<td>7.18</td>
<td>7.59</td>
<td>0.41</td>
</tr>
<tr>
<td>Acetone-(d₆)</td>
<td>21.0</td>
<td>42.2</td>
<td>7.11</td>
<td>7.57</td>
<td>0.46</td>
</tr>
<tr>
<td>CDCl₃</td>
<td>4.8</td>
<td>39.1</td>
<td>6.97</td>
<td>7.10</td>
<td>0.13</td>
</tr>
</tbody>
</table>

*For proton assignments, see Figure 2.13.*

*Dielectric constants are given for the corresponding proteo-solvents.*

*Reichardt empirical solvent polarity scale value (kcal mol\(^{-1}\)). Larger values indicate more polar solvents. Note that the \(E_T\) values given here are for the corresponding proteo-solvents.*

Pagani *et al.*\(^{125,126}\) have argued that the Reichardt solvent polarity scale, which is based on empirical measurements of solvent polarity in zwitterionic systems, is a better indicator of solvent polarity than dielectric constant values for describing the spectroscopic properties of pyridinium amides (see Section 2.1.1.2). The Reichardt solvent polarity scale places solvent polarity in a somewhat different order than the dielectric constant values, so that methanol is now higher in polarity than DMSO. When the difference in chemical shift between H₆ and H₅ was reordered according to the Reichardt solvent polarity scale, the H₆-H₅ value in methanol-\(d₄\)
was still much lower than expected. Apart from this anomalously low H$_6$-$H_5$ value in methanol-$d_4$, the general trend of an increasing difference between H$_6$ and H$_5$ with increasing solvent polarity still holds when the Reichardt scale is used instead of the dielectric constant scale. This again suggests that the contribution of the zwitterionic resonance form to the structure of H$_2$L$_m$ in solution increases with increasing solvent polarity.

UV-visible absorption spectroscopy was also used to study the effect of solvent polarity on the structure of H$_2$L$_m$ in solution. The absorbance of H$_2$L$_m$ in various solvents was recorded every 0.5 nm between 190 and 900 nm, and the wavelength and molar absorptivity at $\lambda_{max}$ for each peak are shown in Table 2.4. In most solvents, three absorption maxima were observed in the UV region and these have been labelled peaks 1, 2 and 3 (with increasing wavelength) in Table 2.4. All three peaks absorbed strongly (with molar absorptivities of between 13,200 and 35,800 L mol$^{-1}$ cm$^{-1}$) and the strongest absorption was observed for peak 2 in each solvent. In methanol, peak 1 was not observed, while in acetone, peak 1 was obscured by the strong absorption of the solvent in this region. Because the tail end of the longest wavelength peak of H$_2$L$_m$ in each solvent extended well into the visible region, H$_2$L$_m$ was strongly yellow coloured in these solvents. Expansion of the baseline did not reveal any other absorption maxima beyond 500 nm. Spectra were not recorded in water or alkanes due to the extremely low solubility of H$_2$L$_m$ in these solvents.

All three peaks for H$_2$L$_m$ in Table 2.4 show solvatochromic behaviour, and the change in $\lambda_{max}$ wavelength with changing solvent polarity seems to be slightly greater for peak 2 than for peaks 1 and 3. Although the wavelength at $\lambda_{max}$ generally decreases with increasing solvent polarity, the wavelength at $\lambda_{max}$ is unexpectedly long in a few solvents. For example, when solvent polarity is ordered according to dielectric constant values (Table 2.4), all three peaks for DMSO occur at longer wavelength than expected. However, if the $\lambda_{max}$ wavelengths shown in Table 2.4 are reordered according to the Reichardt solvent polarity scale ($E_T$, in kcal mol$^{-1}$), methanol and isopropanol are higher in polarity than DMSO and all three peaks show a much clearer pattern of decreasing wavelength at $\lambda_{max}$ with increasing solvent polarity. An example of this can be shown by plotting the wavelength at $\lambda_{max}$ as a function of $E_T$ for peak 2 (Figure 2.16), which shows a much clearer trend of decreasing $\lambda_{max}$ with increasing solvent polarity than when $\lambda_{max}$ is plotted as a function of dielectric constant (Figure 2.15). A similar trend is observed if the wavelength at $\lambda_{max}$ of peaks 1 and 3 are plotted against $E_T$, although the total shift from the highest to the lowest polarity solvent used is slightly lower for peaks 1 and 3 than for peak 2.
Table 2.4: $\lambda_{\text{max}}$ and $\varepsilon$ values for $\text{H}_2\text{L}_m$, determined by UV-visible absorption spectroscopy in different solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dielectric constant</th>
<th>$E_T$</th>
<th>DN</th>
<th>Peak 1</th>
<th>Peak 2</th>
<th>Peak 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMSO</td>
<td>46.7</td>
<td>45.1</td>
<td>29.8</td>
<td>276.0 (19,700)</td>
<td>339.0 (32,900)</td>
<td>379.0 (27,600)</td>
</tr>
<tr>
<td>Methanol</td>
<td>32.7</td>
<td>55.4</td>
<td>30.0</td>
<td>321.5 (26,200)</td>
<td>368.5 (25,100)</td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td>20.7</td>
<td>42.2</td>
<td>17.0</td>
<td>339.0 (35,800)</td>
<td>377.0 (28,100)</td>
<td></td>
</tr>
<tr>
<td>Isopropanol</td>
<td>17.9</td>
<td>48.4</td>
<td>36.0</td>
<td>271.5 (17,100)</td>
<td>331.5 (31,400)</td>
<td>374.5 (25,400)</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>8.93</td>
<td>40.7</td>
<td>1.0</td>
<td>276.5 (19,700)</td>
<td>341.0 (34,600)</td>
<td>380.5 (26,200)</td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td>4.81</td>
<td>39.1</td>
<td>4.0</td>
<td>277.5 (13,200)</td>
<td>341.5 (23,500)</td>
<td>381.0 (17,500)</td>
</tr>
</tbody>
</table>

$^a$ Wavelength at $\lambda_{\text{max}}$ (in nm) and molar absorptivities at this wavelength ($\varepsilon$, L mol$^{-1}$ cm$^{-1}$). The concentration of $\text{H}_2\text{L}_m$ was constant in each solution (36.0 µmol L$^{-1}$).

$^b$ Reichardt empirical solvent polarity scale value (kcal mol$^{-1}$). Larger values indicate more polar solvents.$^{129}$

$^c$ Donor numbers (kcal mol$^{-1}$). Larger numbers indicate more Lewis basic solvents.$^{137}$

$^d$ Peak 1 was not observed in methanol.

$^e$ Peak 1 in acetone was obscured by the strong absorption of the solvent in this region.

Because peak maxima occur at significantly shorter wavelengths for $\text{H}_4\text{L}_m^{2+}$ than $\text{H}_2\text{L}_m$ in methanol (Figure 2.14), it could be argued that the shorter $\lambda_{\text{max}}$ wavelength observed for $\text{H}_2\text{L}_m$ in methanol and isopropanol compared to the other solvents are due to partial protonation in these protic solvents. However, no change to the UV-visible absorption spectra were observed upon adding sodium hydroxide to these solutions, which rules out this possibility. The trends observed in these UV-visible spectroscopic studies therefore strongly suggest that the contribution of the zwitterionic resonance form to the structure of $\text{H}_2\text{L}_m$ in solution increases with increasing solvent polarity, in agreement with the $^1$H NMR spectral data of $\text{H}_2\text{L}_m$ in different solvents. The UV-visible absorption data also agree with the studies conducted by Pagani et al.$^{125}$ on related compounds (summarised in Section 2.1.1.2), where the wavelength at $\lambda_{\text{max}}$ for the $\text{R}_1/\text{R}_2 = \text{SO}_2\text{p-tol}/\text{H}$ substituted pyridinium amide (see Figure 2.1 for structure) was found to decrease with increasing solvent polarity. In this system, the difference between the longest and shortest $\lambda_{\text{max}}$ wavelengths in the solvents used was 11 nm (Table 2.1), compared to between 6 and 20 nm for $\text{H}_2\text{L}_m$ (depending on which of the three observed absorption maxima is being considered for the $\text{H}_2\text{L}_m$ compound). A clear trend of decreasing $\lambda_{\text{max}}$ with increasing solvent polarity was not observed for the $\text{R}_1/\text{R}_2 = \text{NO}_2/\text{H}$ and $\text{NO}_2/\text{NO}_2$ substituted pyridinium amides studied by Pagani et al.$^{125}$
Figure 2.15: Variation of wavelength at $\lambda_{\text{max}}$ with solvent dielectric constant value for peak 2 of H$_2$L$_{m}$, determined by UV-visible absorption spectroscopy.

Figure 2.16: Variation of wavelength at $\lambda_{\text{max}}$ with Reichardt solvent polarity value ($E_T$) for peak 2 of H$_2$L$_{m}$, determined by UV-visible absorption spectroscopy.
Table 2.4 also illustrates that the molar absorptivities ($\varepsilon$) at $\lambda_{\text{max}}$ change somewhat in different solvents. When ordered according to the Reichardt solvent polarity scale, there seems to be a general trend of higher molar absorptivities in mid-polarity solvents and lower molar absorptivities in higher and lower polarity solvents, although the reason for this is not clear.

Reichardt solvent polarity values ($E_T$) are determined from the longest wavelength $\pi$ to $\pi^*$ intramolecular charge transfer absorption band observed in the UV-visible absorption spectrum of a highly solvatochromic pyridinium N-phenolate betaine dye, known as Reichardt’s dye. Although Reichardt’s dye is capable of interacting with electron-pair accepting solvents, this dye molecule lacks functional groups which interact significantly with electron-pair donating solvents. The $E_T$ scale therefore accounts for the Lewis acidity of solvents, but does not account for the Lewis basicity. Because $\text{H}_2\text{L}_m$ contains both Lewis acidic and Lewis basic functional groups, the $E_T$ scale does not adequately account for the interaction of solvents with the Lewis acidic functional groups on $\text{H}_2\text{L}_m$, such as the pyridinium nitrogen atoms or the carboxamide N-H hydrogen atoms. To overcome this limitation, multiparameter solvent polarity scales can be used. These scales introduce a second empirical solvent polarity parameter that accounts for the Lewis basicity of the solvent. One such scale which has been developed incorporates the donor number (DN) parameter, a scale established by Gutmann et al. by measuring the negative of the enthalpy of formation for the reaction of the target solvent with antimony pentachloride in dilute 1,2-dichloroethane. Because antimony pentachloride is a strong Lewis acid, donor numbers (in kcal mol$^{-1}$) provide an empirical measure of the Lewis basicity of the target solvent, with minimal effects from the Lewis acidic properties of the solvent. Thus, using $E_T$ as a measure of the solvent Lewis acidity and DN as a measure of the solvent Lewis basicity, the following linear solvation energy relationship has been developed:

$$Q = Q_0 + \alpha E_T + \beta \text{DN}$$

Where $Q$ and $Q_0$ are the values for the solvent-dependent physicochemical process being investigated for the target substrate (such as chemical shift or $\lambda_{\text{max}}$) in the solvent and in the gas phase (or in an inert solvent), respectively. The $\alpha$ and $\beta$ terms are regression coefficients which describe the relative sensitivity of the physicochemical process to the solvent Lewis acidity and basicity, respectively. These $\alpha$ and $\beta$ terms will depend on the particular target substrate and the
physicochemical process, and can be determined from stepwise multiple linear regression analysis.\textsuperscript{129,138}

For H\textsubscript{2}L\textsubscript{m}, the value of Q\textsubscript{0} is unknown because this compound is not soluble in inert low polarity solvents, and because the theoretical UV-visible absorption and \textsuperscript{1}H NMR spectra of H\textsubscript{2}L\textsubscript{m} in the gas phase have not been calculated. Hence, the \( \alpha \) and \( \beta \) terms have not been determined for H\textsubscript{2}L\textsubscript{m}. Therefore, the extent to which the UV-visible absorption and \textsuperscript{1}H NMR spectra of H\textsubscript{2}L\textsubscript{m} depend upon the Lewis acidity and basicity of the investigated solvents is currently unknown. More detailed studies will need to be carried out to determine these effects. However, if the DN values of the solvents given in Table 2.4 are taken into account, it is possible to gauge in a crude manner that the trend of decreasing \( \lambda_{\text{max}} \) with increasing solvent polarity (Figure 2.16 and Table 2.4) will become more pronounced (provided that the \( \beta \) term in the equation above is not negligible). This is because the DN values for the higher polarity solvents are significantly higher than for the lower polarity solvents, increasing the net solvent polarity to a greater extent. In other words, the \( E_T \) values plotted in Figure 2.16 under-represent the actual solvent polarity, especially for the higher polarity solvents.

Other multiparameter solvent polarity scales have also been established, such as those of Kamlet and Taft,\textsuperscript{129} Drago,\textsuperscript{137} and Catalán.\textsuperscript{140} These solvent polarity scales introduce further empirically-derived terms to those given in the formula above in order to quantify solvent polarity values with greater precision. However, these scales are beyond the scope of the work here and would require more detailed studies to be carried out in a larger set of solvents.

UV-visible absorption spectra of H\textsubscript{2}L\textsubscript{m} were also recorded in various mixtures of methanol and dichloromethane (Figure 2.17). These were recorded for every 10\% increase in ratio of methanol in dichloromethane and spectra were also recorded at 95\% and 5\% methanol in dichloromethane (the latter two spectra are not shown in Figure 2.17). Absorbances below the solvent cut-off wavelengths (where the solvent itself begins to absorb strongly) for each solvent mixture are not shown in Figure 2.17. These results indicate that as the percentage of methanol in dichloromethane increases, all three peak maxima decrease in molar absorptivities and all three peaks shift to shorter wavelengths, which is consistent with the data in Table 2.4. Additionally, as the methanol percentage increases, the shortest wavelength peak (peak 1 in Table 2.4) gradually decreases until it becomes a barely perceptible shoulder. Therefore, only two peak
maxima are observed in 100% methanol, whereas three peak maxima are observed in 100% dichloromethane.

Figure 2.17: UV-visible absorption spectra of H$_2$L$_m$ (36.0 µmol L$^{-1}$) in various mixtures of methanol and dichloromethane. Solid lines depict spectra in 100% methanol and 100% dichloromethane, while dashed lines represent spectra for methanol-dichloromethane mixtures. All peak maxima decrease steadily in absorbance from 100% dichloromethane to 100% methanol.

Figure 2.17 also illustrates that the change in the wavelengths and molar absorptivities at $\lambda_{\text{max}}$ are non-linear with changing solvent ratio. A large decrease in peak wavelength and molar absorptivity was observed with the initial addition of a small amount of methanol, and this was then followed by a more gradual change in peak wavelength and molar absorptivity as the relative amount of methanol in dichloromethane increased further. This is further illustrated in Figure 2.18, where the wavelength at $\lambda_{\text{max}}$ for peak 2 has been plotted as a function of methanol to dichloromethane ratio. In 100% dichloromethane, $\lambda_{\text{max}}$ occurs at 341 nm. With the addition of just 5% methanol, $\lambda_{\text{max}}$ decreases by a reasonably large amount (5 nm). As the relative amount of methanol increases further, the decrease in $\lambda_{\text{max}}$ is approximately linear, reaching 321.5 nm at 100% methanol. A similar trend is also observed if peaks 1 and 3 are plotted likewise, although above 70% methanol, peak 1 becomes a shoulder and is no longer a peak, adding greater error to the wavelength data above 70% methanol. These observations for H$_2$L$_m$ are essentially the opposite to the change in the wavelength at 1000 L mol$^{-1}$ cm$^{-1}$ ($\lambda_{e1000}$) observed
for the ruthenium-pyridinium amidate complex described by Albrecht and Wright et al. (Section 2.1.1.3),\textsuperscript{131} where a sharp increase in $\lambda_{4100}$ was observed when a small (just 1\%) amount of dichloromethane was added to the complex in methanol, followed by a more gradual and approximately linear increase in $\lambda_{4100}$ with increasing percent methanol in dichloromethane.

![Figure 2.18](image)

**Figure 2.18:** Variation of wavelength at $\lambda_{\text{max}}$ with increasing amounts of methanol in dichloromethane, plotted for the peak 2 of the UV-visible absorption spectra of $H_2L_m$

Both $^1$H NMR and UV-visible spectroscopies have therefore provided evidence that the zwitterionic resonance form becomes more predominant for $H_2L_m$ in solution as the solvent polarity increases and are in general agreement with other pyridinium amides published in the literature.

### 2.3.2.3 Fluorescence spectroscopy of $H_2L_m$

Fluorescence spectroscopy was used to determine whether $H_2L_m$ would fluoresce if excited with light of specific wavelengths. The methanol and dichloromethane solutions of $H_2L_m$ that were prepared for UV-visible absorption spectroscopy experiments (where the absorbance at the $\lambda_{\text{max}}$ peaks are close to 1) in Section 2.3.2.2 were used for these studies. Emission spectra were recorded at a variety of excitation wavelengths and these were chosen at the wavelengths of
each peak maximum, each valley, and at a wavelength half way between each peak maximum and the neighbouring valley observed in the UV-visible absorption spectra of H$_2$L$_m$ in methanol and dichloromethane (Figure 2.17). The emission spectra were recorded from a wavelength 20 nm longer than the excitation wavelength (to ensure that the Raman transition was not observed) through to 900 nm, so that second (and sometimes higher) order diffractions from the fluorimeter grating were observed. Comparison of the intensity of the second order diffractions to the intensity of any fluorescence peaks emitted from H$_2$L$_m$ in solution was used as a crude estimate of the fluorescence efficiency$^{127}$ (that is, the relative amount of the excited photons that return to the ground state by the emission of a photon versus the amount that return to the ground state by non-radiative processes – a value also known as the quantum yield). In methanol, a broad fluorescence signal was observed between 400 and 600 nm, with a peak maximum at approximately 460 nm (Figure 2.19). This peak was observed in the emission spectrum for each excitation wavelength used, except, of course, where excitation wavelengths were used that were longer than the emission wavelength. The independence of the wavelength of this emission peak with changing excitation wavelength suggests that this peak is due to fluorescence from H$_2$L$_m$ and is not due to Raman scattering of the incident light. This was further confirmed by the absence of this peak in the blank fluorescence spectrum of the methanol solvent.

Figure 2.19: Fluorescence emission spectrum of H$_2$L$_m$ in methanol, using excitation wavelengths of 322 nm (dotted line) and 368 nm (dashed line)
Figure 2.19 shows two representative emission spectra of H$_2$L$_m$ in methanol, recorded using excitation wavelengths of 322 nm and 368 nm (the wavelength at $\lambda_{\text{max}}$ for peaks 2 and 3 of the UV-visible absorption spectrum in methanol). When compared to the sharp second order diffractions observed at 644 nm and 736 nm, the 460 nm fluorescence peak is reasonably high in intensity. However, this method for estimating fluorescence efficiencies is rather crude and fluorescence quantum yields should be measured at a constant excitation wavelength to determine the fluorescence efficiencies relative to standard fluorescing compounds. Figure 2.19 shows that the second order diffraction changes considerably in intensity between data recorded at 322 nm and 368 nm, when calibrated relative to the intensity of the fluorescence signal. For most molecules, the quantum yield of the fluorescence peak is independent of the excitation wavelength,$^{141}$ so this suggests that the intensity of the second order diffraction changes significantly with changes in excitation light wavelength, assuming that the intensity of the excitation light remains constant (note, however, that the intensity of the excitation light does vary somewhat because no lamp has a constant emission intensity across its entire wavelength range).$^{141}$ This large change in the intensity of the second order diffraction peak with changing excitation wavelengths indicates that the method$^{127}$ used to estimate fluorescence efficiencies (by comparing the intensities of the sample fluorescence peak and the second order diffraction peak) is very limited.

The reason that the fluorescence peak of H$_2$L$_m$ in methanol is not smooth is probably due to the large number of vibrational energy levels in this molecule. A large number of signals are indeed observed in the infrared spectrum of H$_2$L$_m$ in the solid state (Section 2.5.9). Because molecules fluoresce from the lowest vibrational energy level of the first excited electronic state to a variety of vibrational energy levels in the ground electronic state, a large number of peaks are expected in the fluorescence spectrum of H$_2$L$_m$.

The fluorescence emission spectrum of H$_2$L$_m$ in dichloromethane (Figure 2.20) is similar to the fluorescence emission spectrum in methanol. Figure 2.20 shows the emission spectra of H$_2$L$_m$ in dichloromethane, recorded at excitation wavelengths of 341 nm and 381 nm (the wavelengths at $\lambda_{\text{max}}$ for peaks 2 and 3 in the UV-visible absorption spectrum of H$_2$L$_m$ in dichloromethane). Like the fluorescence emission spectra of H$_2$L$_m$ in methanol, a broad fluorescence emission peak is observed in dichloromethane, which is relatively high in intensity compared to the sharp second order diffraction peaks. Also like the fluorescence emission spectra in methanol, this emission peak is not smooth, presumably due to the large number of vibrational energy levels.
in the ground electronic state of H$_2$L$_m$. This fluorescence signal extends from about 400 to 600 nm, with a peak maximum at approximately 475 nm, suggesting that, like the UV-visible absorption spectrum of H$_2$L$_m$, the peak maximum of the H$_2$L$_m$ fluorescence signal shifts to slightly longer wavelengths in lower polarity solvents.

![Figure 2.20](image)

**Figure 2.20:** Fluorescence emission spectrum of H$_2$L$_m$ in dichloromethane, using excitation wavelengths of 341 nm (dotted line) and 381 nm (dashed line)

Traore *et al.*\(^{127}\) have recorded the fluorescence spectra of a simple pyridinium amide (structure shown in Figure 2.2) in *n*-hexane and in water. The fluorescence spectrum of this compound in *n*-hexane showed a broad fluorescence signal with a peak maximum at approximately 500 nm, which was very low in intensity compared to the intensity of the Raman band. Like the fluorescence spectra of H$_2$L$_m$, this band was not smooth, which was ascribed to transitions from the ground vibrational energy level of the excited electronic state to different vibrational energy levels of the ground electronic state. In contrast, the broad fluorescence signal of this compound in water (peak maximum at about 360 nm) was significantly higher in intensity than the intensity of the Raman band. However, this compound was shown to undergo protonation in water and so the emission spectrum was actually recorded for the pyridinium amine rather than for the pyridinium amide.\(^{127}\)
2.4 Conclusions and future work

Although the very low solubility of the new acyclic pyridinium amide (H$_2$L$_a$) precluded NMR and UV-visible absorption studies of this compound, the higher solubility of the new macrocyclic pyridinium amide compound (H$_2$L$_m$) enabled the effects of protonation and solvent polarity upon the spectroscopic properties to be studied. Protonation of H$_2$L$_m$ to give H$_4$L$_m$$^{2+}$ using trifluoroacetic caused downfield shifts for most of the $^1$H and $^{13}$C NMR signals in DMSO-$d_6$, and the peak maxima of the transitions observed in the absorption spectra in methanol shifted to shorter wavelengths upon protonation. NMR and UV-visible spectroscopic studies were consistent with there being a strong effect of the solvent polarity on the electronic structure of H$_2$L$_m$ in solution. With increasing solvent polarity, larger differences in $^1$H NMR chemical shifts between protons H$_6$ and H$_5$ (as per Figure 2.13) and shifting of the UV-visible absorption peak maxima to shorter wavelengths were observed. This is consistent with an increase in contribution of the zwitterionic resonance form relative to the imine resonance form as solvent polarity increases, in agreement with several published studies of other pyridinium amides and pyridinium amidates.

2.5 Experimental

2.5.1 General procedures

Solvents were dried using standard drying agents. Thus, acetonitrile was collected by distillation over CaH$_2$; dichloromethane was dried overnight over 3Å molecular sieves;$^{142}$ 1,4-dioxane was passed through a column of activated alumina and stored over 4Å molecular sieves overnight; THF was dried over sodium/benzophenone and collected by distillation,$^{143}$ and triethylamine was dried using CaH$_2$ and collected by fractional distillation. The reagent, 1,2-phenylenediamine was purified by recrystallisation from toluene and stored in the dark under nitrogen after drying thoroughly under vacuum.$^{143}$ Potassium tert-butoxide, iron(III) chloride and cobalt(II) bromide were stored in an inert atmosphere glovebox and were dispensed into sealed glass vessels under a nitrogen atmosphere. Iron(II) chloride was synthesised according to a literature procedure.$^{144}$ Copper(II) chloride, manganese(II) chloride, sodium acetate and sodium carbonate were dried under high vacuum for five hours at 120 °C, 150 °C, 160 °C and
Compounds were characterised by elemental analysis, mass spectrometry, and $^1$H NMR, $^{13}$C NMR, IR, and UV-visible absorption spectroscopies. NMR spectra were recorded at either 300, 400 or 500 MHz, using Bruker Avance 300, Bruker DRX-400, and Bruker Ascend 500 spectrometers, respectively. NMR spectra were run at room temperature in either chloroform-$d_1$ (with 0.03% v/v TMS as internal standard), DMSO-$d_6$, methanol-$d_4$ or acetone-$d_6$ (used as received from Cambridge Chemical Isotope Laboratories). Proton NMR chemical shifts are reported relative to TMS (0.00 ppm) for chloroform-$d_1$, and relative to the proteo-solvent signal for DMSO-$d_6$ (2.50 ppm), methanol-$d_4$ (3.31 ppm) and acetone-$d_6$ (2.05 ppm). Reported $^{13}$C NMR chemical shifts are $^1$H-decoupled and are calibrated relative to the residual solvent signals at 77.16 ppm (chloroform-$d_1$), 39.52 ppm (DMSO-$d_6$), 49.00 ppm (methanol-$d_4$) and 29.84 (acetone-$d_6$). The $^{31}$P NMR chemical shifts are $^1$H-decoupled and are reported relative to 85% H$_3$PO$_4$ as an external standard (0.00 ppm).$^{145}$

Elemental analyses were obtained from the Campbell Microanalytical Laboratory, University of Otago, Dunedin. All values are given as percentages. Infrared spectra were obtained on a PerkinElmer Fourier Transform Infrared Spectrometer with a universal ATR reflectance sampling accessory. High resolution mass spectra were obtained using a Bruker micoOTOF-Q mass spectrometer in ESI positive or negative ion modes. The samples for these mass spectra were dissolved in either methanol, acetonitrile, or dichloromethane/methanol, depending on the sample solubility. In each experimental procedure given below, the term “M$^{x+}$” given in the mass spectral data denotes the expected composition of compound, without loss or addition of any atoms or ions. UV-visible absorption spectra were recorded using a PerkinElmer Lamda 35 double-beam UV-visible spectrometer (10 nm slit width; 480 nm min$^{-1}$ scan speed) and quartz cuvette cells were used for these experiments. In the experimental procedures given below, the wavelengths at the peak maxima of the UV-visible absorptions ($\lambda_{max}$) are given in nm and the molar absorptivities ($\epsilon$, in L mol$^{-1}$ cm$^{-1}$) at these wavelengths are given inside brackets. Electronic transitions that appear as shoulders rather than as peak maxima have been abbreviated

200 °C, respectively. All other chemicals were obtained from commercial suppliers and used without further purification. Solvents were dispensed with gas-tight syringes and reactions were carried out under nitrogen atmospheres unless otherwise stated. Some reactions were performed under stringently degassed conditions, using at least four freeze-pump-thaw degassing cycles inside Schlenk tubes. The reactions where stringently degassed conditions are used are stated in the appropriate procedures sections below.
“sh” and the $\lambda_{\text{max}}$ and $\varepsilon$ values are given for the mid-point of each shoulder. Fluorescence spectra were recorded in methanol or dichloromethane using a PerkinElmer LS 55 Luminescence spectrometer.

X-ray crystallographic data were obtained on mounted single crystals irradiated with graphite monochromatised Mo Kα radiation (0.71073 Å), collected on a Siemens SMART APEX CCD. Structures were solved and refined using SHELXL-97 (Sheldrick, 1997). Mercury version 3.3 (Cambridge Crystallographic Data Centre, 2013) was used to view crystal structures. Crystal structure data are given in Appendix A.

**2.5.2 Synthesis of 3-amino-2-chloro-1-methylpyridin-1-ium triflate**

![Chemical structure of 3-amino-2-chloro-1-methylpyridin-1-ium triflate](image)

**Figure 2.21: Chemical structure of 3-amino-2-chloro-1-methylpyridin-1-ium triflate**

Methyl triflate (1.28 mL, 11.3 mmol) was added to a solution of 3-amino-2-chloropyridine (1.22 g, 9.49 mmol) in dichloromethane (20 mL). The solution was stirred at room temperature for 17 hours. The solvent was removed under vacuum and the solid was then suspended in diethyl ether (75 mL), collected by filtration, and washed with diethyl ether (150 mL), to yield pure 3-amino-2-chloro-1-methylpyridin-1-ium triflate as a white solid (2.55 g, 92%).

$^1$H NMR (300 MHz, DMSO-$d_6$, $\delta$): 8.32 (dd, $J_1 = 5.4$ Hz, $J_2 = 1.5$ Hz, 1H, CH), 7.72 (dd, $J_1 = 8.7$ Hz, $J_2 = 1.5$ Hz, 1H, CH), 7.66 (dd, $J_1 = 8.7$ Hz, $J_2 = 5.4$ Hz, 1H, CH), 6.8-7.0 (br s, 2H, NH$_2$), 4.23 (s, 3H, CH$_3$).

$^{13}$C (75.4 MHz, DMSO-$d_6$, $\delta$): 145.8 (C$_3$), 134.7 (C$_6$), 128.9 (C$_2$), 127.9 (C$_4$), 125.2 (C$_5$), 47.5 (CH$_3$).

IR (cm$^{-1}$): 3428 (w), 3340 (m), 3228 (w), 1635 (m), 1584 (m), 1498 (s), 1448 (w), 1352 (w), 1318 (w), 1282 (m), 1245 (s), 1224 (s), 1155 (s), 1026 (s), 795 (s), 786 (m), 756 (m), 701 (m), 634 (s), 573 (m), 517 (s).
ESI-MS $m/z$: $M^+$, calcd for C$_6$H$_8$ClN$_2$, 143.0371; found, 143.0369 (100%, z = +1).


2.5.3 Synthesis of 3,3′-(oxalylbis(azanediyl))bis(2-chloro-1-methylpyridin-1-ium) triflate

![Figure 2.22: Chemical structure of 3,3′-(oxalylbis(azanediyl))bis(2-chloro-1-methylpyridin-1-ium) triflate](image)

Oxalyl chloride (0.203 mL, 2.38 mmol) was added to a suspension of 3-amino-2-chloro-1-methylpyridin-1-ium triflate (1.16 g, 3.96 mmol) in THF (110 mL). The solution was stirred at room temperature for 1 hour and then a solution of triethylamine (0.549 mL, 3.96 mmol) in THF (20 mL) was added dropwise over 1 hour. The solution was then stirred for 1.5 hours at room temperature. The solvent was then removed under vacuum and the solid was dried under vacuum for 2 hours. The solid was suspended in dichloromethane (150 mL) and was then collected by filtration and washed with dichloromethane (60 mL) to yield 3,3′-(oxalylbis(azanediyl))bis(2-chloro-1-methylpyridin-1-ium) triflate as a white solid (1.03 g, 81%).

$^1$H NMR (300 MHz, DMSO-$d_6$, $\delta$): 11.48 (s, 2H, NH), 9.17 (dd, $J_1 = 6.3$ Hz, $J_2 = 0.9$ Hz, 2H, CH), 8.82 (dd, $J_1 = 8.4$ Hz, $J_2 = 0.9$ Hz, 2H, CH), 8.19 (dd, $J_1 = 8.4$ Hz, $J_2 = 6.3$ Hz, 2H, CH), 4.42 (s, 6H, CH$_3$).

$^{13}$C NMR (75.4 MHz, DMSO-$d_6$, $\delta$): 158.1 (C=O), 146.4 (C$_6$), 143.3 (C$_2$), 142.8 (C$_4$), 135.4 (C$_3$), 125.5 (C$_5$), 48.6 (CH$_3$).

IR (cm$^{-1}$): 3290 (br, w), 3097 (w), 1712 (m), 1587 (w), 1504 (m), 1478 (m), 1419 (m), 1272 (s), 1255 (s), 1227 (s), 1180 (m), 1143 (s), 1030 (s), 941 (w), 870 (m), 798 (w), 781 (m), 757 (w), 708 (m), 636 (s), 574 (m), 566 (m), 518 (m), 480 (w), 438 (w).

ESI-MS $m/z$: (M$^{2+} - H^+$), calcd for C$_{14}$H$_{13}$Cl$_2$N$_4$O$_2$, 339.0410; found, 339.0400 (100%, z = +1).
Anal. Calcd for C\textsubscript{16}H\textsubscript{14}Cl\textsubscript{6}N\textsubscript{4}O\textsubscript{8}S\textsubscript{2}: C, 30.06; H, 2.21; N, 8.76. Found: C, 30.53; H, 2.09; N, 8.83.

X-ray quality crystals were grown by slow vapour diffusion of chloroform into a saturated solution of 3,3’-(oxalylbis(azanediyl))(bis-2-chloro-1-methylpyridin-1-ium) triflate in ethanol. Results are given in Appendix A.

2.5.4 Synthesis of $N^1,N^2$-bis(1-methyl-2-($p$-tolylimino)-1,2-dihydropyridin-3-yl)oxalamide ($H_2L_a$)

![Chemical structure of $N^1,N^2$-bis(1-methyl-2-($p$-tolylimino)-1,2-dihydropyridin-3-yl)oxalamide ($H_2L_a$)](image)

$p$-Toluidine (0.248 g, 2.31 mmol) and 3,3’-(oxalylbis(azanediyl))bis(2-chloro-1-methylpyridin-1-ium) triflate (1.476 g, 2.31 mmol) were refluxed in acetonitrile (25 mL) for 5 minutes. Another portion of $p$-toluidine (0.248 g, 2.31 mmol in 25 mL acetonitrile) was then added to the solution. After a further 5 minutes under reflux, a solution of $p$-toluidine (4.95 g, 4.62 mmol) in acetonitrile (50 mL) was added to a pressure-equalised dropping funnel attached to the reaction vessel. The solution in the dropping funnel was then added in four equal portions to the refluxing solution over 40 minutes. The solution was refluxed for a further 40 minutes after all the $p$-toluidine had been added and the solution was then cooled to room temperature. DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) (1.55 mL, 10.4 mmol) was added and the solution was stirred at room temperature for 1 hour. The yellow-orange precipitate was collected by filtration and was washed with acetonitrile (150 mL). Yield: 0.835 g (75%). The solubility of this product was very low in solvents suitable for characterisation and was characterised by IR, mass spectrometry and elemental analysis.
IR (cm$^{-1}$): 3253 (m), 1680 (m), 1643 (m), 1568 (s), 1455 (w), 1417 (w), 1370 (m), 1248 (w), 1237 (w), 1201 (s), 1152 (m), 1098 (m), 1039 (m), 929 (w), 900 (w), 869 (w), 844 (w), 826 (m), 787 (w), 758 (s), 732 (s), 719 (w), 675 (w), 639 (w), 588 (w), 569 (s), 529 (s), 482 (w), 443 (m).

ESI-MS m/z: (M + 2H$^+$), calcd for C$_{28}$H$_{30}$N$_6$O$_2$, 241.1215; found, 241.1200 (100%, z = +2). (M + H$^+$), calcd for C$_{28}$H$_{29}$N$_6$O$_2$, 481.2352; found, 481.2338 (5%, z = +1).

Anal. Calcd for C$_{28}$H$_{28}$N$_6$O$_2$·H$_2$O: C, 68.69; H, 5.97; N, 17.17. Found, C, 68.52; H, 5.76; N, 17.49.

2.5.5 Synthesis of 3,3’-(oxalylbis(azanediyl))bis(1-methyl-2-(p-tolylamino)-pyridin-1-ium) trifluoroacetate [H$_4$L$_a$][CF$_3$C(O)O]$_2$

The solubility of the $N^1,N^2$-bis(1-methyl-2-(p-tolylimino)-1,2-dihydropyridin-3-yl)oxalamide (H$_2$L$_a$) ligand was very low in solvents suitable for characterisation, but was much more soluble after the addition of trifluoroacetic acid. The ligand was therefore characterised by $^1$H NMR spectroscopy, $^{13}$C NMR spectroscopy, and mass spectrometry after trifluoroacetic acid (16 µL, 0.208 mmol) was added to a suspension of $N^1,N^2$-bis(1-methyl-2-(p-tolylimino)-1,2-dihydropyridin-3-yl)oxalamide (H$_2$L$_a$, 0.020 g, 0.042 mmol) in DMSO-$d_6$ (0.7 mL), forming the protonated ligand, 3,3’-(oxalylbis(azanediyl))bis(1-methyl-2-(p-tolylamino)pyridin-1-ium) trifluoroacetate ([H$_4$L$_a$][CF$_3$C(O)O]$_2$).
\(^1\)H NMR (300 MHz, DMSO-\(d_6\), \(\delta\)): 10.17 (s, 2H, C(O)NH), 9.74 (s, 2H, NH), 8.50 (dd, \(J_1 = 6.4\) Hz, \(J_2 = 1.2\) Hz, 2H, CH), 8.00 (dd, \(J_1 = 7.8\) Hz, \(J_2 = 1.2\) Hz, 2H, CH), 7.45 (dd, \(J_1 = 7.8\) Hz, \(J_2 = 6.4\) Hz, 2H, CH), 7.06 (d, \(J = 8.4\) Hz, 4H, CH), 6.85 (d, \(J = 8.4\) Hz, 4H, CH), 3.99 (s, 6H, N-CH\(_3\)), 2.19 (s, 6H, C-CH\(_3\)).

\(^{13}\)C NMR (75.4 MHz, DMSO-\(d_6\), \(\delta\)): 161.9 (trifluoroacetate C=O), 158.4 (q, \(J_{13C-19F} = 37.0\) Hz, trifluoroacetate CF\(_3\)), 156.4 (C=O), 147.0 (pyridinium C-NHR), 142.3 (pyridinium CH), 141.5 (pyridinium CH), 135.7 (\(p\)-tolyl C-NHR), 134.4 (\(p\)-tolyl C-CH\(_3\)), 129.2 (\(p\)-tolyl CH), 126.2 (pyridinium C-NHC(O)R), 121.9 (\(p\)-tolyl CH), 116.8 (pyridinium CH), 44.5 (N-CH\(_3\)), 20.4 (C-CH\(_3\)).

2.5.6 Synthesis of 4-chloro-1-methyl-3-nitropyridin-1-ium triflate

![Chemical structure of 4-chloro-1-methyl-3-nitropyridin-1-ium triflate](image)

Figure 2.25: Chemical structure of 4-chloro-1-methyl-3-nitropyridin-1-ium triflate

Methyl triflate (4.69 mL, 41.4 mmol) was added in three equal portions over 4 hours to a suspension of 4-chloro-3-nitropyridine (5.47 g, 34.5 mmol) in dichloromethane (400 mL) at room temperature. The solution was stirred for a further 16 hours at room temperature. Most of the solution was then carefully decanted off and the off-white precipitate was collected by filtration and washed with dichloromethane (450 mL) and diethyl ether (300 mL). Yield: 10.04 g (90%).

\(^1\)H NMR (400 MHz, DMSO-\(d_6\), \(\delta\)): 8.96 (d, \(J = 2\) Hz, 1H, CH), 7.81 (dd, \(J_1 = 7.6\) Hz, \(J_2 = 2\) Hz, 1H, CH), 6.56 (d, \(J = 7.6\) Hz, 1H, CH), 3.78 (s, 3H, CH\(_3\)).

\(^{13}\)C NMR (100.6 MHZ, DMSO-\(d_6\), \(\delta\)): 167.2 (C\(_4\)), 144.0 (C\(_2\)), 142.6 (C\(_6\)), 137.4 (C\(_3\)), 122.6 (C\(_5\)), 43.9 (CH\(_3\)).
IR (cm⁻¹): 3053 (br, m), 1646 (m), 1573 (m), 1552 (s), 1372 (w), 1350 (m), 1252 (s), 1222 (s), 1163 (s), 1092 (m), 1026 (s), 934 (m), 839 (m), 807 (m), 767 (m), 708 (w), 693 (w), 633 (s), 572 (m), 515 (s), 427 (m).

ESI-MS m/z: (M⁺), calcd for C₆H₆ClN₂O₂, 173.0112; found, 173.0114 (35%, z = +1). (M⁺ – NO₂), calcd for C₆H₆ClN, 127.0183; found, 127.0189 (100%, z = +1).

Anal. Calcd for C₇H₆ClF₃N₂O₅S: C, 26.06; H, 1.87; N, 8.68. Found: C, 26.37; H, 1.86; N, 8.72.

2.5.7 Synthesis of 4,4’-(1,2-phenylenebis(azanediyl))bis(1-methyl-3-nitropyridin-1-ium) triflate

Figure 2.26: Chemical structure of 4,4’-(1,2-phenylenebis(azanediyl))bis(1-methyl-3-nitropyridin-1-ium) triflate

1,2-phenylenediamine (1.69 g, 15.6 mmol) was added to a suspension of 4-chloro-1-methyl-3-nitropyridin-1-ium triflate (10.04 g, 31.2 mmol) in 1,4-dioxane (220 mL). Triethylamine (4.37 mL, 31.4 mmol) was added and the solution was heated to reflux. After 20 hours under reflux, the solution was cooled to room temperature. The precipitate was collected by filtration and washed with dichloromethane (300 mL), yielding 4,4’-(1,2-phenylenebis(azanediyl))bis(1-methyl-3-nitropyridin-1-ium) triflate as a pale brown solid (9.53 g, 90%).

¹H NMR (400 MHz, DMSO-d₆, δ): 10.85 (s, 2H, NH), 9.66 (d, J = 1.2 Hz, 2H, CH), 8.33 (dd, J₁ = 7.6 Hz, J₂ = 1.2 Hz, 2H, CH), 7.71-7.73 (m, 2H, phenyl CH), 7.62-7.65 (m, 2H, phenyl CH), 7.31 (d, J = 7.6 Hz, 2H, CH), 4.07 (s, 6H, CH₃).

¹³C NMR (100.6 MHz, DMSO-d₆, δ): 149.7 (pyridinium C-NHR), 145.4 (pyridinium CH), 145.3 (pyridinium CH), 133.0 (phenyl C), 130.6 (phenyl CH), 130.2 (pyridinium C-NO₂), 128.8 (phenyl CH), 113.1 (pyridinium CH), 45.4 (CH₃).
IR (cm⁻¹): 3294 (br, m), 3058 (br, m), 1663 (s), 1557 (s), 1501 (w), 1412 (w), 1377 (w), 1353 (w), 1274 (s), 1250 (s), 1211 (s), 1183 (m), 1152 (s), 1119 (m), 1029 (s), 948 (m), 896 (w), 871 (w), 795 (m), 769 (m), 757 (m), 696 (w), 633 (s), 573 (m), 560 (w), 516 (m), 493 (m), 459 (w), 395 (w).

ESI-MS m/z: (M^{2+}), calcd for C₁₈H₁₈N₆O₄, 191.0689; found, 191.0694 (100%, z = +2). (M^{2+} – H^+), calcd for C₁₈H₁₇N₆O₄, 381.1300; found, 381.1296 (75%, z = +1).

Anal. Calcd for C₂₀H₁₈F₆N₆O₁₀S₂: C, 35.30; H, 2.67; N, 12.35. Found: C, 35.61; H, 2.77; N, 12.13.

2.5.8 Synthesis of 4,4’-(1,2-phenylenebis(azanediyl))bis(3-amino-1-methylpyridin-1-ium) triflate

Figure 2.27: Chemical structure of 4,4’-(1,2-phenylenebis(azanediyl))bis(3-amino-1-methylpyridin-1-ium) triflate

A bag containing dihydrogen gas (2 L, 1 atmosphere) was attached to a flask containing a suspension of 4,4’-(1,2-phenylenebis(azanediyl))bis(1-methyl-3-nitropyridin-1-ium) triflate (9.53 g, 14.0 mmol) and 10% Pd/C (0.650 g) in ethanol (600 mL). After 40 hours at room temperature, the solution was filtered through Celite and the solvent was removed from the filtrate under vacuum, yielding 4,4’-(1,2-phenylenebis(azanediyl))bis(3-amino-1-methylpyridin-1-ium) triflate as a pale orange solid (7.62 g, 88%).

¹H NMR (400 MHz, DMSO-­⁶, δ): 8.72 (s, 2H, NH), 7.75 (dd, J₁ = 6.8 Hz, J₂ = 1.6 Hz, 2H, CH), 7.67 (d, J = 1.6 Hz, 2H, CH), 7.47-7.52 (m, 4H, phenyl CH), 6.70 (d, J = 6.8 Hz, 2H, CH), 5.85 (s, 4H, NH₂), 3.93 (s, 6H, CH₃).
13C NMR (100.6 MHz, DMSO-<i>d</i>6, δ): 143.0 (pyridinium C-NHR), 134.5 (pyridinium CH), 134.2 (pyridinium C-NH2), 132.7 (phenyl CH), 127.9 (phenyl CH), 127.1 (phenyl CH), 125.6 (pyridinium CH), 106.2 (pyridinium CH), 45.2 (CH3).

IR (cm⁻¹): 3379 (br, w), 3215 (br, m), 1630 (m), 1587 (w), 1541 (s), 1510 (w), 1485 (m), 1343 (m), 1276 (s), 1255 (s), 1241 (s), 1166 (s), 1025 (s), 993 (w), 874 (w), 856 (w), 812 (m), 775 (m), 758 (w), 635 (s), 572 (m), 514 (s), 451 (w).

ESI-MS m/z: (M²⁺), calcd for C18H22N6, 161.0948; found, 161.0792 (100%, z = +2). (M²⁺ – H⁺), calcd for C18H21N6, 321.1822; found, 321.1827 (6%, z = +1).


2.5.9 Synthesis of (5E,18aE)-8,12,12,16-tetramethyl-8,10,14,16-tetrahydro-11H-benzo[e]dipyrido[3,4-b:4',3'-h][1,4,7,10]tetraazacyclotridecine-11,13(12H)-dione (H₂Lₘ)

Figure 2.28: Chemical structure of (5E,18aE)-8,12,12,16-tetramethyl-8,10,14,16-tetrahydro-11H-benzo[e]dipyrido[3,4-b:4',3'-h][1,4,7,10]tetraazacyclotridecine-11,13(12H)-dione (H₂Lₘ)

60% sodium hydride (2.46 g, 61.5 mmol) was added to a solution of 4,4’-(1,2-phenylenebis(azanediyl))bis(3-amino-1-methylpyridin-1-ium) triflate (7.62 g, 12.3 mmol) in acetonitrile (1 L). After 10 minutes at room temperature, the excess sodium hydride was removed via air-free filtration. The filtrate was heated to 70 °C under nitrogen and dimethylmalonyl dichloride (2.27 mL, 17.2 mmol in 20 mL acetonitrile) was added dropwise to the filtrate over 2 hours. The solution was stirred for a further 2 hours at 70 °C and was then cooled to room temperature and was stirred at room temperature for 16 hours. The solvent was removed under vacuum and the residue was dried for 3 hours under vacuum. The orange solid
was then dissolved in deionised water (350 mL) and sodium carbonate (6.58 g, 61.5 mmol) was added. The aqueous solution was extracted with dichloromethane (3 x 350 mL) and the combined dichloromethane fractions were dried over magnesium sulfate and then filtered. The filtrate was dried for 5 hours under vacuum and the yellow-brown solid was then dissolved in a minimum amount of 9:1 dichloromethane/methanol and was purified by column chromatography on basic alumina (20 x 7 cm column, 1:0 to 39:1 dichloromethane/methanol), collecting the bright yellow band. The solvent was removed under vacuum to yield (5E,18aE)-8,12,12,16-tetramethyl-8,10,14,16-tetrahydro-11H-benzo[e]dipyrido[3,4-b:4’,3’-h][1,4,7,10]-tetraazacyclotridecine-11,13(12H)-dione (H$_2$L$_m$) as a bright yellow solid (1.05 g, 20%).

$^1$H NMR (400 MHz, DMSO-$d_6$, δ): 11.25 (s, 2H, NH), 8.73 (d, J = 2.0 Hz, 2H, pyridinium CH), 7.64 (dd, J$_1$ = 7.2 Hz, J$_2$ = 2.0 Hz, 2H, pyridinium CH), 7.47-7.49 (m, 2H, phenyl CH), 7.09 (d, J = 7.2 Hz, 2H, pyridinium CH), 7.01-7.03 (m, 2H, phenyl CH), 3.78 (s, 6H, N-CH$_3$), 1.45 (s, 6H, C-CH$_3$).

$^1$H NMR (300 MHz, methanol-$d_4$, δ): 8.32 (d, J = 1.8 Hz, 2H, pyridinium CH), 7.59 (dd, J$_1$ = 7.2 Hz, J$_2$ = 1.8 Hz, 2H, pyridinium CH), 7.49-7.52 (m, 2H, phenyl CH), 7.18 (d, J = 7.2 Hz, 2H, pyridinium CH), 7.06-7.10 (m, 2H, phenyl CH), 3.81 (s, 6H, N-CH$_3$), 1.60 (s, 6H, C-CH$_3$).

$^1$H NMR (300 MHz, acetone-$d_6$, δ): 11.47 (br s, 2H, NH), 8.86 (s, 2H, pyridinium CH), 7.57 (d, J = 6.6 Hz, 2H, pyridinium CH), 7.48-7.51 (m, 2H, phenyl CH), 7.11 (d, J = 6.6 Hz, 2H, pyridinium CH), 7.01-7.04 (m, 2H, phenyl CH), 3.88 (s, 6H, N-CH$_3$), 1.54 (s, 6H, C-CH$_3$).

$^1$H NMR (300 MHz, chloroform-$d_1$, δ): 11.40 (br s, 2H, NH), 8.88 (d, J = 1.8 Hz, 2H, pyridinium CH), 7.39-7.42 (m, 2H, phenyl CH), 7.10 (dd, J$_1$ = 7.2 Hz, J$_2$ = 1.8 Hz, 2H, pyridinium CH), 7.04-7.07 (m, 2H, phenyl CH), 6.97 (d, J = 7.2 Hz, 2H, pyridinium CH), 3.71 (s, 6H, N-CH$_3$), 1.67 (s, 6H, C-CH$_3$).

$^{13}$C NMR (100.6 MHz, DMSO-$d_6$, δ): 175.1 (C=O), 146.0 (pyridinium C=NR), 136.7 (phenyl C), 136.4 (pyridinium CH), 132.4 (pyridinium C-NHR), 127.9 (pyridinium CH), 122.0 (phenyl CH), 117.4 (phenyl CH), 102.2 (pyridinium CH), 53.3 (C-CH$_3$), 44.3 (N-CH$_3$), 26.0 (C-CH$_3$).

IR (cm$^{-1}$): 3469 (br, w), 3141 (br, m), 2933 (br, w), 1639 (s), 1616 (m), 1559 (s), 1516 (m), 1483 (m), 1449 (w), 1426 (w), 1385 (m), 1341 (w), 1322 (m), 1287 (w), 1261 (w), 1235 (w), 1206 (s), 1178 (m), 1125 (m), 1091 (w), 1035 (w), 958 (w), 925 (m), 895 (m), 865 (s), 782 (w), 739 (m), 636 (w), 614 (w), 588 (w), 571 (m), 534 (w), 483 (w), 457 (m).
ESI-MS \( m/z \): (M + H\(^+\)), calcd for C\(_{23}\)H\(_{25}\)N\(_6\)O\(_2\), 417.2034; found, 417.2032 (100%, \( z = +1 \)). (M + 2H\(^+\)), calcd for C\(_{23}\)H\(_{26}\)N\(_6\)O\(_2\), 209.1053; found, 209.1059 (25%, \( z = +2 \)). (M + Na\(^+\)), calcd for C\(_{23}\)H\(_{24}\)N\(_6\)NaO\(_2\), 439.1853; found, 439.1828 (2.5%, \( z = +1 \)).

UV-vis (DMSO) \( \lambda_{\text{max}} \), nm (\( \varepsilon \), L mol\(^{-1}\) cm\(^{-1}\)): 276 (19,700), 339 (32,900), 379 (27,600). (CH\(_3\)OH) \( \lambda_{\text{max}} \), nm (\( \varepsilon \)): 321.5 (26,200), 368.5 (25,100). (Acetone) \( \lambda_{\text{max}} \), nm (\( \varepsilon \)): 339 (35,800), 377 (38,100). (Isopropanol) \( \lambda_{\text{max}} \), nm (\( \varepsilon \)): 271.5 (17,100), 341 (34,600), 380.5 (26,200). (CHCl\(_3\)) \( \lambda_{\text{max}} \), nm (\( \varepsilon \)): 277.5 (13,200), 341.5 (23,500), 381 (17,500).

Anal. Calcd for C\(_{23}\)H\(_{24}\)N\(_6\)O\(_2\).H\(_2\)O: C, 63.58; H, 6.03; N, 19.34; Found: C, 63.77; H, 6.09; N, 19.20.

2.5.10 Synthesis of 8,12,12,16-tetramethyl-11,13-dioxo-10,11,12,13,14,19-hexahydro-5H-benzo[e]dipyrido[3,4-b:4’,3’-h][1,4,7,10]tetraazacyclotridecine-8,16-diium trifluoroacetate ([H\(_4\)L\(_m\)][CF\(_3\)C(O)O])

![Chemical structure of 8,12,12,16-tetramethyl-11,13-dioxo-10,11,12,13,14,19-hexahydro-5H-benzo[e]dipyrido[3,4-b:4’,3’-h][1,4,7,10]tetraazacyclotridecine-8,16-diium trifluoroacetate ([H\(_4\)L\(_m\)][CF\(_3\)C(O)O])](image)

Figure 2.29: Chemical structure of 8,12,12,16-tetramethyl-11,13-dioxo-10,11,12,13,14,19-hexahydro-5H-benzo[e]dipyrido[3,4-b:4’,3’-h][1,4,7,10]tetraazacyclotridecine-8,16-diium trifluoroacetate ([H\(_4\)L\(_m\)][CF\(_3\)C(O)O])

For NMR studies, (5E,18aE)-8,12,12,16-tetramethyl-8,10,14,16-tetrahydro-11H-benzo[e]-dipyrido[3,4-b:4’,3’-h][1,4,7,10]tetraazacyclotridecine-11,13(12H)-dione (H\(_2\)L\(_m\), 0.010 g, 0.024 mmol) was dissolved in DMSO-\( d_6 \) (0.7 mL) and trifluoroacetic acid (9.2 \( \mu \)L, 0.12 mmol) was added. After stirring for a few minutes in air at room temperature, \(^1\)H and \(^{13}\)C NMR spectra were obtained. For UV-visible absorption studies, trifluoroacetic acid (202 \( \mu \)L of a 41 mM stock solution in methanol; 8.3 \( \mu \)mol total amount) was added to a solution of H\(_2\)L\(_m\) (0.00090 g, 2.2 \( \mu \)mol) in methanol (60.0 mL). A 3.0 mL aliquot of this solution was added to a cuvette (blanked using a methanol solution) and the UV-visible absorption spectrum was obtained.
$^1$H NMR (300 MHz, DMSO-$d_6$, $\delta$): 9.96 (br s, 2H, NH), 8.98 (br s, 2H, R-NH-C(O)R’), 8.65 (d, $J = 1.8$ Hz, 2H, pyridinium CH), 8.38 (dd, $J_1 = 7.5$ Hz, $J_2 = 1.8$ Hz, 2H, pyridinium CH), 7.84-7.88 (m, 2H, phenyl CH), 7.60 (d, $J = 7.5$ Hz, 2H, pyridinium CH), 7.50-7.53 (m, 2H, phenyl CH), 4.10 (s, 6H, N-CH$_3$), 1.56 (s, 6H, C-CH$_3$).

$^{13}$C NMR (75.4 Hz, DMSO-$d_6$, $\delta$): 172.3 (C=O), 161.9 (trifluoroacetate C=O), 158.4 (q, $J_{^{13}C-^{19}F} = 37.0$ Hz, trifluoroacetate CF$_3$), 150.4 (pyridinium RC-NH-R’), 143.0 (pyridinium CH), 142.6 (pyridinium CH), 130.8 (phenyl C), 127.2 (phenyl CH), 125.1 (phenyl CH), 122.0 (pyridinium RC-NH-C(O)R’), 106.9 (pyridinium CH), 50.9 (C-CH$_3$), 45.3 (N-CH$_3$), 23.3 (C-CH$_3$).

UV-vis (CH$_3$OH) $\lambda_{\text{max}}$, nm ($\varepsilon$, L mol$^{-1}$ cm$^{-1}$): 308 (sh, 21,300), 319 (30,900).
Chapter 3: Synthesis, Structures, and Spectroscopic Properties of New Metal-Pyridinium Amide Complexes

3.1 Introduction

This chapter describes the synthesis and spectroscopic properties of a variety of transition metal complexes of the new acyclic (H$_2$L$_a$) and macrocyclic (H$_2$L$_m$) pyridinium amide ligands. These complexes were designed and synthesised for several reasons: 1) to synthesise iron, cobalt and manganese complexes as catalysts for the oxidation of dye substrates by hydrogen peroxide (discussed in Chapter 4); 2) to synthesise rhodium complexes of ligand L$_m$ as catalysts for small molecule activation (discussed in Chapter 5); 3) to study the effects of the strongly donating pyridinium amide moieties on the oxidation state of the metal centres; 4) to extend the range of known transition metal-pyridinium amide complexes, which remain rare, and to synthesise the first known examples of manganese-, iron-, and cobalt-pyridinium amide complexes; and 5) to synthesise the first known metal complexes of macrocyclic pyridinium amide ligands and to investigate the effect that macrocyclisation has on the structure of the metal complexes produced, in comparison to analogous acyclic pyridinium amide complexes.

3.1.1 Transition metal complexes of pyridinium amides

Although a large number of pyridinium amide ligands have been published in the literature, only a handful of different transition metals have been coordinated to these ligands. Only pyridinium amide complexes with molybdenum, nickel, copper, zinc, ruthenium, rhodium, or palladium metal centres have so far been published. Most studies have involved transition metal-pyridinium amide complexes based on nickel and palladium, and the structures of many of these complexes were discussed in Section 1.4. For all of these nickel and palladium complexes, the metal centres are in the +II oxidation state, and these complexes are square planar and diamagnetic.$^{4-9}$
Copper(I) and zinc(II) complexes of a tripodal pyridinium amide ligand have been synthesised by metallation of the free ligand with [Cu(I)(MeCN)$_4$][PF$_6$] or Zn(II)(OTf)$_2$ in acetonitrile (Figure 3.1).

Both complexes are four-coordinate. The ligand coordinates to the metal centre through one tertiary amine nitrogen atom and the nitrogen atoms of three pyridinium amide functional groups, holding the metal centre in an approximately trigonal pyramidal coordination geometry. The complexes were diamagnetic and were characterised by elemental analysis, NMR spectroscopy, infrared spectroscopy, and mass spectrometry. X-ray crystallography of the zinc(II) complex and the copper(I) complex where R = Bn (Figure 3.1) was used to verify their structures. For the zinc(II) complex, the oxygen atom of the triflate anion was reasonably close to the zinc centre, forming a long, weak zinc-oxygen covalent bond.

**Figure 3.1: Copper(I) and zinc(II) complexes of a tripodal pyridinium amide ligand**

A copper(II) complex of the substituted pyridinium amide ligand shown in Figure 3.2 has also been synthesised. This complex contains two pyridinium amide ligands, which are each bidentate and coordinate to the square planar copper(II) metal centre through a pyridinium amide nitrogen atom and the oxygen atom of a deprotonated hydroxyl group. This complex was synthesised from the corresponding free ligand and bis(acetylacetonato)copper(II) in dichloromethane, followed by recrystallisation from dichloromethane and ethyl acetate. Although IR spectroscopy and elemental analysis results were reported, the compound was not characterised further. Similar substituted pyridinium amide ligands were used to synthesise octahedral molybdenum(VI) complexes (Figure 3.2) from the corresponding free ligand, bis(acetylacetonato)dioxomolybdenum(VI), and triethylamine in refluxing methanol. This was followed by recrystallisation from methanol and ethyl acetate. Elemental analyses for the molybdenum(VI) complexes agreed with the expected formulations and IR spectroscopy results were given. However, these molybdenum(VI) complexes were not characterised further.
Several square planar diamagnetic rhodium(I)-pyridinium amide carbonyl complexes have been synthesised (Figure 3.3) in order to study the donor properties of pyridinium amide ligands, via the analysis of the carbonyl IR stretching frequencies of these complexes. These results were discussed in Section 1.3. The Rh\(^{1}(\text{CO})_{2}(\text{Cl})(\text{L})\) complexes (\(\text{L} = \text{pyridinium amide}\)) used in these studies were synthesised by reacting the free pyridinium amide ligand with [Rh\(^{1}(\text{Cl})(\text{CO})_{2}\)]\(_{2}\) in toluene.\(^{4,5}\)

An octahedral diamagnetic ruthenium(II)-pyridinium amide complex (Figure 3.4) has been synthesised by reacting a free pyridinium amide ligand with [Ru\(^{II}\text{Cl}_{2}(p\text{-cymene})]_{2}\), 2,2’-bipyridine-4,4’-dicarboxylic acid, and ammonium thiocyanate in \(N,N\)-dimethylformamide. The product was purified by column chromatography on Sephadex LH-20 and was studied as a sensitizer for dye-sensitised solar cells. Formation of the complex was confirmed by NMR spectroscopy, infrared spectroscopy, mass spectrometry, and elemental analysis.\(^{12}\)
3.1.2 Iron, cobalt, and manganese complexes of macrocyclic N-donating ligands

Iron, cobalt, and manganese complexes of the macrocyclic pyridinium amide ligand, $L_m$, were targeted as potential catalysts for the oxidation of dye substrates by hydrogen peroxide. The structures of these compounds are discussed in Section 3.2.3, and investigations of their catalytic properties are discussed in Chapter 4. The structures of these metal-$L_m$ complexes are expected to be similar to the structures of metal-TAML complexes (see Section 1.6.3). The latter are known to be highly effective oxidation catalysts. This section therefore summaries the structures and spectroscopic properties of iron-, cobalt-, and manganese-TAML complexes.

Iron complexes of TAML ligands are usually synthesised by reaction of the free $H_4TAML$ ligand with anhydrous iron(II) chloride or iron(III) chloride in the presence of a strong base (such as sodium hydride, $n$-butyl lithium or potassium tert-butoxide) in THF under stringently air- and water-free conditions.\cite{92,135,147} X-ray crystallography and elemental analysis of these paramagnetic Fe-TAML complexes indicates that they are five-coordinate in the solid state, with an axial chloride or water ligand and an iron(III) metal centre.\cite{55,97,104} The ability of Fe(III)-TAML complexes to catalyse the oxidation of various substrates by peroxides was described in Section 1.6.3. These Fe(III)-TAML complexes are either dianionic (when the axial ligand is chloride, $[\text{Fe}^{\text{III}}(\text{TAML})(\text{Cl})]^2-$) or monoanionic (when the axial ligand is water, $[\text{Fe}^{\text{III}}(\text{TAML})(\text{H}_2\text{O})]^-$). The countercation(s) depend on the base used and they are often exchanged for bulkier cations, such as $\text{PPh}_4^+$ or $\text{NEt}_4^+$, to alter the solubility of the complex, and to obtain more crystalline samples.\cite{92,135,147} EPR spectroscopies and DFT studies suggest that the iron centre of Fe(III)-TAMLs is six-coordinate in aqueous solutions, with two axial water ligands.\cite{55,97} Spectroscopic studies also suggest that Fe(III)-TAMLs are oxidised to the Fe(V) oxidation state in the presence of excess peroxides.\cite{62,80,83} Using strong oxidants, a few Fe-
TAML complexes have been isolated in oxidation states higher than +III. For example, a stable paramagnetic Fe(IV)-TAML complex, \([\text{NEt}_4][\text{Fe}^{\text{IV}}(\text{MAC}^*)(\text{Cl})]\), has been synthesised by oxidising \([\text{NEt}_4]_2[\text{Fe}^{\text{III}}(\text{MAC}^*)(\text{Cl})]\) with ceric ammonium nitrate in dichloromethane (see Figure 1.27 for the structure of various TAML ligands, such as MAC*). X-ray crystallography, Mössbauer spectroscopy, and EPR spectroscopy suggested that the iron centre of this complex is in the +IV oxidation state and is high-spin (spin = 2).\(^{81,148}\) In a related study, a low-spin (spin = 1) iron(IV) TAML complex, \([\text{Fe}^{\text{IV}}(\text{MAC}*)(\text{CN}^\text{Bu})_2]\), was synthesised by oxidising \([\text{Li}]_2[\text{Fe}^{\text{III}}(\text{MAC}*)(\text{Cl})]\) with ceric ammonium nitrate in dichloromethane, followed by isolation of the \([\text{Li}]_2[\text{Fe}^{\text{IV}}(\text{B}(\text{Cl})_2)(\text{Cl})]\) complex. This complex was then added to water and the axial chloride ligand was exchanged for a cyano ligand using excess sodium cyanide, and the \([\text{Li}]_2[\text{Fe}^{\text{IV}}(\text{B}(\text{Cl})_2)(\text{CN})]\) product was then isolated.\(^{104}\) In solution, a spin = ½ square pyramidal iron(V) TAML complex, \(\text{Fe}^{\text{V}}(\text{B}^*)(\text{O})\), has been characterised at -60 °C in n-butyronitrile by mass spectrometry, reactivity studies, and DFT calculations, and also by EPR, Mössbauer, and X-ray absorption spectroscopies. This iron(V) complex was synthesised by reacting \([\text{PPh}_4][\text{Fe}^{\text{III}}(\text{B}^*)(\text{H}_2\text{O})]\) with excess \(m\)-chloroperbenzoic acid at -60 °C in n-butyronitrile.\(^{83}\)

Cobalt(III) complexes of TAML ligands are normally synthesised by reaction of the free \(\text{H}_4\text{TAML}\) ligand with cobalt(II) chloride in THF under rigorously air- and water-free conditions, in the presence of a strong base (such as \(n\)-butyl lithium or lithium diisopropylamide). Upon exposure of the solution to air, the complex oxidises to the Co(III) oxidation state and the products are then isolated. High resolution negative ion mass spectrometry of these complexes agree with the expected formulation of \([\text{Co}^{\text{III}}(\text{TAML})]^\text{−}\).\(^{18,150-152}\) The countercation is often exchanged for bulkier counterions, such as \(\text{PPh}_4^+\), \(\text{NEt}_4^+\), or \(\text{NBu}_4^+\), to alter the solubility of the complex and to grow X-ray quality crystals. X-ray crystallographic studies show that the Co(III) centre is four-coordinate and square planar, and sits close to the plane defined by the four amidate nitrogen atoms.\(^{18,106,150-152}\) In contrast, Fe(III)-TAMLs are five-coordinate in the solid state.\(^{55,97,104}\) EPR studies suggest that the cobalt centres of Co(III)-TAMLs are in the \(S = 1\) spin state, and relatively sharp contact-shifted proton NMR signals confirm that the cobalt centres are paramagnetic.\(^{150,152}\) Like the Fe(III)-TAML complexes, the cobalt centres of Co(III)-TAMLs can be oxidised to oxidation states higher than +III. For example, oxidation of
[NEt₄][Co₃⁺(B)] with ceric ammonium nitrate in dry dichloromethane yielded an air-stable Co⁴⁺(B) complex. X-ray crystallography indicated that the Co(IV) centre remains square planar, and elemental analysis also agreed with the expected formulation. Analysis of the phenyl ring C-C bond lengths in the Co⁴⁺(B) complex suggested that oxidation of the [NEt₄][Co₃⁺(B)] complex is not entirely metal-centred, and also suggested that partial oxidation of the TAML phenyl ring may occur. EPR studies, however, suggested that the [NEt₄][Co₃⁺(B)] complex has one unpaired electron, which is located primarily on the metal centre.¹⁵⁰

Manganese complexes of several TAML complexes have also been isolated and these have shown promise as catalysts for oxidation reactions.¹⁵³,¹⁵⁴ Air-stable manganese(V)-oxo-TAML complexes, [Mn⁵⁺(TAML)(O)]⁺ are usually synthesised by reacting the free H₄TAML ligand with a strong base (tert-butyl lithium or lithium bis(trimethylsilyl)amide) and Mn³⁺Cl₂ (or Mn³⁺(acac)₃) in THF under air- and water-free conditions. The complexes are then oxidised to the Mn(V) oxidation state in situ using tert-butyl hydroperoxide. After product isolation, the lithium countercation is often exchanged for NEt₄⁺ or PPh₄⁺. Proton NMR spectroscopy of these [Mn⁵⁺(TAML)(O)]⁺ complexes indicates that they are diamagnetic. Furthermore, X-ray crystallography confirms that the manganese centre of these complexes is five-coordinate in the solid state, with the manganese atom sitting significantly out of the plane defined by the four amidate nitrogen atoms, on the side towards the metal-oxo bond.¹⁵³-¹⁵⁶ This is similar to the crystal structures of Fe(III)(TAML)(X) complexes (X = Cl or H₂O), where the five-coordinate iron atom also sits significantly out of the tetraamidate plane, on the side towards the axial ligand.⁵⁵,⁹⁷,¹⁰⁴ Although Mn(III)-TAML complexes have not been isolated, it is believed that they are formed prior to the addition of tert-butyl hydroperoxide.¹⁷,¹⁵³ Mn(IV)-TAML complexes also have not been isolated, even though cyclic voltammetry has suggested that the [NEt₄][Mn⁵⁺(B)(O)] TAML complex can be reduced to a formal Mn(IV) oxidation state. The possibility of ligand non-innocence in these manganese-TAML complexes was not investigated.¹⁵⁶
3.1.3 Nickel, palladium, and copper complexes of macrocyclic N-donating ligands

This section discusses the structural and spectroscopic properties of various macrocyclic N-donating ligands with nickel, palladium, and copper metal centres, so that their properties can be compared to nickel, palladium, and copper complexes of the new macrocyclic (Lₘ) and acyclic (Lₐ) pyridinium amide ligands. These are described further in Sections 3.2.2 and 3.2.4. Although ligand Lₘ is similar in structure to some TAML ligands (see Section 1.5), of the three different types of metal centres discussed in this section, only nickel complexes of TAML ligands have been published.¹⁵⁷ Therefore, this section also discusses the structural and spectroscopic properties of nickel, palladium, and copper complexes of several other macrocyclic ligands that contain four strongly donating nitrogen donors. Many different classes of these ligands are known, and this section focuses primarily on some of the most common macrocyclic tetra-nitrogen donor ligands: porphyrins, corroles, and dibenzo-tetramethyl-tetraaza[14]annulenes (abbreviated herein as TMTAAs). The general structures of these ligands are shown in Figure 3.5.

![Figure 3.5: General structures of free porphyrin, corrole, and TMTAA ligands. Many different substituted derivatives of these ligands have been studied](image)

An air-stable nickel(III)-TAML complex has been synthesised by reaction of the free H₄MAC* TAML ligand (see Figure 1.27 for the structure of this ligand) with Ni⁰(PPh₃)₂(Br)₂ in dry, deoxygenated THF, in the presence of excess lithium bis(trimethylsilyl)amide.¹⁵⁷ Oxidation of the isolated nickel(II) complex with excess benzoyl peroxide in ethanol yielded the Li[Ni⁺⁺(MAC*)] complex, and the lithium countercation was then exchanged for tetraethylammonium, followed by product isolation. X-ray crystallography of the [NEt₄][Ni⁺⁺(MAC*)] complex indicated that the nickel(III) centre has a distorted square planar...
geometry, with the metal centre sitting slightly above the tetraamidate plane (by 0.09 Å). EPR studies confirmed that [NEt₄][Ni⁺⁺⁺(MAC*)] is paramagnetic, and suggested that this complex may axially ligate in solution in the presence of potential ligands, such as trimethylphosphine, ethanol, pyridines, or cyanide.

In contrast to the Ni(III)-MAC* TAML complex, most isolated nickel and palladium complexes of porphyrin, corrole, and TMTAA ligands are diamagnetic, with square planar (or slightly distorted square planar) metal centres that are in the +II oxidation state. Even though the X-ray crystal structures of these complexes demonstrate that TMTAA ligands are significantly more distorted than porphyrin or corrole ligands, the metal centre still remains relatively planar in the Ni(II)-TMTAA and Pd(II)-TMTAA complexes. Although electrochemical studies suggest that some of these complexes can be oxidised to species with formal Ni(III) or Pd(III) oxidation states, they have not been isolated and the ligands are often redox non-innocent. An exception to this is the recent isolation and characterisation of a stable octahedral Pd(III)-porphyrin complex, where the metal centre was shown to be paramagnetic, with one unpaired electron. A few octahedral Ni(II)-porphyrin complexes have also been isolated. Spectroscopic studies suggest that these complexes are paramagnetic, with two unpaired electrons, as would be expected for a $d^8$ octahedral complex. These octahedral complexes are synthesised by the reaction of diamagnetic square planar Ni(II)-porphyrin complexes with potential donor ligands, such as pyridines. The porphyrin ligands of these complexes are usually substituted with electron-withdrawing functionalities, which decreases the electron density at the Ni(II) centre and enables binding of the axial ligands. Analysis of the X-ray crystal structures of these octahedral Ni(II)-porphyrin complexes reveals that the porphyrin cavity expands upon axial ligation. This has been attributed to occupation of the non-bonding $d_{x^2-y^2}$ orbital by one electron, which increases the Ni-N bond lengths and decreases the distortion of the macrocyclic ligand, therefore relieving some of the strain in this ligand. The planarity of the metal centre therefore increases relative to the analogous four-coordinate Ni(II)-porphyrin complexes.

Copper complexes of porphyrin and TMTAA ligands are usually paramagnetic, with square planar (or close to square planar) Cu(II) metal centres. Spectroscopic studies suggest that these complexes have one unpaired electron, as would be expected for a metal centre with a $d^9$ square planar geometry. As for the Ni(II) and Pd(II) complexes of porphyrin, corrole, and TMTAA ligands described above, electrochemical studies suggest that the Cu(II) metal centre can be oxidised to a formal Cu(III) metal centre, but these complexes have not been isolated.
For the Cu(II)-porphyrin complexes, the porphyrin ligand is usually non-innocent, and so the ligand oxidises as well as the metal centre to form porphyrin radical cation complexes that have formal Cu(III) metal centres. Numerous Cu(II)-porphyrin and Cu(II)-TMTAA complexes have been characterised by X-ray crystallography, and these results confirm that the Cu(II) metal centres are close to planarity, as has also been found for the Ni(II) and Pd(II) complexes of porphyrin, corrole, and TMTAA ligands described in the previous paragraph.

In contrast to the paramagnetic Cu(II)-porphyrin and Cu(II)-TMTAA complexes, most copper-corrole complexes have square planar diamagnetic Cu(III) metal centres. This has been attributed to the fact that corrole ligands are stronger N-donors than most porphyrin and TMTAA ligands, and can therefore stabilise metal centres in higher oxidation states. X-ray crystal structures of these complexes indicate that the Cu(III) atom remains close to the plane defined by the four corrole atoms, although the corrole ligand itself is usually somewhat saddled. NMR studies of Cu(III)-corroles demonstrate that the proton NMR signals broaden and shift considerably as the temperature increases. For most Cu(III)-corroles, proton NMR signals remain sharp and non-contact shifted at room temperature, and broadening only occurs at elevated temperatures. However, some Cu(III)-corroles have broadened and contact-shifted proton NMR signals at room temperature, suggesting that these complexes are paramagnetic. It has been postulated that this is due to rapid equilibrium between a diamagnetic Cu(III)-corrole species and a paramagnetic Cu(II)-corrole radical cation species, and that the contribution from the latter species increases with increasing temperature. DFT and spectroscopic studies suggest that this is because the Cu(II) radical cation species is only slightly higher in energy than the Cu(III) species. The large energy gap between the HOMO and LUMO orbitals for square planar Cu(III) complexes would suggest that the observed paramagnetism is not due to the formation of a square planar high-spin Cu(III) complex.

3.1.4 Complexes with unsupported ruthenium-ruthenium bonds

Ruthenium complexes containing direct ruthenium-ruthenium bonds that are not supported by ligands chelating between the two metal centres are described in this section, and the spectroscopic and crystallographic evidence for these structures are discussed. These particular ruthenium complexes are discussed herein because spectroscopic studies suggest that an
unsupported ruthenium-ruthenium bond is present in a ruthenium complex of the new macrocyclic pyridinium amide ligand, Lₘ, discussed below (see Section 3.2.5).

A large number of complexes with direct ruthenium-ruthenium bonds have been published in the literature. For the vast majority of these complexes, the metal-metal bond is supported by chelating ligands that bridge between the two metal centres, stabilising the ruthenium-ruthenium bond. Most of these supported ruthenium-ruthenium complexes have a “paddlewheel”-type structure, where four bidentate ligands coordinate to both metal centres. An example of this class of supported metal-metal bound complexes is Ru₂(OAc)₄. Replacement of the methyl group on the acetate ligands of this complex with other functionalities has led to the development of a large suite of related paddlewheel-type ruthenium-ruthenium complexes. N,O-donating ligands (such as amidates and oxopyridinates) and N,N’-donating ligands (such as aminopyridinates, formamidates, and triazenates) can also form paddlewheel-type ruthenium-ruthenium dimers. For most of these complexes, one metal centre is in the +II oxidation state and the other metal centre is in the +III oxidation state, although Ru(II)-Ru(II) and Ru(III)-Ru(III) paddlewheel-type dimers are also known.

In contrast to the supported metal-metal bound complexes, unsupported ruthenium-ruthenium complexes are rare and are usually based on ruthenium complexes with corrole, porphyrin, tetraazaannulene, or catecholate ligands. The rest of this section focuses on unsupported ruthenium-ruthenium bound complexes of macrocyclic N-donating ligands, because of their structural similarities to the ruthenium-ruthenium dimer of the new pyridinium amide macrocyclic ligand Lₘ, which is discussed in Section 3.2.5.

Air-stable neutral ruthenium(III)-ruthenium(III) dimers of the corrole ligands, 2,3,8,12,17,18-hexaethyl-7,13-dimethylcorrole (hedmc) and 8,12-diethyl-2,3,7,13,17,18-hexamethylcorrole (dehmc) have been synthesised and characterised (Figure 3.6). These complexes were synthesised by reacting the free ligand (H₃hedmc or H₃dehmc) with triethylamine and excess [Ruᵖ²(COD)Cl₂]₂ in 2-methoxyethanol. After heating for 20 to 30 minutes under reflux in air, the solvent was removed under vacuum, and the complexes were purified by recrystallisation and column chromatography on basic alumina, to give [Ruᵖ²(hedmc)]₂ and [Ruᵖ²(dehmc)]₂ in 72% and 51% yield, respectively. Mass spectrometry, UV-visible absorption spectroscopy and X-ray crystallography confirmed that these dimers were indeed synthesised.
Figure 3.6: Chemical structures of [Ru$^{III}$](hedmc)$_2$ and [Ru$^{III}$](dehmc)$_2$

[Ru$^{III}$](hedmc)$_2$ and [Ru$^{III}$](dehmc)$_2$ are diamagnetic. Equivalence of the positions in the $^1$H NMR spectra of these complexes indicated that each ligand is two-fold symmetric, and that each ligand is symmetric with the other ligand. The methylene positions of the ethyl groups were found to be diastereotopic. This has been postulated as evidence of a metal-metal bond, because one of the CH$_2$ protons points towards the metal-metal bond, while the other CH$_2$ proton points away from the metal-metal bond, and so these two protons are shielded to different extents.  

All of the $^1$H NMR signals occurred in the expected regions and were not contact-shifted. The simplified orbital splitting diagram for eclipsed metal-metal complexes, where each metal centre is five-coordinate, is shown in Figure 3.7. This diagram predicts that the [Ru$^{III}$](hedmc)$_2$ and [Ru$^{III}$](dehmc)$_2$ complexes are diamagnetic, and also predicts that the ruthenium-ruthenium bond is a formal triple bond. Although this bond is a formal triple bond, studies have shown that the energy barrier to rotation about the metal-metal bond for complexes of the geometry shown in Figure 3.7 is very small when the $\delta^*$ orbital is fully occupied. The orbital splitting diagram is similar if the two ligands are staggered, except that the two $\delta$ orbitals become degenerate and non-bonding, and the two $\sigma^*(M-N)$ orbitals also become degenerate. Using these splitting diagrams, ruthenium(II)-ruthenium(II) and ruthenium(II)-ruthenium(III) dimers would be paramagnetic, with formal bond orders of 2 and 2.5, respectively. Because monomeric ruthenium(III) species are also expected to be paramagnetic, the absence of signals in the EPR spectrum of the [Ru$^{III}$](hedmc)$_2$ and [Ru$^{III}$](dehmc)$_2$ complexes suggested that only the diamagnetic ruthenium(III)-ruthenium(III) complexes were synthesised.
Figure 3.7: Orbital splitting diagram for an eclipsed homodimer, where each metal centre is five-coordinate. Electrons are added to illustrate the bond order of eclipsed $d^5-d^5$ metal-metal bound $\text{[Ru}^{\text{III}}(\text{L})_2$ complexes

X-ray crystallography of $\text{[Ru}^{\text{III}}(\text{hedmc})_2$ demonstrated that the two ligands are rotated 180° relative to one another. The crystal structure also showed that the ligands are slightly domed, and that the ruthenium centres sit out of the plane defined by the four corrole nitrogen atoms, on the side towards the metal-metal bond. This was attributed to the strong interaction between the two ruthenium centres and steric repulsions between the ligands. The short ruthenium-ruthenium bond length (2.166(1) Å) was consistent with a ruthenium-ruthenium triple bond, as expected.\textsuperscript{182}

Cyclic voltammetry has been used to study changes to the oxidation states of $\text{[Ru}^{\text{III}}(\text{hedmc})_2$ and $\text{[Ru}^{\text{III}}(\text{dehmc})_2$ in dichloromethane solutions containing 0.1 mol $\text{L}^{-1}$ tetra-$n$-butylammonium perchlorate. Upon reducing the ruthenium(III)-ruthenium(III) complexes, two reversible one-electron reductions were observed, which were ascribed to reduction of the ruthenium(III)-ruthenium(III) metal centre to ruthenium(II)-ruthenium(III) and then to ruthenium(II)-ruthenium(II) (Figure 3.8). Upon oxidation of the $\text{[Ru}^{\text{III}}(\text{hedmc})_2$ and
[Ru\textsuperscript{III}(dehmc)]\textsubscript{2} complexes, two reversible one-electron oxidations occurred, and it has been concluded that these are due to oxidation of the ruthenium(III)-ruthenium(III) species to a ruthenium(III)-ruthenium(IV) species and then to a ruthenium(IV)-ruthenium(IV) species. As the potential increased further, a two-electron oxidation process occurred. Thin-layer UV-visible spectroelectrochemistry suggested that this two-electron oxidation was not metal-centred and was instead due to a one electron oxidation of each corrole ligand of the ruthenium(IV)-ruthenium(IV) dimer. Further oxidations and reductions were outside of the potential range of the solvents used in these cyclic voltammetry studies. Figure 3.8 illustrates that as the oxidation state of the metal centres increased, the bond order also increased, as predicted by the orbital splitting diagram given in Figure 3.7. None of the oxidised or reduced species of the ruthenium(III)-ruthenium(III)-corrole dimers have been isolated.\textsuperscript{187}

![Diagram](image)

**Figure 3.8: Species observed in the electrochemical reduction and oxidation of [Rh\textsuperscript{III}(hedmc)]\textsubscript{2} and [Rh\textsuperscript{III}(dehmc)]\textsubscript{2} dimers by cyclic voltammetry**

Ruthenium(III)-ruthenium(III) dimers have also been synthesised of the corrole ligand, 5,10,15-tris(pentafluorophenyl)corrole (tpfc) (Figure 3.9). The method used to synthesise [Ru\textsuperscript{III}(tpfc)]\textsubscript{2} was very similar to the procedures used to synthesise [Ru\textsuperscript{III}(hedmc)]\textsubscript{2} and [Ru\textsuperscript{III}(dehmc)]\textsubscript{2}. Like these complexes, [Ru\textsuperscript{III}(tpfc)]\textsubscript{2} is diamagnetic and air-stable, and the two corrole ligands are oriented \(180^\circ\) relative to one another in the X-ray crystal structure. Also like [Ru\textsuperscript{III}(hedmc)]\textsubscript{2} and [Ru\textsuperscript{III}(dehmc)]\textsubscript{2}, the tfpc ligands are domed, and the metal atoms sit out of the plane defined by the four nitrogen atoms, on the side towards the metal-metal bond. The ruthenium-ruthenium bond length (2.182 Å) was similar to the ruthenium-ruthenium bond lengths of [Ru\textsuperscript{III}(hedmc)]\textsubscript{2} (2.166 Å) and other complexes with ruthenium-ruthenium triple bonds. Significant doming of the tfpc ligands is thought to be a consequence of the steric repulsion between the adjacent
pentafluorobenzene rings. As for the cyclic voltammograms of [Ru\textsuperscript{III}(hedmc)]\textsubscript{2} and [Ru\textsuperscript{III}(dehmc)]\textsubscript{2}, the cyclic voltammogram of [Ru\textsuperscript{III}(tpfc)]\textsubscript{2} showed two reversible metal-centred reduction waves and three metal-centred reversible oxidation waves.\textsuperscript{188}

Figure 3.9: Chemical structure of [Ru\textsuperscript{III}(tpfc)]\textsubscript{2}

Unsupported Ru-Ru bonds are also known to form in ruthenium complexes of the porphyrin ligands octaethylporphyrin (OEP) and tetraphenylporphyrin (TPP) (Figure 3.10). [Ru\textsuperscript{II}(OEP)]\textsubscript{2} has been studied much more extensively than [Ru\textsuperscript{II}(TPP)]\textsubscript{2}. Both complexes were synthesised by heating the corresponding Ru\textsuperscript{II}(porphyrin)(py)\textsubscript{2} complex (py = pyridine) overnight at 210 °C under high vacuum (about 10\textsuperscript{-5} torr). For the [Ru\textsuperscript{II}(TPP)]\textsubscript{2} complex, Ru\textsuperscript{II}(TPP)(py)\textsubscript{2} had to be lyophilised to an amorphous state before pyridine dissociation occurred.\textsuperscript{191}

Figure 3.10: Chemical structures of the free porphyrin ligands, octaethylporphyrin (H\textsubscript{2}OEP) and tetraphenylporphyrin (H\textsubscript{2}TPP), used to synthesise dimeric ruthenium complexes
Although sharp $^1$H NMR signals were observed for both [Ru$^{	ext{II}}$(OEP)]$_2$ and [Ru$^{	ext{II}}$(TPP)]$_2$, these signals were contact-shifted, suggesting that both complexes are paramagnetic. For example, $^1$H NMR signals for [Ru$^{	ext{II}}$(OEP)]$_2$ were observed between 3.4 and 25.5 ppm in benzene-$d_6$, and between -14.2 and 13.4 ppm for [Ru$^{	ext{II}}$(TPP)]$_2$ in toluene-$d_8$. Unlike the ruthenium(III)-ruthenium(III) corrole dimers, [Ru$^{	ext{II}}$(OEP)]$_2$ and [Ru$^{	ext{II}}$(TPP)]$_2$ are very air-sensitive and react with a large variety of substrates to produce monomeric ruthenium(II) complexes.

Solution magnetic moments for [Ru$^{	ext{II}}$(OEP)]$_2$ and [Ru$^{	ext{II}}$(TPP)]$_2$ indicated that each complex has two unpaired electrons and so, based on the orbital splitting diagram shown in Figure 3.7, each ruthenium centre is in the +II oxidation state, with a formal double bond between the two metal centres. This differs from the ruthenium(III)-ruthenium(III) corrole dimers, where both metal centres are in the +III oxidation state. It has been postulated that this difference is due to both the smaller cavity size of the corrole ligand and the more electronegative corrole ligand, which stabilises metal centres in higher oxidation states than porphyrin ligands. This is because corrole ligands have three formally negatively charged nitrogen donor atoms and one neutral nitrogen donor atom, while porphyrin ligands have only two formally negatively charged nitrogen-donors and two neutral nitrogen-donors.

An X-ray crystal structure of [Ru$^{	ext{II}}$(OEP)]$_2$ has been obtained. The crystal was grown in $n$-pentane and two $n$-pentane molecules were observed in the crystal structure. As for the
ruthenium(III)-ruthenium(III) corrole dimers, the two porphyrin ligands are slightly domed, and the ruthenium atoms sit out of the plane defined by the four nitrogen atoms, on the side towards the metal-metal bond. The orientation of the two porphyrin ligands was found to distort away from a fully eclipsed geometry, with a twist angle of 23.8(1)° between the two ligands. The only major change expected for the orbital splitting diagram of this complex (as given in Figure 3.7) is that energy gap between the δ and δ* orbitals decreases as the porphyrin ligands rotate away from a fully eclipsed geometry. Since both of these orbitals are completely filled in the [RuII(OEP)]2 complex, the ruthenium-ruthenium bond order is not affected by this rotation. Despite the presence of a formal ruthenium-ruthenium double bond and a geometry intermediate between an eclipsed and a staggered geometry in the solid state, the equivalence of the two OEP ligands of [RuII(OEP)]2 by 1H NMR spectroscopy suggests that rotation of these ligands about the metal-metal bond in solution is rapid on the NMR timescale. This was not unexpected, because other studies have shown that the energy barrier to rotation about the formal double bond of [RuII(porphyrin)]2 dimers is very small. The ruthenium-ruthenium bond length (2.408(1) Å) of [RuII(OEP)]2 was found to be close to the bond length expected for ruthenium-ruthenium double bonds, and was significantly longer than the Ru(III)-Ru(III) triple bond observed for ruthenium corrole dimers (about 2.2 Å).

Cyclic voltammetry suggested that it may be relatively easy to chemically oxidise the [RuII(OEP)]2 complex to produce stable Ru(II)-Ru(III) and Ru(III)-Ru(III) dimers. Using one equivalent of an oxidant (silver tetrafluoroborate, ferrocenium hexafluorophosphate or tris(4-bromophenyl)ammonium hexachloroantimonate), [RuII(OEP)]2 was selectively oxidised to the air-sensitive mixed-valence [RuII/III(OEP)]2+ dimer (Figure 3.11). When two equivalents of the oxidant were used, the air-sensitive [RuIII(OEP)]22+ dimer was selectively synthesised instead. After isolation, elemental analyses of these compounds agreed with the expected formulations. Sharp contact-shifted 1H NMR signals indicated that the [RuII/III(OEP)]2+ dimer is paramagnetic, while sharp non-contact shifted 1H NMR signals indicated that the [RuIII(OEP)]22+ dimer is diamagnetic, as would be expected based on the simple orbital splitting diagrams proposed for these complexes (Figure 3.7). Like the [RuII(OEP)]2 complex, 1H NMR spectroscopy showed that the ligands in both complexes are four-fold symmetric, that the two ligands are equivalent, and that the methylene groups are diastereotopic. These results suggested that the symmetry is maintained after oxidation. In contrast to these Ru(II)-Ru(II)-OEP and Ru(II)-Ru(III)-OEP complexes, attempts to isolate Ru(II)-Ru(II)-corrole and Ru(II)-Ru(III)-corrole dimers from the Ru(III)-Ru(III)-corrole complexes were unsuccessful.
Figure 3.11: Chemical oxidation of the [Ru\textsuperscript{II}OEP]\textsubscript{2} dimer to [Ru\textsuperscript{II/III}OEP]\textsubscript{2}\textsuperscript{+} and [Ru\textsuperscript{III}OEP]\textsubscript{2}\textsuperscript{2+} using one and two equivalents of an oxidant, respectively (oxidants = AgBF\textsubscript{4}, [Fe(Cp)\textsubscript{2}]PF\textsubscript{6} or tris(4-bromophenyl)ammonium hexachloroantimonate)

A mixed-valence [Ru\textsuperscript{II/III}(TPP)]\textsubscript{2}[PF\textsubscript{6}] complex has been characterised by X-ray crystallography.\textsuperscript{195} As for the [Ru\textsuperscript{II}(OEP)]\textsubscript{2} complex, the TPP ligands are domed; the ruthenium atoms sit out of the plane defined by the four nitrogen atoms, on the side towards the metal-metal bond; and the orientation of the two porphyrin ligands are distorted away from a fully eclipsed geometry, with a twist angle of 29.4° between the two ligands. The Ru(II)-Ru(III) bond length of [Ru\textsuperscript{II/III}(TPP)]\textsubscript{2}[PF\textsubscript{6}] (2.293(2) Å) is similar to the Ru-Ru bond lengths of other Ru(II)-Ru(III) mixed-valence complexes (2.24-2.30 Å), and is intermediate between the Ru(II)-Ru(II) bond length of [Ru\textsuperscript{II}(OEP)]\textsubscript{2} (2.408(1) Å) and the Ru(III)-Ru(III) bond length of ruthenium corrole dimers (about 2.2 Å). EPR spectroscopy and solution magnetic susceptibility measurements showed that [Ru\textsuperscript{II/III}(TPP)]\textsubscript{2}[PF\textsubscript{6}] has one unpaired electron, as expected.\textsuperscript{195}

Ruthenium-ruthenium dimers of the porphyrin ligands tetra-\textit{p}-tolylporphyrin (TTP) and octaethyltetraazaazaporphyrin (OETAP) have also been isolated.\textsuperscript{193,196} TTP is structurally related to the TPP porphyrin, and contains four \textit{p}-tolyl groups on each porphyrin ligand instead of four phenyl groups, while OETAP is structurally related to OEP, and contains nitrogen atoms instead of CH groups at each of the four methine bridge positions. Both complexes were synthesised using the same method as for the OEP and TPP ruthenium(II)-ruthenium(II) dimers. Spectral data for the [Ru\textsuperscript{II}(TTP)]\textsubscript{2} and [Ru\textsuperscript{II}(OETAP)]\textsubscript{2} complexes suggests that, like the [Ru\textsuperscript{II}(TPP)]\textsubscript{2} and [Ru\textsuperscript{II}(OEP)]\textsubscript{2} dimers, both ruthenium centres are in the +II oxidation state.\textsuperscript{191,193,196,197}
Dibenzotetramethylenetetraaza[14]annulenes (TMTAAs) (Figure 3.5) are another class of ligand that are known to form dimeric ruthenium complexes with unsupported ruthenium-ruthenium bonds. Two different routes have been used to synthesise [Ru(TMTAA)]$_2$ complexes. One route leads directly to the formation of a mixed-valence [Ru$^{II/III}$TMTAA]$_2$ complex, whereas the other route leads directly to a [Ru$^{II}$TMTAA]$_2$ complex. In the first route, [Ru$^{II/III}$TMTAA]$_2$[BF$_4$] was synthesised by reaction of ruthenium(II)-ruthenium(III) acetate chloride (Ru$_2$(OAc)$_4$Cl) with H$_2$TMTAA and NaBF$_4$ in ethanol. Like the isolated ruthenium(II)-ruthenium(III) porphyrin dimers, [Ru$^{II/III}$TMTAA]$_2$[BF$_4$] is air-sensitive. Solid-state magnetic moments confirmed that the complex was paramagnetic, with one unpaired electron. Cyclic voltammetry showed that the [Ru$^{II/III}$TMTAA]$_2$[BF$_4$] complex could be reversibly oxidised to [Ru$^{III}$TMTAA]$_2^{2+}$ and reversibly reduced to [Ru$^{II}$TMTAA]$_2$, and this was also achieved chemically using ferrocenium tetrafluoroborate and sodium borohydride, respectively. Like the Ru(II)-Ru(II) and Ru(III)-Ru(III) porphyrin dimers, the [Ru$^{II}$TMTAA]$_2$ and [Ru$^{III}$TMTAA]$_2$[BF$_4$]$_2$ complexes were air-sensitive and were characterised under air-free conditions. Mass spectrometry, $^1$H NMR spectroscopy, and solid state magnetic moments suggested that the ruthenium-ruthenium bonds remained intact in these complexes, and that the [Ru$^{II}$TMTAA]$_2$ complex is paramagnetic (with two unpaired electrons), while the [Ru$^{III}$TMTAA]$_2$[BF$_4$]$_2$ complex is diamagnetic. As for the [Ru$^{III}$(corrole)]$_2$ complexes, $^1$H NMR spectroscopy showed that for all three TMTAA dimers ([Ru$^{II}$TMTAA]$_2$, [Ru$^{II/III}$TMTAA]$_2$[BF$_4$] and [Ru$^{III}$TMTAA]$_2$[BF$_4$]$_2$), the two ligands are symmetrically equivalent and each half of each ligand is also symmetrically equivalent.

The second route used to synthesise ruthenium TMTAA dimers directly from non-ruthenium-ruthenium bound complexes involved thermally displacing the π-bound COD ligand of a COD-bridged (TMTAA)Ru$^{II}$(COD)Ru$^{II}$(TMTAA)-THF complex by refluxing this complex in toluene for two hours. This route yielded the [Ru$^{II}$(TMTAA)]$_2$ dimer directly. Spectroscopic characterisation revealed that this complex was identical to the [Ru$^{II}$TMTAA]$_2$ complex synthesised from the [Ru$^{II/III}$TMTAA]$_2$[BF$_4$] dimer described in the previous paragraph. An X-ray crystal structure of [Ru$^{II}$TMTAA]$_2$ was obtained and showed some interesting differences from the [Ru$^{II}$(OEP)]$_2$ crystal structure. Instead of twisting slightly, the two TMTAA ligands were rotated approximately 90° to one another, and the M-N bonds about each ligand were therefore maintained in a fully eclipsed geometry. The displacement of the ruthenium atoms out of the plane defined by the four nitrogen atoms was significantly larger for [Ru$^{II}$(TMTAA)]$_2$ than for the [Ru$^{II}$(OEP)]$_2$ porphyrin and [Ru$^{III}$(corrole)]$_2$ dimers, and the TMTAA ligands were also significantly more distorted than the OEP and tpfc ligands. The
TMTAA ligand formed a saddle shape instead of a dome shape, with the benzene rings bending towards the metal-metal bond and the methyl groups bending away from the metal-metal bond.\textsuperscript{199} The saddle shape is believed to arise from steric repulsions between the methyl protons and the phenyl protons of the adjacent TMTAA ligands.\textsuperscript{198} Like the \([\text{Ru}^{II}(\text{OEP})]\textsubscript{2} \text{dimer}, the ruthenium-ruthenium bond length of \([\text{Ru}^{II}(\text{TMTAA})]\textsubscript{2} (2.3829(4) \text{ Å}) was close to the expected length of other ruthenium-ruthenium double bonds.\textsuperscript{199} The \([\text{Ru}^{II}(\text{TMTAA})]\textsubscript{2} \text{ dimer synthesised via this second route was selectively oxidised to the mixed-valence } [\text{Ru}^{II/III}(\text{TMTAA})]_2[\text{BPh}_4] \text{ dimer using ferrocenium tetr phenylborate in THF. An X-ray crystal structure of } [\text{Ru}^{II/III}(\text{TMTAA})]_2[\text{BPh}_4] \text{ also showed that the two ligands are oriented 90° relative to each other and have highly distorted saddle shapes. The } \text{Ru(II)}-\text{Ru(III)} \text{ bond length (2.2784(4) Å) was about 0.1 Å shorter than the } \text{Ru(II)}-\text{Ru(II)} \text{ bond length of } [\text{Ru}^{II}(\text{TMTAA})]_2 \text{ and was close to the } \text{Ru(II)}-\text{Ru(III)} \text{ bond lengths of } [\text{Ru}^{II/III}(\text{TPP})]_2[\text{PF}_6] \text{ (2.293(2) Å)} \text{ and other } \text{Ru(II)}-\text{Ru(III)} \text{ dimers (2.24-2.30 Å).}\textsuperscript{195}

Therefore, in summary, ruthenium-ruthenium dimers containing unsupported metal-metal bonds have been isolated in the \text{Ru(II)}-\text{Ru(II)}, \text{Ru(II)}-\text{Ru(III)}, and \text{Ru(III)}-\text{Ru(III)} oxidation states. Starting from the corresponding free ligand, corrole dimers have been isolated in the \text{Ru(III)}-\text{Ru(III)} oxidation state, while TMTAA dimers have been isolated in the \text{Ru(II)}-\text{Ru(III)} oxidation state, and porphyrin dimers have been isolated in the \text{Ru(II)}-\text{Ru(II)} oxidation state. Furthermore, \text{Ru(II)}-\text{Ru(II)} TMTAA dimers can be synthesised by thermal displacement of the COD-bridged \text{Ru(II)}-\text{Ru(II)} TMTAA dimer. Although the corrole dimers have only been isolated in the \text{Ru(III)}-\text{Ru(III)} oxidation state, cyclic voltammetry showed that higher and lower oxidation states are also accessible. For the porphyrin and TMTAA dimers, complexes in all three oxidation states (\text{Ru(II)}-\text{Ru(II)}, \text{Ru(II)}-\text{Ru(III)} and \text{Ru(III)}-\text{Ru(III)}) have been isolated, using the \text{Ru(II)}-\text{Ru(II)} or \text{Ru(II)}-\text{Ru(III)} dimers as precursors. Of all the isolated species, only the corrole \text{Ru(III)}-\text{Ru(III)} dimers were air-stable.

### 3.1.5 Complexes with unsupported rhodium-rhodium bonds

This section discusses the structures of complexes with direct unsupported rhodium-rhodium bonds that have been published in the literature, and describes spectroscopic and crystallographic evidence for these structures. These complexes are described here for comparison of their structural and spectroscopic properties to a rhodium-rhodium dimeric
complex of the new macrocyclic pyridinium amide ligand (Lₘ), which is discussed in Section 3.2.6.

Like the ruthenium dimers discussed in Section 3.1.4, a large number of complexes have been published in the literature that have direct rhodium-rhodium bonds. Also like the ruthenium-ruthenium dimers, in the vast majority of these complexes the rhodium-rhodium bond is supported by bridging ligands, for example, in the Rh₂(OAc)₄ paddlewheel-type dimer. However, unlike the ruthenium-ruthenium dimeric complexes, where complexes have been isolated in the Ru(II)-Ru(II), Ru(II)-Ru(III), and Ru(III)-Ru(III) oxidation states, for most rhodium-rhodium complexes, both metal centres are in the +II oxidation state, and only a handful of these complexes have been isolated in the mixed Rh(II)-Rh(III) oxidation state. Rhodium-rhodium complexes with supporting ligands that chelate between the two metal centres usually have either one or two axial ligands (that is, where one metal centre is five-coordinate and the other is six-coordinate, or where both metal centres are six-coordinate, respectively), although compounds are also known that are not axially ligated.

A number of rhodium-rhodium complexes with unsupported metal-metal bonds are known. These can be divided into two main categories: those that are six-coordinate about each metal centre, and those that are five-coordinate about each metal centre. Rhodium-rhodium dimers of monodentate or chelating ligands are usually six-coordinate about each metal centre, whereas rhodium-rhodium dimers of macrocyclic ligands (such as porphyrins and TMTAAAs) are often five-coordinate about each metal centre. Some examples of these complexes are provided in this section, focusing on complexes with macrocyclic ligands.

Rhodium(II)-rhodium(II) dimeric complexes of the TMTAA ligand, and of the porphyrin ligands OEP, TPP, and TTP (see Figure 3.5 and Figure 3.10 for the structure of TMTAA and porphyrin ligands) have been synthesised and reported in the literature. These complexes are five-coordinate about each metal centre and are not otherwise axially ligated. Using the orbital splitting diagram shown in Figure 3.7, and the fact that both the metal centres have seven d-electrons, it has been proposed that these complexes have formal rhodium-rhodium single bonds, which agrees with the diamagnetism of these complexes.
[Rh$^{II}$](OEP)$_2$ has been synthesised by dissolving Rh$^{III}$](OEP)(H) in degassed benzene, followed by recrystallisation from degassed toluene under an argon atmosphere. Gas-liquid chromatography indicated that the hydride ligand was lost as dihydrogen gas, and elemental analysis of the complex agreed with a formulation of [Rh$^{II}$](OEP)$_2$-(toluene). Rh$^{II}$](OEP)$_2$ has also been synthesised by reacting Rh$^{III}$](OEP)(H) with a slight excess of (2,2,6,6-tetramethylpiperidin-1-yl)oxy (TEMPO) under a nitrogen atmosphere in dry degassed benzene.

For the [Rh$^{II}$](OEP)$_2$ complexes synthesised via either route, magnetic susceptibility measurements and sharp non-contact shifted $^1$H NMR signals suggested that the [Rh$^{II}$](OEP)$_2$ complex was diamagnetic, as expected. Like the [Ru$^{II}$](OEP)$_2$ complex (Section 3.1.4), each ligand in the $^1$H NMR spectrum of [Rh$^{II}$](OEP)$_2$ was four-fold symmetric, and the two ligands were equivalent. Also like [Ru$^{II}$](OEP)$_2$, the methylene protons of [Rh$^{II}$](OEP)$_2$ were diastereotopic by $^1$H NMR spectroscopy, providing further evidence for a metal-metal bond. Proton NMR line broadening studies have suggested that the rhodium-rhodium bond of [Rh$^{II}$](OEP)$_2$ is rather weak (Rh-Rh bond energy of about 16.5 kcal mol$^{-1}$), and consequently reacts with a wide variety of substrates to produce monomeric complexes and Rh-L-Rh bridged complexes. These are discussed further in Chapter 5.

A [Rh(OEP)]$_2 ^{2+}$ complex has been synthesised by reaction of Rh$^{III}$](OEP)I with a stoichiometric amount of AgX (where X = BF$_4^-$, PF$_6^-$ or ClO$_4^-$) in dry dichloromethane. Unlike the analogous [Ru$^{III}$](OEP)$_2 ^{2+}$ complex (synthesised by oxidation of [Ru$^{II}$](OEP)$_2$ with AgBF$_4$), where both ruthenium centres are in the +III oxidation state, it has been postulated that the rhodium centres of [Rh(OEP)]$_2 ^{2+}$ remain in the +II oxidation state, and that the porphyrin ligands are oxidised by one electron to form porphyrin radical cations. Interactions between the radical cations of each porphyrin ligand then produce a $\pi$-$\pi$ interporphyrin radical cation bond. The formulation for the rhodium complex was therefore [Rh$^{III}$](OEP$^{•+}$)$_2$[X)$_2$ and not [Rh$^{III}$](OEP)$_2$[X]$^2$. Evidence for this structure included: the presence of diamagnetic non-contact shifted $^1$H NMR signals; significant changes to the porphyrin $\pi$-system relative to [Rh(OEP)]$_2$, as shown by shifting and splitting of the electronic transitions in the UV-visible absorption spectrum, and significant upfield shifts of the $^1$H NMR signals relative to [Rh$^{II}$](OEP)$_2$; the appearance of a low energy band at 920 nm in the UV-visible absorption spectrum, which was attributed to transitions from the bonding to the antibonding orbitals of the interporphyrin $\pi$-$\pi$ interaction; the observation that the complex did not dissociate under conditions where the [Rh$^{II}$](OEP)$_2$ complex readily dissociates, suggesting that the Rh(II)-Rh(II) bond is strengthened by the interporphyrin $\pi$-$\pi$ interaction; and the diastereotopic methylene protons, which suggested that the rhodium-rhodium bond remains intact.
[Rh\textsuperscript{II}(TPP)]\textsubscript{2}, [Rh\textsuperscript{II}(TTP)]\textsubscript{2}, and [Rh\textsuperscript{II}(TXP)]\textsubscript{2} (see Figure 3.10 for the structure of the TPP ligand; TTP is the \textit{p}-tolyl analogue of TPP, and TXP is the 3,5-xylyl analogue of TPP) have been synthesised by irradiation of the corresponding Rh\textsuperscript{III}(porphyrin)H complex under a stream of argon.\textsuperscript{204,205} Proton NMR spectra of these complexes in benzene-\textit{d}\textsubscript{6} showed that these complexes are also diamagnetic, and like the analogous [Ru\textsuperscript{II}(TPP)]\textsubscript{2} and [Ru\textsuperscript{II}(TTP)]\textsubscript{2} complexes, all of the methine CH protons are equivalent and all of the pyrrole CH protons are equivalent. Also like the analogous ruthenium complexes, two sets of \textit{ortho} proton and two sets of \textit{meta} protons were observed on the aromatic rings of the phenyl/\textit{p}-tolyl/3,5-xylyl substituents, suggesting that these aromatic groups are oriented perpendicular to the rest of the porphyrin molecule and also suggesting that the complex is dimeric.\textsuperscript{204,205} When very bulky porphyrin ligands, such as tetramesitylporphyrin (TMP) or 2,4-6-triisopropylphenylporphyrin (TTiPP) were used, the rhodium(II) radical complexes, [Rh\textsuperscript{II}(TMP)]\textbullet and [Rh\textsuperscript{II}(TTiPP)]\textbullet were synthesised instead of dimeric rhodium(II) complexes.\textsuperscript{206,207}

A rhodium dimer of the TMTAA ligand (see Figure 3.5 for the structure of this ligand), [Rh\textsuperscript{II}(TMTAA)]\textsubscript{2}, has been synthesised by refluxing H\textsubscript{2}TMTAA with Rh\textsubscript{2}(OAc)\textsubscript{4} overnight in degassed ethanol. The complex precipitated out of solution and was recrystallised from benzene.\textsuperscript{15} As for the [Ru\textsuperscript{II}(TMTAA)]\textsubscript{2} complex, each ligand of the [Rh\textsuperscript{II}(TMTAA)]\textsubscript{2} dimer was two-fold symmetric by \textsuperscript{1}H NMR spectroscopy and the two ligands were equivalent. Unlike the OEP, TPP, and TTP porphyrin rhodium dimers, none of the functional groups of the TMTAA ligand were oriented perpendicular to the ligand plane, and so \textsuperscript{1}H NMR spectroscopy was not used to verify the formation of a dimeric complex.\textsuperscript{15} However, mass spectrometry and X-ray crystallography confirmed that a dimeric [Rh\textsuperscript{II}(TMTAA)]\textsubscript{2} complex was indeed synthesised.\textsuperscript{15,208} Like the [Ru\textsuperscript{II}(TMTAA)]\textsubscript{2} complex, the two TMTAA ligands of [Rh\textsuperscript{II}(TMTAA)]\textsubscript{2} were saddle-shaped by X-ray crystallography, and were oriented approximately 90° to each other, with the rhodium atoms sitting significantly out of the plane defined by the four nitrogen atoms, on the side towards the metal-metal bond. The saddle shape was attributed to steric repulsions between the methyl protons and the phenyl protons of the adjacent TMTAA ligands.\textsuperscript{208} The rhodium-rhodium bond length of [Rh\textsuperscript{II}(TMTAA)]\textsubscript{2} (2.612 Å) was within the expected range for single unsupported Rh(II)-Rh(II) bonds.\textsuperscript{186}

Proton NMR line broadening has been used to determine the approximate strength of the rhodium-rhodium bond in [Rh\textsuperscript{II}(TMTAA)]\textsubscript{2}. These studies have estimated that the Rh(II)-Rh(II) bond dissociation enthalpy is about 22 kcal mol\textsuperscript{-1}, suggesting that this bond is stronger than the
Rh(II)-Rh(II) bond of [Rh\textsuperscript{II}(OEP)]\textsubscript{2} (where the bond dissociation enthalpy was estimated to be 16.5 kcal mol\textsuperscript{-1}).\textsuperscript{208} This was also reflected in the longer Rh(II)-Rh(II) bond length of [Rh\textsuperscript{II}(OEP)]\textsubscript{2} (2.81 Å) than [Rh\textsuperscript{II}(TMTAA)]\textsubscript{2} (2.612 Å). Beyond this reported rhodium-rhodium bond length, further details for the X-ray crystal structure of the [Rh\textsuperscript{II}(OEP)]\textsubscript{2} complex have not been published.\textsuperscript{209}

Spectroscopic and X-ray crystallographic data for the Rh(II)-Rh(II)-porphyrin and Rh(II)-Rh(II)-TMTAA dimers discussed above strongly suggest that each metal centre is five-coordinate, with no other axial ligand on the metal centre. In contrast, the phthalocyanine complex, [Rh\textsuperscript{II}(pc)]\textsubscript{2} (see Figure 3.12 for the structure of this ligand) has been axially ligated by pyridine to form a [Rh\textsuperscript{II}(pc)(py)]\textsubscript{2} complex.\textsuperscript{210} The diamagnetic [Rh\textsuperscript{II}(pc)]\textsubscript{2} complex was synthesised by heating the monomeric complex, [H][Rh\textsuperscript{III}(X)\textsubscript{2}(pc)] (where X = Cl or Br) under vacuum at 300 °C for 24 hours. [Rh\textsuperscript{II}(pc)(py)]\textsubscript{2} was then synthesised by dissolving the [Rh\textsuperscript{II}(pc)]\textsubscript{2} complex in pyridine, followed by evaporation of the solvent under vacuum and washing of the solid residue with diethyl ether. X-ray quality crystals of [Rh\textsuperscript{II}(pc)(py)]\textsubscript{2}·2C\textsubscript{6}H\textsubscript{6} were grown by slow evaporation of a 1:2 pyridine/benzene solution of [Rh\textsuperscript{II}(pc)]\textsubscript{2}. Analysis of the [Rh\textsuperscript{II}(pc)(py)]\textsubscript{2}·2C\textsubscript{6}H\textsubscript{6} X-ray crystal structure revealed a Rh(II)-Rh(II) bond length of 2.741(2) Å, which was within the range of rhodium-rhodium bond lengths expected for unsupported Rh(II)-Rh(II) dimers. In contrast to the Rh(II)-Rh(II)-porphyrin and Rh(II)-Rh(II)-TMTAA dimers, the rhodium atoms of [Rh\textsuperscript{II}(pc)(py)]\textsubscript{2}·2C\textsubscript{6}H\textsubscript{6} were found to be close to the centre of the plane defined by the four nitrogen atoms. This was ascribed to the presence of the axial pyridine ligands. Further analysis of the [Rh\textsuperscript{II}(pc)(py)]\textsubscript{2}·2C\textsubscript{6}H\textsubscript{6} crystal structure showed that the two phthalocyanine ligands were twisted by 42(1)° relative to each other, and were slightly domed in order to minimise steric repulsions. The proton NMR spectrum of [Rh\textsuperscript{II}(pc)(py)]\textsubscript{2} in pyridine-\textit{d}\textsubscript{5} showed a high degree of symmetry, with two sharp non-contact shifted signals (one for the \textit{ortho} protons on the phenyl rings and the other for the \textit{meta} protons). The addition of other N-donor solvents (such as imidazole and pyrazine) to [Rh\textsuperscript{II}(pc)]\textsubscript{2} have also been shown to form [Rh\textsuperscript{II}(pc)(L)]\textsubscript{2} complexes by \textsuperscript{1}H NMR spectroscopy.\textsuperscript{210}
Addition of one equivalent of trimethylphosphine to the substituted Rh(II)-Rh(II)-phthalocyanine dimer, [RhII(Rpc)]₂ (see Figure 3.12 for ligand structure), in benzene-d₆ has been shown to afford a mono-axially ligated complex, [RhII(Rpc)]₂(PMe₃), by ¹H NMR spectroscopy. Addition of a second equivalent of trimethylphosphine afforded the bis-axially ligated complex, [RhII(Rpc)]₂(PMe₃)₂, while the addition of another two equivalents of trimethylphosphine cleaved the rhodium-rhodium bond to form the monomeric RhIII(Rpc)(PMe₃)₂ complex. The RhIII(Rpc)(PMe₃)₂ complex was paramagnetic and neutral overall because it is best described as a rhodium(III) complex with a singly-reduced π-radical anionic ligand (Rpc⁻). As expected, the two Rpc ligands of [RhII(Rpc)]₂(PMe₃) were inequivalent by ¹H NMR spectroscopy, whereas the two Rpc ligands of [RhII(Rpc)]₂ and [RhII(Rpc)]₂(PMe₃)₂ were equivalent. For all three dimeric complexes, the α and β methylene groups of the n-pentyl chains were diastereotopic, suggesting that the rhodium-rhodium bond remains intact after the addition of trimethylphosphine.²¹¹ Proton NMR line broadening studies were attempted to estimate the rhodium-rhodium bond strength of the [RhII(Rpc)]₂ complex. The lack of any broadening up to 140 °C in benzene-d₆ suggested that the rhodium-rhodium bond is significantly stronger for [RhII(Rpc)]₂ than for [RhII(OEP)]₂ and [RhII(TMTAA)]₂. This may explain why Rh(II)-Rh(II) phthalocyanine dimers become six-coordinate in the presence of pyridine and other neutral donors, while the Rh(II)-Rh(II) bonds of [RhII(OEP)]₂ and [RhII(TMTAA)]₂ cleave in the presence of pyridine.²¹²

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**Figure 3.12: Chemical structures of the free phthalocyanine ligands, H₂pc and H₂Rpc**
X-ray crystal structures have also been published for a number of dimeric rhodium(II)-rhodium(II) complexes of monodentate and chelating ligands that contain unsupported metal-metal bonds.\textsuperscript{186} Most of these complexes are six-coordinate about each rhodium centre. Some examples include the acetonitrile and propionitrile complexes, the $p$-tolylisocyanide complex $\text{[Rh}^\text{II}(\text{CN-}p\text{-tolyl})_4(\text{I})_2][\text{PF}_6]_2$;\textsuperscript{213} $\text{[Rh}^\text{II}(\text{NCMe})_5][\text{BF}_4]_4$ and $\text{[Rh}^\text{II}(\text{NCEt})_5][\text{BF}_4]_4$;\textsuperscript{214} and the chelating complex, $\text{[Rh}^\text{II}(\text{dmg})_2(\text{PPh}_3)]_2$ (dmg = the monoanion of dimethylglyoxime).\textsuperscript{215} See Figure 3.13 for the structures of these complexes. All of these complexes are diamagnetic, and the Rh(II)-Rh(II) bond lengths are usually within the expected range for rhodium-rhodium single bonds. For the rhodium dimers of chelating ligands, the ligands coordinated to one metal centre are usually in a staggered orientation relative to the ligands about the other metal centre in the solid state. The chelating ligand complex, $\text{[Rh}^\text{II}(\text{dmg})_2(\text{PPh}_3)]_2$, was unusual in that the rhodium-rhodium bond was exceptionally long (2.936(2) $\text{Å}$). This has been attributed to the presence of the triphenylphosphine axial ligands, which prevent the dmg ligands from bending away from the rhodium-rhodium bond to minimise steric strain, and so the strain is instead relieved by lengthening of the metal-metal bond.\textsuperscript{215} This was later confirmed by replacing the triphenylphosphine axial ligands of $\text{[Rh}^\text{II}(\text{dmg})_2(\text{PPh}_3)]_2$ with pyridine axial ligands, which did not hinder the dmg ligands from distorting away from the rhodium-rhodium bond. Consequently, unlike the $\text{[Rh}^\text{II}(\text{dmg})_2(\text{PPh}_3)]_2$ complex, the rhodium-rhodium bond length of $\text{[Rh}^\text{II}(\text{dmg})_2(\text{py})]_2$ (2.726(1) $\text{Å}$) was within the expected range for a Rh(II)-Rh(II) single bond.\textsuperscript{186}

\begin{figure}[h]
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\caption{Examples of Rh(II)-Rh(II) dimeric complexes of monodentate and chelating ligands}
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3.2 Synthesis, structures, and spectroscopic properties of metal complexes of the new pyridinium amide ligands

3.2.1 Iron and cobalt complexes of acyclic ligand Lₐ

Iron and cobalt complexes of macrocyclic pyridinium amide ligand (Lₘ) were two target complexes that were studied as catalysts for the oxidation of substrates by hydrogen peroxide. This work is described in Chapter 4. Before these metal complexes were synthesised, attempts were made to synthesise iron and cobalt complexes of the acyclic pyridinium amide ligand (Lₐ), in order to find conditions that may be suitable for the synthesis of the iron-Lₘ and cobalt-Lₘ complexes, and to analyse the structures and spectroscopic properties of these complexes. Iron-Lₐ and cobalt-Lₐ complexes were also synthesised to study their potential behaviour as catalysts for the oxidation of substrates by hydrogen peroxide, in comparison to the catalytic behaviour of the macrocyclic iron-Lₘ and cobalt-Lₘ complexes (see Chapter 4).

Iron-Lₐ and cobalt-Lₐ complexes were successfully synthesised using the procedures described below. However, despite many purification attempts, these complexes were not successfully isolated in a pure form. Spectroscopic studies suggest that this is at least in part due to the formation of a large number of iron(III)-Lₐ and cobalt(III)-Lₐ products, with different numbers of metal centres and ligands.

Using conditions similar to those used to synthesise Fe³⁺-TAML complexes, H₂Lₐ and excess potassium tert-butoxide (5 equivalents) were added to thoroughly-degassed THF inside a Schlenk tube. The solution was again degassed via freeze-pump-thaw degassing cycles. A small excess (1.2 equivalents) of anhydrous iron(II) chloride was then added, followed by further freeze-pump-thaw degassing cycles. After sealing the Schlenk tube under vacuum, the solution was stirred at room temperature for 1 hour and then at 50 °C for 1.5 hours, until the reaction had reached completion (by TLC analysis). Careful neutralisation of the solution in air using glacial acetic acid (1 mol L⁻¹) in THF gave a green product which was purified by column chromatography on silica gel (see Section 3.4.3 for detailed procedure). The absence of signals in the ¹H NMR spectrum of this product suggests that it is paramagnetic, as would be expected for iron(II) or iron(III) complexes.
High resolution positive ion mass spectrometry of the columned product suggests that many iron-Lₐ complexes were synthesised. All of the major signals in this mass spectrum were identified, and their m/z values were very close to the expected m/z values of the predicted structures (Table 3.1). The relative intensities of these signals were calibrated relative to the highest intensity peak in the mass spectrum, at 100%. Most of these major signals have been identified as [(Fe³⁺)ₙ(Lₐ)ₙ₊₁ + xH⁺]^(n+x-2)⁺ species, where n = 1 to 4 and x = 1 to 4. The oxalamide bond of the Lₐ ligands in these iron(III)-Lₐ species must be transoidal in order for each metal centre to coordinate to more than one Lₐ ligand. This is because a cis oxalamide bond would result in a metal-Lₐ complex which is too sterically strained to allow coordination of more than one Lₐ ligand to one metal centre. In a transoidal orientation, there are up to six donors on each Lₐ ligand which can coordinate to metal centres (two carboxamide nitrogen donors, two pyridinium amide nitrogen donors and two carboxamide carbonyl oxygen donors), and each Lₐ ligand can coordinate to up to two iron(III) metal centres (Figure 3.14).

Two possible geometries for these [(Fe³⁺)ₙ(Lₐ)ₙ₊₁ + xH⁺]^(n+x-2)⁺ complexes are given in Figure 3.14, using n = 2 as an example. In the proposed tridentate geometry given on the right hand side of Figure 3.14, each octahedral iron(III) metal centre coordinates to three donors on each Lₐ ligand, while in the proposed bidentate geometry given on the left hand side of Figure 3.14, each octahedral iron(III) metal centre coordinates to two donors on each Lₐ ligand. In the former geometry, the two Lₐ ligands occupy the meridional coordination sites on each iron(III) centre, while in the latter geometry, only four of the six coordination sites on each iron(III) centre coordinate to the Lₐ ligands, leaving two coordination sites available for the coordination of axial ligands such as chloride or acetate. Although the measured m/z values for the [(Fe³⁺)ₙ(Lₐ)ₙ₊₁ + xH⁺]^(n+x-2)⁺ species did not correspond to the presence of chloride or acetate ligands, these ligands are expected to be weakly coordinated and, like iron-TAML complexes, are expected to be lost in the electrospray ionisation process. Similar effects were observed in the mass spectra of metal-Lₐ complexes, which are discussed in the following sections. Overall, the bidentate coordination mode is probably less likely than the tridentate coordination mode due to coordinative unsaturation and greater steric strain in the former coordination mode.
Table 3.1: Iron-$L_a$ species identified in the high resolution ESI positive ion mass spectrum of the iron-$L_a$ complex synthesised from the reaction of $H_2L_a$ with FeCl$_2$ and K'BuO, followed by neutralisation with acetic acid and partial purification by column chromatography on silica gel

| $z$ | Fe$^{II}L_a$ | Fe$^{III}$(L$_a$)$_2$ | (Fe$^{III}$(L$_a$)$_3$ | (Fe$^{III}$(L$_a$)$_4$ | (Fe$^{III}$(L$_a$)$_5$

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<td>([Fe$^{II}$(L$<em>a$)$^2$]$^0 + H^+$), calcd for C$</em>{28}$H$<em>{32}$Fe$</em>{11}$N$_6$O$_2$, 535.1540; found 535.1526 (15%)</td>
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<td>+2</td>
<td>([Fe$^{III}$(L$<em>a$)$^2$]$^1 + 3H^+$), calcd for C$</em>{56}$H$<em>{103}$Fe$</em>{17}$N$_{15}$O$_7$, 837.6337; found, 837.6320 (40%)</td>
<td>([Fe$^{III}$(L$<em>a$)$^3$]$^2 + 2H^+$), calcd for C$</em>{140}$H$<em>{143}$Fe$</em>{30}$N$<em>{30}$O$</em>{10}$, 872.2695; found, 872.2687 (6%)</td>
<td>([Fe$^{III}$(L$<em>a$)$^4$]$^3 + 3H^+$), calcd for C$</em>{140}$H$<em>{143}$Fe$</em>{30}$N$<em>{30}$O$</em>{10}$, 654.4540; found, 654.4517 (20%)</td>
<td>([Fe$^{III}$(L$<em>a$)$^5$]$^4 + 4H^+$), calcd for C$</em>{140}$H$<em>{143}$Fe$</em>{30}$N$<em>{30}$O$</em>{10}$, 523.7646; found, 523.7624 (15%)</td>
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<td>+3</td>
<td>([Fe$^{III}$(L$<em>a$)$^3$]$^3 + 4H^+$), calcd for C$</em>{56}$H$<em>{103}$Fe$</em>{17}$N$_{15}$O$_7$, 837.6337; found, 837.6320 (40%)</td>
<td>([Fe$^{III}$(L$<em>a$)$^4$]$^4 + 3H^+$), calcd for C$</em>{112}$H$<em>{106}$Fe$</em>{33}$N$_{30}$O$_8$, 694.2225; found 694.2209 (40%)</td>
<td>([Fe$^{III}$(L$<em>a$)$^5$]$^5 + 2H^+$), calcd for C$</em>{140}$H$<em>{143}$Fe$</em>{30}$N$<em>{30}$O$</em>{10}$, 872.2695; found, 872.2687 (6%)</td>
<td>([Fe$^{III}$(L$<em>a$)$^6$]$^6 + H^+$), calcd for C$</em>{140}$H$<em>{143}$Fe$</em>{30}$N$<em>{30}$O$</em>{10}$, 523.7646; found, 523.7624 (15%)</td>
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<tr>
<td>+4</td>
<td>([Fe$^{III}$(L$<em>a$)$^4$]$^4 + 4H^+$), calcd for C$</em>{56}$H$<em>{103}$Fe$</em>{17}$N$_{15}$O$_7$, 837.6337; found, 837.6320 (40%)</td>
<td>([Fe$^{III}$(L$<em>a$)$^5$]$^5 + 3H^+$), calcd for C$</em>{112}$H$<em>{106}$Fe$</em>{33}$N$_{30}$O$_8$, 694.2225; found 694.2209 (40%)</td>
<td>([Fe$^{III}$(L$<em>a$)$^6$]$^6 + 2H^+$), calcd for C$</em>{140}$H$<em>{143}$Fe$</em>{30}$N$<em>{30}$O$</em>{10}$, 872.2695; found, 872.2687 (6%)</td>
<td>([Fe$^{III}$(L$<em>a$)$^7$]$^7 + H^+$), calcd for C$</em>{140}$H$<em>{143}$Fe$</em>{30}$N$<em>{30}$O$</em>{10}$, 523.7646; found, 523.7624 (15%)</td>
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<tr>
<td>+5</td>
<td>([Fe$^{III}$(L$<em>a$)$^5$]$^5 + 4H^+$), calcd for C$</em>{56}$H$<em>{103}$Fe$</em>{17}$N$_{15}$O$_7$, 837.6337; found, 837.6320 (40%)</td>
<td>([Fe$^{III}$(L$<em>a$)$^6$]$^6 + 3H^+$), calcd for C$</em>{112}$H$<em>{106}$Fe$</em>{33}$N$_{30}$O$_8$, 694.2225; found 694.2209 (40%)</td>
<td>([Fe$^{III}$(L$<em>a$)$^7$]$^7 + 2H^+$), calcd for C$</em>{140}$H$<em>{143}$Fe$</em>{30}$N$<em>{30}$O$</em>{10}$, 872.2695; found, 872.2687 (6%)</td>
<td>([Fe$^{III}$(L$<em>a$)$^8$]$^8 + H^+$), calcd for C$</em>{140}$H$<em>{143}$Fe$</em>{30}$N$<em>{30}$O$</em>{10}$, 523.7646; found, 523.7624 (15%)</td>
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Figure 3.14: Possible structures for the Fe\textsuperscript{III}\textsubscript{2}(L\textsubscript{a})\textsubscript{3} species observed in the high resolution positive ion mass spectrum the iron-L\textsubscript{a} complex. The terminal L\textsubscript{a} ligands of this species have varying degrees of protonation (at the positions denoted by the bolded hydrogen atoms). The acetate/chloride ligands (L) on the proposed bidentate coordination mode compound are not observed in the mass spectrum.
In both the tridentate structure and the bidentate structure given in Figure 3.14, the two nitrogen atoms and one oxygen atom at the end of each terminal Lₐ ligand (there are two terminal Lₐ ligands in total for each (Fe^{III})ₙ(Lₐ)ₙ₊₁ species) are not coordinated to a metal centre and are most likely protonated in the isolated complexes. However, in the mass spectrum, some of these protons are easily lost, and this explains why a number of species with different levels of protonation are observed for each (Fe^{III})ₙ(Lₐ)ₙ₊₁ complex of a specific n value. A maximum of five different species are therefore reasonably possible for each (Fe^{III})ₙ(Lₐ)ₙ₊₁ complex of a specific n value, although in practice, the greatest number of species actually observed in the mass spectrum for any (Fe^{III})ₙ(Lₐ)ₙ₊₁ complex was three, presumably because the formation of highly charged species is not very favourable.

In addition to the numerous iron(III)-Lₐ species observed in the high resolution mass spectrum of the iron-Lₐ complex purified by column chromatography, one of the major signals corresponded to the predicted mass of an iron(II)-Lₐ species. The m/z value for this iron(II)-Lₐ species corresponded to the predicted mass of a [Fe^{II}(Lₐ)] + H⁺ complex, which presumably (like the Pd^{II}(Lₐ) complex described in Section 3.2.2) has a cis oxalamide bond, so that one Lₐ ligand coordinates to one metal centre. Although the predicted mass suggests that this [Fe^{II}(Lₐ)] + H⁺ species has a four-coordinate metal centre, in solution the iron(II)-Lₐ complex is probably six-coordinate with two axial ligands (chloride and/or acetate), which are readily lost during the electrospray ionisation process. Although the presence of chloride and/or acetate axial ligands would give rise to an anionic species (see Figure 3.15), neither iron(II)-Lₐ nor iron(III)-Lₐ species were observed in the high resolution negative ion mass spectrum of the iron-Lₐ complex purified by column chromatography. It is currently unknown whether the iron-Lₐ sample submitted for mass spectrometry contained a mixture of iron(II)-Lₐ and iron(III)-Lₐ complexes or whether this mixture arose from oxidation or reduction of the sample during the electrospray ionisation process.

Only one further major species was observed in the high resolution positive ion mass spectrum of the purified iron-Lₐ complex, other than the iron(III)-Lₐ and iron(II)-Lₐ species described above. This signal corresponded to the predicted mass of the free ligand (H₂Lₐ + H⁺, z = +1, 20%), which may suggest that the free ligand has not completely reacted. However, the free ligand has also been observed in the mass spectra of most of the synthesised metal-Lₘ complexes (discussed in the following sections), even when ^1H NMR spectroscopy confirms that all of the free ligand has reacted. Therefore, it is more likely that the appearance of free ligand in the mass
spectrum of the iron-Lₐ complex is due to partial demetallation during the electrospray ionisation process. Given this observation, it is possible that some of the multinuclear iron-Lₐ species might also have formed during the electrospray ionisation process.

\[
\text{Figure 3.15: Proposed structure for the Fe}^{II}(\text{L}ₐ) \text{ species observed in the high resolution positive ion mass spectrum of the Fe-Lₐ complex purified by column chromatography. The acetate/chloride axial ligands (L) on this species are not observed in the mass spectrum.}
\]

The large number of major species observed in the high resolution positive ion mass spectrum of iron-Lₐ might actually be fragments of a complex with a larger structure. It may even be possible that the metal-Lₐ complex has a single structure (for example, only (Fe^{III})₅(Lₐ)₆), that undergoes fragmentation in the mass spectrum to give smaller species. To test whether single or multiple products are present in the iron-Lₐ product, mass spectra were obtained of the front, centre, and tail of the wide product band on the silica column used to purify the crude product. Although each mass spectrum was run under the same conditions, the relative intensities of the product species (as identified in Table 3.1) changed substantially, suggesting that there are indeed multiple species in the purified iron-Lₐ product. Different relative intensities were also obtained when a neutral alumina column was used to purify the iron-Lₐ product.

A cobalt complex of ligand Lₐ was synthesised using a method very similar to the procedure used to synthesise the iron-Lₐ complex. Anhydrous cobalt(II) bromide was used instead of iron(II) chloride under thoroughly degassed conditions. The reaction was slower than for the analogous iron-Lₐ synthesis reaction, requiring 20 minutes at room temperature and then 6 hours at 50 °C before the reaction reached completion (by TLC). The product was neutralised and isolated as per the iron-Lₐ complex (see Section 3.4.4 for more detail).
Table 3.2 shows all of the major species that were identified in the high resolution positive ion mass spectrum of the purified cobalt-Lₐ complex. Like the iron-Lₐ complex (Table 3.1), a variety of major species were observed, which closely fit the calculated \([(\text{Co}^{III})_n(L_\text{a})_{n+1} + x\text{H}^+\] \(n+x-2\)) \(m/z\) values. The structures of these cobalt-Lₐ species are expected to be very similar to the structures of the iron-Lₐ species (Figure 3.14). For both complexes, a maximum \(n\) value of four was observed. As for iron-Lₐ, a small amount (relative to the total intensity of all the cobalt(III) species) of a cobalt(II) species (\(\text{Co}^{II}L_\text{a} + \text{H}^+\)) was observed in the mass spectrum of the cobalt-Lₐ complex. Also like iron-Lₐ, mass spectra of the cobalt-Lₐ product purified by different methods, and mass spectra of different parts of the product band isolated from the silica column showed different relative intensities of the major species, suggesting that multiple cobalt-Lₐ species are present that are not separated properly during the chromatography procedure.

Because the mass spectra of the iron-Lₐ and cobalt-Lₐ complexes suggested that multiple products are formed, many different purification methods were attempted to separate these products. These included extractions, recrystallisations, and column chromatography on silica, neutral alumina, basic alumina, and reverse-phase silica, using a variety of eluents. However, none of these techniques were successful in isolating only one (or even only a few) \(M_nL_{n+1}\) species, perhaps because these are fragments of larger \(M_nL_{n+1}\) species. Therefore, these complexes were not characterised further. They also were not used for oxidation studies (Chapter 4), because a consistent product formulation between different synthesised batches of these complexes was difficult to obtain, and different \(M_nL_{n+1}\) species may catalyse reactions to different extents, which would make consistent data difficult to obtain. Because the structure of the \(\text{H}_2L_m\) macrocycle is much more rigid than the structure of acyclic ligand \(\text{H}_2L_a\), multiple \(M_nL_{n+1}\) species are not expected for iron-Lₐ and cobalt-Lₐ complexes. These are discussed in Section 3.2.3.
Table 3.2: Cobalt-Lₐ species identified in the high resolution ESI positive ion mass spectrum of the cobalt-Lₐ complex synthesised from the reaction of H₂Lₐ with CoBr₂ and K’BuO, followed by neutralisation with acetic acid and partial purification by column chromatography on silica gel

<table>
<thead>
<tr>
<th>z</th>
<th>Co⁺Lₐ</th>
<th>Co⁺⁺(Lₐ)₂</th>
<th>(Co⁺⁺)(Lₐ)₃</th>
<th>(Co⁺⁺)(Lₐ)₄</th>
<th>(Co⁺⁺)(Lₐ)₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>+1</td>
<td>([Co⁺⁺(Lₐ)₂]⁺ + H⁺), 538.1522; found, 538.1455 (60%)</td>
<td>([Co⁺⁺(Lₐ)₃]⁺ + 3H⁺), 509.1900; found, 509.1844 (95%)</td>
<td>([Co⁺⁺(Lₐ)₄]⁺ + 2H⁺), 777.2581; found, 777.2559 (100%)</td>
<td>([Co⁺⁺(Lₐ)₅]⁺ + 2H⁺), 518.5078; found, 518.5031 (60%)</td>
<td>([Co⁺⁺(Lₐ)₆]⁺ + 3H⁺), 697.2202; found, 697.2207 (5%)</td>
</tr>
<tr>
<td>+2</td>
<td>([Co⁺⁺(Lₐ)₃]⁺ + 2H⁺), 269.5797; found, 269.5767 (32%)</td>
<td>([Co⁺⁺(Lₐ)₄]⁺ + H⁺), 339.7960; found, 339.7921 (35%)</td>
<td>([Co⁺⁺(Lₐ)₅]⁺ + 3H⁺), 518.5078; found, 518.5031 (60%)</td>
<td>([Co⁺⁺(Lₐ)₆]⁺ + 4H⁺), 657.2012; found, 657.2006 (2%)</td>
<td>([Co⁺⁺(Lₐ)₇]⁺ + 5H⁺), 797.2202; found, 797.2207 (3%)</td>
</tr>
<tr>
<td>+3</td>
<td>([Co⁺⁺(Lₐ)₄]⁺ + 4H⁺), 339.7960; found, 339.7921 (35%)</td>
<td>([Co⁺⁺(Lₐ)₅]⁺ + 3H⁺), 518.5078; found, 518.5031 (60%)</td>
<td>([Co⁺⁺(Lₐ)₆]⁺ + 2H⁺), 697.2202; found, 697.2207 (5%)</td>
<td>([Co⁺⁺(Lₐ)₇]⁺ + 5H⁺), 797.2202; found, 797.2207 (3%)</td>
<td>([Co⁺⁺(Lₐ)₈]⁺ + 6H⁺), 937.2202; found, 937.2207 (2%)</td>
</tr>
<tr>
<td>+4</td>
<td>([Co⁺⁺(Lₐ)₅]⁺ + 2H⁺), 389.1327; found, 389.1286 (25%)</td>
<td>([Co⁺⁺(Lₐ)₆]⁺ + 4H⁺), 518.5078; found, 518.5031 (60%)</td>
<td>([Co⁺⁺(Lₐ)₇]⁺ + 3H⁺), 657.2012; found, 657.2006 (2%)</td>
<td>([Co⁺⁺(Lₐ)₈]⁺ + 5H⁺), 797.2202; found, 797.2207 (3%)</td>
<td>([Co⁺⁺(Lₐ)₉]⁺ + 6H⁺), 937.2202; found, 937.2207 (2%)</td>
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3.2.2 A palladium complex of acyclic ligand La

Analysis of the mass spectral data for the iron-La and cobalt-La complexes (Section 3.2.1) suggested that the presence of six-coordinate iron and cobalt metal centres along with the presence of a transoidal La ligand resulted in the formation of multiple MnLn+1 products. Therefore, in this section, a palladium complex of ligand La was synthesised to see if a single product would form. The palladium centre of this complex is expected to be square planar, with an oxidation state of +II. This may result in the formation of a monomeric complex with one metal centre and one La ligand (PdII(La)) that has a cis-oriented oxalamide bond, without forming complexes that contain multiple La ligands and multiple metal centres. This palladium-La complex was also synthesised in order to obtain information about conditions that may be suitable for metallating macrocyclic ligand H2Ln with palladium, and to compare the structures and spectroscopic properties of the Pd-Ln and Pd-La complexes (see Section 3.2.4). Indeed, a monomeric diamagnetic palladium-La complex with a formulation of PdII(La) was successfully synthesised, purified, and characterised. These results are given below.

PdII(La) was synthesised by reacting free ligand H2La with a stoichiometric amount of palladium acetate in refluxing THF (see Section 3.4.2 for experimental details). After heating for 12 hours under reflux, the orange precipitate was collected by filtration and was washed with THF. Pure PdII(La) (Figure 3.16) was obtained in 42% yield after column chromatography on basic alumina.

![Figure 3.16: Synthesis of complex PdII(La) from acyclic ligand H2La](image-url)
NMR spectroscopy, mass spectrometry, and elemental analysis confirmed a formulation of PdII(La). Proton and 13C NMR spectroscopies (in CDCl3) indicated that the complex is diamagnetic, and that the chemical shifts for the positions on both halves of the symmetric molecule (as drawn in Figure 3.16) are identical. The highest intensity peak in the high resolution positive ion mass spectrum corresponded to the predicted mass of PdII(La) + H⁺, and the only other observed signals were very minor. Elemental analysis of the palladium complex agreed with a formulation of PdII(La), with one water of crystallisation. Unfortunately, despite many attempts to grow suitable crystals, an X-ray crystal structure of PdII(La) was not obtained. Nevertheless, it is expected that the PdII(La) complex will have a square planar d8 structure with a cis-oxalamide bond, and it is also expected that the trans-oxalamide bond of the free ligand (H2La) has undergone rotation to form this complex. This structure was expected because square planar geometries are common for four-coordinate d8 metal complexes with strong-field ligands.216 This has indeed been found for most palladium(II) complexes of other tetra-nitrogen donating macrocyclic ligands discussed in Section 3.1.3 (of porphyrin, corrole and TMTAA ligands).160,161,167 Although the pyridinium amide groups are drawn in the imine resonance form in Figure 3.16, both the imine resonance form and the zwitterionic resonance form are expected to contribute to the structure of this complex (see Figure 2.12 for the two resonance forms of this ligand).

The procedure used to synthesise PdII(La) was repeated using a 2:1 ratio of Pd(OAc)2/H2La, to see whether a complex with a formula of (PdII)2(La)(OAc)2 could be synthesised. Unlike PdII(La), the oxalamide bond of (PdII)2(La)(OAc)2 might be expected to be transoidal. However, in this reaction only the PdII(La) complex was synthesised and no “(PdII)2(La)(OAc)2” complex was observed, indicating that the former product is favoured in these reactions. Reactions were also repeated in the presence of a large excess of palladium acetate, and also at different temperatures and reaction times. In each case, no (PdII)2(La)(OAc)2 complex was observed.

UV-visible absorption spectroscopy of PdII(La) in dichloromethane showed one band in the visible region, which is assigned to a d-d transition, with a peak maximum at 751 nm (ε = 369 L mol⁻¹ cm⁻¹). Any other d-d transitions that may be present in the complex were obscured by strongly allowed transitions that extend well into the visible region. Four other strong absorptions were observed, with peak maxima at 314 nm (32,800 L mol⁻¹ cm⁻¹), 359 nm (21,100 L mol⁻¹ cm⁻¹), 437 nm (15,400 L mol⁻¹ cm⁻¹), and 471 nm (11,600 L mol⁻¹ cm⁻¹). There is possibly a fifth strong absorption at about 251 nm, which was observed as a shoulder (about
47,000 L mol\(^{-1}\) cm\(^{-1}\)) on the strong solvent absorption peak that appears in this region. Because some of these strong absorptions occur in the visible region, very dilute solutions of Pd\(\text{II}(\text{La})\) remained strongly yellow in colour. These strongly allowed absorptions probably arise from charge transfer transitions, and also from the transitions between orbitals in one ligand, the latter of which were also observed in the UV-visible absorption spectrum of the free macrocyclic ligand (H\(_2\text{La}\), see Section 2.3.2), where they were also found to extend significantly into the visible region. Although the very low solubility of H\(_2\text{La}\) in most solvents prevented UV-visible absorption spectra from being obtained, this compound presumably (like other pyridinium amides studied in the literature)\(^{125-127}\) also absorbs strongly in the visible region.

### 3.2.3 Iron, cobalt, and manganese complexes of macrocyclic ligand L\(_\text{m}\)

Iron, cobalt, and manganese complexes of macrocyclic ligand L\(_\text{m}\) were synthesised for their use as catalysts in oxidation reactions, which are described in Chapter 4. These metals were chosen because iron, cobalt, and manganese complexes of porphyrin and TAML ligands (which are structurally related to ligand L\(_\text{m}\)) are known to be effective catalysts for a variety of oxidation reactions.\(^{17,20,21,85}\) Paramagnetic iron-L\(_\text{m}\) and cobalt-L\(_\text{m}\) complexes were successfully synthesised and purified, and the characterisation data agreed with formulations of Fe\(\text{III}(\text{L}_\text{m})\)Cl and Co\(\text{III}(\text{L}_\text{m})\)Br, respectively (see below for more detail). A paramagnetic manganese-L\(_\text{m}\) complex was also synthesised, but was not successfully purified, even though a wide variety of purification techniques were employed. Spectroscopic and reactivity studies described below suggest that this is due in part to ready inter-conversion between a Mn(II)-L\(_\text{m}\) species and a Mn(III)-L\(_\text{m}\) species, which prevented these species from being separated, even after deliberate oxidation or reduction of the crude mixture of manganese-L\(_\text{m}\) complexes.

Fe\(\text{III}(\text{L}_\text{m})\)Cl was synthesised by reacting free ligand H\(_2\text{L}_\text{m}\) with a small excess of anhydrous iron(III) chloride, in the presence of a moderate excess of sodium acetate. The reaction was conducted in dry methanol under stringently air-free conditions inside a Schlenk tube (see Section 3.4.6 for experimental details). After 25 hours at 60 °C, TLC plates showed that all of the free ligand had reacted. The reaction products were isolated by cooling the solution to room temperature, followed by filtration to remove undissolved solids. A large excess of sodium chloride was then added to the filtrate to exchange any acetate ligands coordinated to iron centre in the crude complex for chloride, followed by removal of the solvent under vacuum. Pure
Fe$^{III}$($L_m$)Cl was subsequently obtained in 58% yield after column chromatography on neutral alumina.

The absence of signals in the $^1$H NMR spectrum of the iron-$L_m$ complex suggested that it is paramagnetic, and elemental analysis indicated that the complex has a formulation of Fe$^{III}$($L_m$)Cl·H$_2$O. Despite many attempts to grow suitable crystals, X-ray quality crystals were not obtained, and it is not known whether the water molecule is present as an axial ligand or as a water of crystallisation. Therefore, this complex could be five-coordinate or six-coordinate about the iron centre. The former is more likely in the solid state, because related Fe(III)(TAML)(X) complexes (where X = Cl or H$_2$O) are known to be five-coordinate in the solid state.$^{55,97,104}$ A four-coordinate metal centre for the iron-$L_m$ complex is unlikely based on the structure of other known Fe(III) complexes.$^{17}$ Two possible formulations can be drawn if the complex is five-coordinate: a Fe$^{III}$($L_m$)Cl·H$_2$O complex with an axial chloride ligand and one water of crystallisation, or a [Fe$^{III}$($L_m$)(H$_2$O)]Cl complex, with an axial water ligand and a chloride counteranion. The former seems more likely, because a large excess of sodium chloride was added to the complex during product isolation. Also, the fact that the complex travels as a narrow band with a high R$_f$ value on neutral alumina using 19:1 dichloromethane/methanol as the eluent suggests that the iron complex is neutral, because a charged complex would be expected to move much more slowly on this column. Although it may be possible to determine whether this complex is five- or six-coordinate in the solid state by measuring the magnetic susceptibility, this was not conducted here due to time constraints and the small amount of product synthesised.

In the high resolution positive ion mass spectrum of Fe$^{III}$($L_m$)Cl·H$_2$O, the only major species corresponded to a formulation of [Fe$^{III}$($L_m$)]$^+$. This is probably because any axial ligand(s) on this complex are rather labile, and would be easily lost in the mass spectrum during the electrospray ionisation process. This has been also been observed in the mass spectra of other axially ligated metal(III)-$L_m$ complexes, which are discussed below.

Co($L_m$)Br was synthesised using a method that was closely related to the procedure used to synthesise Fe$^{III}$($L_m$)Cl, and employed cobalt(II) bromide as the metal source (see Section 3.4.7 for more detail). Both reactions took a similar length of time to reach completion at 60 °C. After the reaction had reached completion, the solution was exposed to air for 45 minutes to oxidise
the expected cobalt(II) product to cobalt(III). The product was then isolated by addition of a large excess of sodium bromide to the filtered solution, followed by removal of the solvent under vacuum. Chromatography on neutral alumina gave the pure Co$^{\text{III}}$(L$_m$)Br product in 53% yield.

Like Fe$^{\text{III}}$(L$_m$)Cl, Co$^{\text{III}}$(L$_m$)Br is also a paramagnetic complex. Elemental analysis agreed with a formulation of Co$^{\text{III}}$(L$_m$)Br·H$_2$O. Despite many attempts, crystals suitable for X-ray crystallographic analysis were not obtained, and it is unknown whether the cobalt centre is six-coordinate (with axial water and bromide ligands), five-coordinate (with an axial water ligand and a bromide counteranion, or with an axial bromide ligand and a water of crystallisation), or four-coordinate (with a bromide counteranion and a water of crystallisation). Based on the crystal structures of various Co(III)-TAML complexes, the latter four-coordinate species may be the most likely structure of the Co(III)-L$_m$ complex in the solid state, and a formulation of [Co$^{\text{III}}$(L$_m$)]Br·H$_2$O may therefore best represent the structure of the complex. Although only the [Co$^{\text{III}}$(L$_m$)]$^+$ unit was observed in the high resolution positive ion mass spectrum, this technique does not clarify whether axial ligands are present on the cobalt centre.

The manganese-L$_m$ complex was synthesised using a method closely related to the procedures used to synthesise the Fe$^{\text{III}}$(L$_m$)Cl and Co$^{\text{III}}$(L$_m$)Br complexes (see Section 3.4.5 for detailed procedure). A small excess of anhydrous manganese(II) chloride was used as the metal source in this reaction, and the reaction was performed under stringently air-free conditions in dry methanol, using a moderate excess of sodium acetate as the base. The reaction was heated in a sealed Schlenk tube at 60 °C, and was much slower than the analogous reactions used to synthesise the iron-L$_m$ and cobalt-L$_m$ complexes, taking 70 hours to reach completion (by TLC). The solution was then exposed to air for 2 hours, followed by removal of the solvent under vacuum. Exchange of the ligand(s)/counteranion(s) with sodium chloride was carried out in water, due to the low solubility of the complex in methanol, and this was followed by removal of the solvent under vacuum.

When the crude manganese-L$_m$ complex was purified by column chromatography on silica gel, two coloured bands were observed on the column: a reasonably narrow orange-brown band, followed immediately behind by a reasonably narrow dark brown band. High resolution positive ion mass spectrometry in water confirmed that both bands contained a manganese-L$_m$ complex, but suggested that the oxidation states of the complexes in these two bands were different. The
mass spectrum of the first band was consistent with a formulation of \([\text{Mn}^{\text{III}}(L_m)]^+\), where any axial ligands coordinated to the metal centre are presumably lost in the mass spectrum during the electrospray ionisation process. Meanwhile, the mass spectrum of the second band was consistent with a formulation of \([\text{Mn}^{\text{II}}(L_m)] + \text{H}^+\). Both these species had a charge of +1 and were separated by just one \(m/z\) mass unit. When the mass spectrum of the crude Mn-L\(_m\) complex was obtained before columnning, the ratio of the Mn(II) species to the Mn(III) species was approximately 0.7:1. After column chromatography, a small amount of the Mn(II) complex was observed in the mass spectrum of the first band, and a small amount of the Mn(III) complex was observed in the mass spectrum of the second band, probably because there was an overlap between the two bands on the silica column. Although the intensity of the minor complex species to the major complex species was lower when mass spectra are obtained of only the front edge of the first band, or of the tail end of the second band, the minor complex was not completely removed in these parts of the band. The mass spectra of all the samples were run under the same conditions, using water as the solvent. Similar results were obtained when acetonitrile was used as the solvent to run the mass spectra. The change in ratio between the two Mn-L\(_m\) species before and after columnning suggests that they are two separate products, rather than being due to partial oxidation or reduction of a single species in the mass spectrum. Proton NMR spectra of the products from each silica column band suggest that both the Mn(II) and the Mn(III) species are paramagnetic, as would be expected.

Changing the eluents and the types of columns used (using neutral alumina, basic alumina, and reverse-phase silica) did not clearly separate the Mn(II) and Mn(III) bands, and for some columns, very little separation was observed. Attempts were therefore made to deliberately reduce or oxidise the product mixture to give only one of the products. A reduction reaction was attempted by stirring a solution of the chloride-exchanged crude manganese-L\(_m\) complex with a large excess of zinc powder in dry degassed THF. After 2 hours at room temperature, the product was purified by passing the solution through a plug of silica gel to remove the excess zinc metal and any zinc salts. A single, dark brown band was observed on the column, suggesting that all of the product may have reduced to the Mn(II) species. However, when the reaction mixture was analysed by mass spectrometry (in either water or acetonitrile), a significant amount of the Mn(III) species was also observed. In contrast, when the mass spectrum was run using a small portion of the reaction mixture (diluted in acetonitrile), only the Mn(II) species was observed, presumably because the small amount of zinc metal still present in the sample prevented oxidation to the Mn(III) species. This suggests that the zinc metal does reduce the Mn(III) species to Mn(II) species, but after removing the reductant, the Mn(II) species is partially
reoxidised back to a Mn(III) species (presumably by the oxygen in air), either on the column or after column chromatography. Similar results were obtained when acetonitrile was used as the solvent for this reaction, and similar results were also obtained when this reaction was performed using either of the Mn-Lₘ product bands from the silica column.

Because the above results suggest that the manganese-Lₘ complex is more stable in air in the +III oxidation state than in the +II oxidation state in the absence of a reductant, the manganese-Lₘ complex was instead deliberately oxidised with tert-butyl hydroperoxide. Studies by Collins et al. have shown that stable diamagnetic Mn(V)-TAML complexes can be synthesised by adding tert-butyl hydroperoxide to various manganese(III)-TAML complexes in THF. A solution of the crude chloride-exchanged Mn-Lₘ complex was therefore stirred with a large excess of tert-butyl hydroperoxide for 1 hour in water, and the solvent was then removed under vacuum. Prior to solvent removal, mass spectrometry of a small portion of this solution showed only the Mn(III) species. No Mn(V) species was observed, and the absence of signals in the ¹H NMR spectrum suggested that the complex remains paramagnetic. Therefore, it was surmised that it may be possible to isolate the Mn(III)-Lₘ complex produced using this procedure. However, after thoroughly drying the Mn(III)-Lₘ residue under vacuum to remove the excess tert-butyl hydroperoxide, a small amount of the Mn(II) species again appeared in the mass spectrum, suggesting that the Mn(III) species partially reduces back to the Mn(II) species in the absence of tert-butyl hydroperoxide, even after prolonged exposure of the solution to air.

Recrystallisations and extractions were also attempted to isolate only one product, but these were unsuccessful. Different salts were also added to the crude manganese-Lₘ product prior to purification, in order to synthesise species with different ligands/counteranions (using salts with bromide, iodide, acetate, tetrafluoroborate, tetraphenylborate, or hexafluorophosphate anions), and also to exchange any countercations that may be present in the product(s) (using salts with lithium, sodium, potassium, or tetraethylammonium cations). Columns, recrystallisations, and extractions of these crude exchanged complexes did not enable the isolation of a complex in only one oxidation state, without contamination by the product in the other oxidation state.

The manganese-Lₘ, iron-Lₘ, cobalt-Lₘ, iron-L₄, and cobalt-L₄ complexes synthesised in this thesis are the first known examples of any pyridinium amides ligand to be coordinated to these transition metal centres. Because the cobalt and iron complexes of macrocyclic ligand Lₘ were
successfully synthesised and purified, these were studied as oxidation catalysts. These studies are described in the next chapter. The manganese complex was not used for these studies because of time constraints, and because a pure product with a single oxidation state could not be isolated.

3.2.4 Nickel, copper, and palladium complexes of macrocyclic ligand $L_m$

Nickel, copper, and palladium complexes of ligand $L_m$ were synthesised to study the effect of this strongly donating ligand on the oxidation state of the metal centres. These complexes were also synthesised so that diamagnetic species can be isolated, in order to compare the NMR spectra of these species to the NMR spectra of the free ligand, and to the palladium complex of the acyclic ligand (Pd$^{II}$(L$_a$)). Based on the proposed structure of the Pd$^{II}$(L$_a$) complex and other related complexes with strongly donating macrocyclic ligands (described in Section 3.1.3), square planar $d^8$ nickel(II)-$L_m$, copper(III)-$L_m$, and palladium(II)-$L_m$ complexes are expected to be diamagnetic. In contrast, the iron-$L_m$, cobalt-$L_m$, and manganese-$L_m$ complexes synthesised and described in the previous section (Section 3.2.3) were paramagnetic. Therefore, these diamagnetic $L_m$ complexes may also aid in understanding the structures of the paramagnetic $L_m$ complexes.

Using the methods described below, the diamagnetic nickel-$L_m$ and palladium-$L_m$ complexes, Ni$^{II}$(L$_m$) and Pd$^{II}$(L$_m$), were synthesised and fully characterised. A copper-$L_m$ complex that was tentatively formulated as Cu$^{III}$(L$_m$)(OH)(H$_2$O) was also successfully synthesised. Although the characterisation data for this complex supported a formulation of Cu$^{III}$(L$_m$)(OH)(H$_2$O) in solution, a formulation of Cu$^{II}$(L$_m$)-H$_2$O could not be ruled out. These results are discussed below. Attempts to grow X-ray quality crystals are ongoing and this should help to clarify the formulation of this complex.

Ni$^{III}$(L$_m$) was successfully synthesised by refluxing ligand H$_2$L$_m$ with a small excess of nickel acetate tetrahydrate and a moderate excess of sodium acetate in methanol (see Section 3.4.8 for full experimental procedure). The reaction was cooled to room temperature after heating for 20 hours under reflux. The orange precipitate that formed was collected by filtration, and was then purified by column chromatography on silica gel, obtaining pure Ni$^{III}$(L$_m$) in 70% yield.
Pd$^{II}$(L$_m$) was obtained using a method closely related to the procedure used to synthesise Ni$^{II}$(L$_m$). The procedure is given in Section 3.4.12, and involves the reaction of ligand H$_2$L$_m$ with a small excess of palladium acetate and a moderate excess of sodium acetate in refluxing methanol. The solution was cooled to room temperature after heating for 28 hours under reflux, and the yellow precipitate that was formed was collected by filtration. Pure Pd$^{II}$(L$_m$) was obtained in 79% yield after column chromatography on silica gel.

Sharp, non-contact shifted $^1$H and $^{13}$C NMR spectra indicated that both the Ni$^{II}$(L$_m$) complex and the Pd$^{II}$(L$_m$) complex were diamagnetic. High resolution positive ion mass spectrometry confirmed that both complexes have metal centres in the +II oxidation state. This is because M$^{II}$(L$_m$) + H$^+$ and M$^{II}$(L$_m$) + Na$^+$ species were observed as the only major species in the mass spectra of the Ni$^{II}$(L$_m$) and Pd$^{II}$(L$_m$) complexes. Elemental analyses were also consistent with formulations of Ni$^{II}$(L$_m$) and Pd$^{II}$(L$_m$), with one water of crystallisation for the nickel complex, and half a water of crystallisation for the palladium complex. A single water of crystallisation has also been observed in the elemental analyses of the Pd$^{II}$(L$_a$), Fe$^{III}$(L$_m$)Cl, and Co$^{III}$(L$_m$)Br complexes described above, suggesting that this is common for metal-L$_a$ and metal-L$_m$ complexes. In the Ni$^{II}$(L$_m$), Pd$^{II}$(L$_m$), and Pd$^{II}$(L$_a$) complexes, it is unlikely that the water molecule is present as an axial ligand, whereas in the iron-L$_m$ and cobalt-L$_m$ complexes, the water molecule could be present as either an axial ligand or as a water of crystallisation, as was discussed in Section 3.2.3.

Table 3.3 and Figure 3.17 show the chemical shifts of selected signals observed in the $^1$H NMR spectra of the Ni$^{II}$(L$_m$) and Pd$^{II}$(L$_m$) complexes, compared to the $^1$H NMR signals of the free deprotonated (H$_2$L$_m$) and protonated (H$_4$L$_m^{2+}$) ligands. All spectra were recorded in DMSO-$d_6$. Note that although the imine resonance form is drawn for the L$_m$ ligand in Figure 3.17, in reality, the zwitterionic resonance form is also expected to contribute to the structure of these complexes in solution (see Section 2.2.2 and Figure 2.11 for the resonance structures of the free L$_m$ ligand).
Table 3.3: $^1$H NMR chemical shifts of metal complexes Ni$^{II}$(L$_m$) and Pd$^{II}$(L$_m$), compared to the free deprotonated (H$_2$L$_m$) and protonated (H$_4$L$_m^{2+}$) ligands

<table>
<thead>
<tr>
<th>Position $^a$</th>
<th>H$_2$L$_m$</th>
<th>Ni$^{II}$(L$_m$)</th>
<th>Pd$^{II}$(L$_m$)</th>
<th>H$_4$L$_m^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.01-7.03 (m)</td>
<td>6.85-6.87 (m)</td>
<td>6.94-6.96 (m)</td>
<td>7.50-7.53 (m)</td>
</tr>
<tr>
<td>2</td>
<td>7.47-7.49 (m)</td>
<td>7.57-7.60 (m)</td>
<td>7.64-7.66 (m)</td>
<td>7.84-7.88 (m)</td>
</tr>
<tr>
<td>3</td>
<td>7.09 (d)</td>
<td>7.31 (d)</td>
<td>7.34 (d)</td>
<td>7.60 (d)</td>
</tr>
<tr>
<td>4</td>
<td>7.64 (dd)</td>
<td>7.65 (dd)</td>
<td>7.71 (dd)</td>
<td>8.38 (dd)</td>
</tr>
<tr>
<td>5</td>
<td>3.78 (s)</td>
<td>3.81 (s)</td>
<td>3.84 (s)</td>
<td>4.10 (s)</td>
</tr>
<tr>
<td>6</td>
<td>8.73 (d)</td>
<td>9.19 (d)</td>
<td>9.01 (d)</td>
<td>8.65 (d)</td>
</tr>
<tr>
<td>7</td>
<td>1.45 (s)</td>
<td>1.42 (s)</td>
<td>1.47 (s)</td>
<td>1.56 (s)</td>
</tr>
</tbody>
</table>

$^a$ Numbered positions are shown in Figure 3.17. Coupling constants are given in procedure Sections 2.5.9, 2.5.10, 3.4.8 and 3.4.12.

$^b$ Abbreviations: s = singlet, d = doublet, dd = doublet of doublets, m = multiplet.

Figure 3.17: Numbered positions for Ni$^{II}$(L$_m$) and Pd$^{II}$(L$_m$) complexes, and for the analogous free deprotonated (H$_2$L$_m$) and protonated (H$_4$L$_m^{2+}$) ligands, used for the comparison of $^1$H NMR chemical shifts. Because the molecule is symmetric about a vertical mirror plane, only one half of the L$_m$ ligand is numbered here.

Table 3.3 illustrates that most of the $^1$H NMR chemical shifts for the Ni$^{II}$(L$_m$) and Pd$^{II}$(L$_m$) complexes are between the chemical shifts of the deprotonated (H$_2$L$_m$) and protonated (H$_4$L$_m^{2+}$) free ligands, as might be expected if two protons are removed from the H$_2$L$_m$ ligand, and are replaced by one electropositive metal centre, coordinating to the four nitrogen atoms. However, a few protons in the Ni$^{II}$(L$_m$) and Pd$^{II}$(L$_m$) complexes do not follow this trend. For example, proton 1 on the phenyl ring is slightly further upfield for these metal complexes than it is for ligand H$_2$L$_m$, and proton 6 on the pyridinium ring is significantly further downfield for the metal complexes than it is for either the H$_2$L$_m$ or the H$_4$L$_m^{2+}$ free ligands. It is interesting that the protons in position 6 of the H$_2$L$_m$ free ligand are also shifted downfield from the corresponding
protons for $\text{H}_2\text{L}_m^{2+}$ free ligand, whereas all the other protons are further upfield for the $\text{H}_2\text{L}_m$ ligand than for the $\text{H}_4\text{L}_m^{2+}$ ligand. This effect was discussed in Section 2.3.2.1. The downfield shift of proton 6 for Ni$^{II}(\text{L}_m)$ and Pd$^{II}(\text{L}_m)$ compared to $\text{H}_2\text{L}_m$ and $\text{H}_4\text{L}_m^{2+}$ could be due to changes in the ring conformation of the macrocycle upon coordination of the metal, which brings proton 6 into a position where it is more deshielded by the adjacent carboxamide group than it is in the $\text{H}_2\text{L}_m$ and $\text{H}_4\text{L}_m^{2+}$ free ligands. All of the $^1\text{H}$ NMR signals (except for position 6) are shifted slightly further downfield for the Pd$^{II}(\text{L}_m)$ complex than they are for the Ni$^{II}(\text{L}_m)$ complex, which is surprising considering that the palladium(II) metal centre is expected to be slightly more electronegative than the nickel(II) metal centre.

Like the structures proposed for the Ni$^{II}(\text{L}_m)$ and Pd$^{II}(\text{L}_m)$ complexes, most nickel and palladium complexes of porphyrin, corrole, and TMTAA ligands (described in Section 3.1.3) have four-coordinate metal(II) centres, with square planar (or slightly distorted square planar) geometries. In contrast, a nickel complex of the MAC* TAML ligand has been isolated with a square planar paramagnetic Ni(III) centre. TAML ligands are stronger N-donors than porphyrin, corrole, and TMTAA ligands, and are therefore able to stabilise metal centres in higher oxidation states. Based on the number and types of donor groups present in the L$_m$ ligand and the expected donating strength of these functional groups, the N-donor strength of ligand L$_m$ is expected to be lower than TAML ligands, but higher than most porphyrin, corrole, and TMTAA complexes. Therefore, although either metal(II) or metal(III) complexes of ligand L$_m$ might be expected with nickel and palladium, Ni$^{II}(\text{L}_m)$ and Pd$^{II}(\text{L}_m)$ seem to be more stable as metal(II) species under the conditions used to synthesise these complexes. However, it was not investigated whether strong oxidants would oxidise the Ni$^{II}(\text{L}_m)$ or Pd$^{II}(\text{L}_m)$ complexes to higher oxidation states. The acyclic Pd$^{II}(\text{L}_a)$ complex also seems to be more stable as a diamagnetic square planar Pd(II) complex than as a higher oxidation state complex (see Section 3.2.2).

A copper-L$_m$ complex tentatively formulated as Cu$^{III}(\text{L}_m)(\text{OH})(\text{H}_2\text{O})$ was synthesised by stirring the $\text{H}_2\text{L}_m$ free ligand with a small excess of anhydrous copper(II) chloride and a moderate excess of sodium acetate in methanol under a nitrogen atmosphere. After 26 hours at room temperature, the red-orange precipitate was collected. This precipitate was purified by column chromatography on silica gel to give a single red-orange band that was collected. On evaporation of this solution, Cu$^{III}(\text{L}_m)(\text{OH})(\text{H}_2\text{O})$ was obtained as a red-orange crystalline solid in 78% yield.
The absence of signals in the $^1$H and $^{13}$C NMR spectra of this copper-L$_m$ complex in DMSO-$d_6$ and in CDCl$_3$ (scanned over a very large chemical shift range) suggests that the complex is paramagnetic in solution. This paramagnetism would be consistent with either a $d^9$ copper(II) metal centre or an octahedral $d^8$ copper(III) metal centre. The high resolution positive ion mass spectrum of this copper-L$_m$ complex suggests that the latter formulation is more likely, because only one major signal was observed in this mass spectrum, which corresponded to a [Cu$^{III}$(L$_m$)]$^+$ species. It would be expected that any axial ligand this complex had would be lost in the mass spectrum during the electrospray ionisation process, as has also been found in the mass spectra of the iron-L$_m$, cobalt-L$_m$, and manganese-L$_m$ complexes (discussed in Section 3.2.3). However, even though neither a [Cu$^{II}$(L$_m$)] + H$^+$ species nor a [Cu$^{II}$(L$_m$)] + Na$^+$ species was observed in the mass spectrum, it may be possible that the metal centre of the copper-L$_m$ complex is in the +II oxidation state and oxidises to a copper(III) species during the electrospray ionisation process.

Elemental analysis of the copper-L$_m$ complex was consistent with a formulation of either Cu$^{III}$(L$_m$)(OH) or Cu$^{II}$(L$_m$)(H$_2$O) in the solid state. Therefore, it also was not possible to rule out a copper(II) metal centre based on elemental analysis. If the metal centre of copper-L$_m$ is indeed in the +III oxidation state, the diamagnetic square pyramidal Cu$^{III}$(L$_m$)(OH) complex would have to ligate in solution to form a paramagnetic octahedral complex (such as Cu$^{III}$(L$_m$)(OH)(H$_2$O)) in order to be consistent with the paramagnetism observed in the $^1$H NMR spectrum. Thus, a square pyramidal geometry (Cu$^{III}$(L$_m$)(OH)) would be preferred in the solid state, whereas an octahedral geometry (Cu$^{III}$(L$_m$)(OH)(H$_2$O)) would be preferred in solution. This behaviour has been well documented for the related $d^5$ iron(III)-TAML complexes.$^{17,97}$ Unfortunately, due to time constraints and the small amount of Cu$^{III}$(L$_m$)(OH)(H$_2$O) synthesised, solid state and solution state magnetic moments were not measured to determine whether this is occurring. Many attempts have also been made to grow X-ray quality crystals of Cu$^{III}$(L$_m$)(OH)(H$_2$O) to confirm the solid state structure, but these have so far been unsuccessful.

In the literature, most copper(III)-corrole complexes are diamagnetic at room temperature, with square planar metal centres and no axial ligands (see Section 3.1.3 for more detail).$^{177-181}$ However, at higher temperatures, broadening and shifting of the copper(III)-corrole proton NMR signals often occurs, and this has been attributed to an equilibrium between the diamagnetic copper(III) species and a paramagnetic copper(II)-corrole radical cation species.$^{179,180,184}$ In contrast to these copper-corrole complexes, most copper-porphyrin and
copper-TMTAA complexes (which contain ligands with weaker donor atoms) are in the +II oxidation state under ambient conditions, and are thus paramagnetic.\textsuperscript{170-172} The higher oxidation state of copper-corrole complexes compared to copper-porphyrin and copper-TMAA complexes has been attributed to the stronger N-donating properties of the corrole ligand than the porphyrin and TMTAA ligands.\textsuperscript{157} Like corrole and porphyrin ligands, the L_{m} ligand is expected to be a strong N-donor, due to the presence of both carboxamide and pyridinium amide N-donor groups. Based on the number and types of donor groups, it might be expected that ligand L_{m} is a stronger N-donor than porphyrin and corrole ligands. However, this has not been confirmed experimentally.

3.2.5 A dimeric ruthenium complex of macrocyclic ligand L_{m}

This section describes the synthesis, characterisation, and spectroscopic properties of a dimeric ruthenium complex of the macrocyclic pyridinium amide ligand L_{m}, and compares this complex to other dimeric ruthenium complexes with strongly donating ligands (such as porphyrins, corroles, and TMTAAAs). These reported complexes display interesting structural properties (see Section 3.1.4). The dimeric ruthenium complex of ligand L_{m} was also synthesised so that it could be compared to the structure of a similar dimeric rhodium complex of ligand L_{m}, which is discussed in Section 3.2.6. This dimeric ruthenium-L_{m} complex was successfully synthesised and purified using the procedure described below. The characterisation data for this complex strongly suggested a formulation of [Ru^{III}(L_{m})]_{2}[BF_{4}]_{2}, with a direct unsupported ruthenium(III)-ruthenium(III) bond. These data are described and discussed below.

[Ru^{III}(L_{m})]_{2}[BF_{4}]_{2} was successfully synthesised by first refluxing the free ligand (H_{2}L_{m}) with a small excess of ruthenium trichloride trihydrate and a moderate excess of sodium carbonate in 2-methoxyethanol for 18 hours. After cooling the solution to room temperature, the excess sodium carbonate was removed by filtration, the solvent was removed under vacuum, and the solid was dried under vacuum to remove most of the 2-methoxyethanol. The counteranions were then exchanged for tetrafluoroborate by stirring the crude product with a large excess of sodium tetrafluoroborate in water, followed by extraction of the product into dichloromethane. Column chromatography on neutral alumina gave the dark purple [Ru^{III}(L_{m})]_{2}[BF_{4}]_{2} product in 59\% yield. See Section 3.4.10 for the detailed experimental procedure. This procedure is similar to the method used to synthesise the [Ru^{III}(corrole)]_{2} dimers, which used [Ru^{II}(COD)Cl]_{2} as the
ruthenium source and triethylamine as the base in refluxing 2-methoxyethanol (see Section 3.1.4 for details).\textsuperscript{182,187}

Spectroscopic data for the ruthenium-L\textsubscript{m} complex agrees with a dimeric formulation of [Ru\textsuperscript{III}(L\textsubscript{m})\textsubscript{2}[BF\textsubscript{4}]\textsubscript{2}. For example, a single major signal was observed in the high resolution positive ion mass spectrum of this complex, which agreed with a formulation of [(Ru\textsuperscript{III})\textsubscript{2}(L\textsubscript{m})\textsubscript{2}]\textsuperscript{2+}, and elemental analysis showed that one tetrafluoroborate anion is present per metal centre, as expected.

Sharp, non-contact shifted \textsuperscript{1}H and \textsuperscript{13}C NMR signals indicate that the [Ru\textsuperscript{III}(L\textsubscript{m})\textsubscript{2}[BF\textsubscript{4}]\textsubscript{2} complex is diamagnetic, as expected based on the simplified orbital splitting diagram shown in Figure 3.7. This scheme has been used previously to rationalise the metal-metal bonding in related dimeric complexes. This orbital splitting diagram also predicts that [Ru\textsuperscript{III}(L\textsubscript{m})\textsubscript{2}[BF\textsubscript{4}]\textsubscript{2} has a formal ruthenium-ruthenium triple bond. The \textsuperscript{1}H and \textsuperscript{13}C NMR chemical shifts observed for the L\textsubscript{m} ligands in [Ru\textsuperscript{III}(L\textsubscript{m})\textsubscript{2}[BF\textsubscript{4}]\textsubscript{2} are also similar to those observed for the diamagnetic Ni\textsuperscript{II}(L\textsubscript{m}) and Pd\textsuperscript{II}(L\textsubscript{m}) complexes. Each half of each L\textsubscript{m} ligand is symmetrically equivalent by \textsuperscript{1}H and \textsuperscript{13}C NMR spectroscopy, and the two L\textsubscript{m} ligands are symmetrically equivalent to each other, suggesting that the [Ru\textsuperscript{III}(L\textsubscript{m})\textsubscript{2}[BF\textsubscript{4}]\textsubscript{2} complex is symmetric about mirror planes parallel and perpendicular to the metal-metal bond (see Figure 3.18 for a possible structure). Therefore, only one \textsuperscript{1}H NMR singlet is observed for the four N-methyl groups of [Ru\textsuperscript{III}(L\textsubscript{m})\textsubscript{2}[BF\textsubscript{4}]\textsubscript{2}, for example. Ru(III)-Ru(III)-corrole dimers, and Ru(II)-Ru(II), Ru(II)-Ru(III), and Ru(III)-Ru(III) dimers of porphyrin and TMTAA ligands are also highly symmetric by NMR spectroscopy.\textsuperscript{182,187,188,191,193-195,197-199} Only the geminal-C-methyl groups of the [Ru\textsuperscript{III}(L\textsubscript{m})\textsubscript{2}[BF\textsubscript{4}]\textsubscript{2} complex are not equivalent by NMR spectroscopy. Instead of all four of these methyl groups being equivalent, two sets of signals are observed by \textsuperscript{1}H and \textsuperscript{13}C NMR spectroscopy (integrating for six protons each in the \textsuperscript{1}H NMR spectrum). This can be rationalised because the geminal-C-methyl groups are oriented perpendicular to the otherwise mostly planar macrocyclic ligand. Two of these groups point away from the metal-metal bond, while the other two point towards the metal-metal bond, and so they will be shielded to different extents. This observation provides further confirmation that the [Ru\textsuperscript{III}(L\textsubscript{m})\textsubscript{2}[BF\textsubscript{4}]\textsubscript{2} complex is dimeric, because a monomeric Ru(III)-L\textsubscript{m} complex with no axial ligands, besides being paramagnetic, would only have one set of geminal-C-methyl signals if the ruthenium atoms are coordinated in the plane of the macrocycle.
Similar effects have been observed in the NMR spectra of the dimeric ruthenium-corrole and ruthenium-porphyrin complexes discussed in Section 3.1.4. For example, $^1$H NMR spectroscopy has shown that corrole and porphyrin ligands containing ethyl groups (such as $[\text{Ru}^{III}(\text{hedmc})]_2$, $[\text{Ru}^{III}(\text{dehmc})]_2$, $[\text{Ru}^{II}(\text{OEP})]_2$, and $[\text{Ru}^{II}(\text{OETAP})]_2$) have diastereotopic methylene protons, and porphyrin ligands that are substituted with aromatic groups at the methine bridge carbons (which are oriented perpendicular to the porphyrin ring – for example, in $[\text{Ru}^{II}(\text{TPP})]_2$ and $[\text{Ru}^{II}(\text{TTP})]_2$) show inequivalence of the ortho protons and inequivalence of the meta protons. These results have also been attributed to the presence of direct ruthenium-ruthenium bonds in these complexes.\textsuperscript{187,191}

![Figure 3.18](image.png)

**Figure 3.18:** Possible structure of $[\text{Ru}^{III}(\text{L}_m)]_2[\text{BF}_4]_2$. The ruthenium-ruthenium bond has been elongated considerably in this figure in order to clearly show the orientation of the two ligands

Like the Ru(III)-Ru(III) corrole dimers discussed in Section 3.1.4, the $[\text{Ru}^{III}(\text{L}_m)]_2[\text{BF}_4]_2$ complex is air-stable.\textsuperscript{187} In contrast, the isolated Ru(II)-Ru(II), Ru(II)-Ru(III), and Ru(III)-Ru(III) dimers of porphyrin and TMTAA ligands published in the literature are highly air-sensitive.\textsuperscript{192,198} The high stability of Ru(III)-Ru(III) corrole dimers has been attributed to the strongly donating corrole ligand.\textsuperscript{182} Thus, the high stability of the $[\text{Ru}^{III}(\text{L}_m)]_2[\text{BF}_4]_2$ complex also suggests that the L\textsubscript{m} ligands donate strongly to the ruthenium(III) metal centres.

The only published example of a ruthenium-pyridinium amide complex was a monomeric six-coordinate ruthenium(II) species, containing one bidentate chelating pyridinium amide ligand, one bidentate bipyridine ligand, and two thiocyanate ligands (see Section 3.1.1 for structure).\textsuperscript{12}
The structure of the \([\text{Ru}^{III}(L_{\text{m}})]_{2}[^{\text{BF}}_{4}]_{2}\) complex differs markedly from this ruthenium(II) complex, and the higher oxidation state of the \([\text{Ru}^{III}(L_{\text{m}})]_{2}[^{\text{BF}}_{4}]_{2}\) complex suggests that the \(L_{\text{m}}\) ligand may be able to stabilise metal centres in high oxidation states than the bidentate chelating pyridinium amide ligand. This is expected, because the bidentate pyridinium amide ligand coordinates to the ruthenium centre through one strongly donating pyridinium amide nitrogen atom and one less strongly donating pyridine nitrogen atom (and weak to moderately strongly donating ancillary ligands), whereas each \(L_{\text{m}}\) ligand coordinates to the ruthenium centre through two strongly donating pyridinium amide nitrogen atoms and two strongly donating carboxamide nitrogen atoms.

Therefore, in summary, characterisation data and the comparison of these data to similar dimeric ruthenium complexes published in the literature strongly suggests that the ruthenium-\(L_{\text{m}}\) complex has a dimeric formulation of \([\text{Ru}^{III}(L_{\text{m}})]_{2}[^{\text{BF}}_{4}]_{2}\). As such, it is the first example of a ruthenium(III) complex of a pyridinium amide and adds to the rare class of ruthenium complexes with direct unsupported metal-metal bonds.

### 3.2.6 A dimeric rhodium complex of macrocyclic ligand \(L_{\text{m}}\)

Rhodium complexes of the macrocyclic ligand \(L_{\text{m}}\) were synthesised because the rhodium complexes of some strongly donating porphyrin, phthalocyanine, and TMTAA ligands show interesting structural properties and reactivities (see Section 3.1.5 and Chapter 5). Some of these complexes have also shown promise as catalysts for small molecule activation reactions.\(^{19,25}\) The results of investigations into the catalytic activation of small molecules by rhodium complexes of ligand \(L_{\text{m}}\) is reported in Chapter 5. Meanwhile, this section describes the synthesis, structure, and spectroscopic properties of the new dimeric rhodium-\(L_{\text{m}}\) complex, \(\text{Na}[\text{Rh}^{III}(L_{\text{m}})]_{2}\text{Cl}\). Spectroscopic data and reactivity studies (discussed below) indicate that this complex is diamagnetic and has a direct rhodium-rhodium bond, with one axial chloride ligand.

\(\text{Na}[\text{Rh}^{III}(L_{\text{m}})]_{2}\text{Cl}\) was synthesised by refluxing a methanol solution of free ligand \(\text{H}_{2}L_{\text{m}}\) with a slight excess of \(\text{RhCl}_{3} \cdot \text{xH}_{2}\text{O}\) (assuming \(\text{x} = 3\)) and a moderate excess of sodium acetate. After heating under reflux for six hours, the solution was cooled to room temperature, and the orange
precipitate was collected by filtration and washed thoroughly with ice-cold methanol, giving Na[[Rh\textsuperscript{II}(L\textsubscript{m})]\textsubscript{2}Cl] in 47% yield.

Both positive and negative ion high resolution mass spectrometries confirm that Na[[Rh\textsuperscript{II}(L\textsubscript{m})]\textsubscript{2}Cl] has a dimeric formulation. In the positive ion mass spectrum, the highest intensity peak is consistent with a formulation of [Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2} + H\textsuperscript{+}]. Like many other axially ligated metal-L\textsubscript{m} complexes described in this chapter, the axial chloride ligand of Na[[Rh\textsuperscript{II}(L\textsubscript{m})]\textsubscript{2}Cl] is probably lost during the electrospray ionisation process. A monomeric complex with a formulation of [Rh\textsuperscript{III}(L\textsubscript{m})]\textsuperscript{+} is also observed in the positive ion mass spectrum of Na[[Rh\textsuperscript{II}(L\textsubscript{m})]\textsubscript{2}Cl] (85% intensity relative to the [Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2} + H\textsuperscript{+}] signal). This species probably arises from heterolytic cleavage of the rhodium-rhodium bond during the electrospray ionisation process. This is not unexpected because, based on similar rhodium dimers of porphyrin and TMTAA ligands, the rhodium-rhodium bond of Na[[Rh\textsuperscript{II}(L\textsubscript{m})]\textsubscript{2}Cl] is expected to be reasonably weak.\textsuperscript{202,208}

In the negative ion mass spectrum of Na[[Rh\textsuperscript{II}(L\textsubscript{m})]\textsubscript{2}Cl], a variety of axially ligated ([Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}(X)\textsubscript{n}]\textsuperscript{n-} dimer species (n = 1 or 2) were identified in the mass spectrum, with chloride, formate, or methanol axial ligands, or a combination of these ligands (Table 3.4). Some species had two axial ligands, while other species had only one axial ligand. Those with two axial ligands were observed as the mono-protonated, monoanionic species and no dianionic or higher charged species were identified. These results therefore suggest that the rhodium-L\textsubscript{m} dimer is readily ligated in the axial positions. These results also suggest that Na[[Rh\textsuperscript{II}(L\textsubscript{m})]\textsubscript{2}Cl] can be readily ligated with a second axial ligand during the electrospray ionisation process, and that the chloride axial ligand may be exchanged during the electrospray ionisation process. The methanol ligand arises from the methanol solvent used to run the mass spectrum, while the formate ligands originate from the sodium formate that was added to the Na[[Rh\textsuperscript{II}(L\textsubscript{m})]\textsubscript{2}Cl] sample to obtain the mass spectrum. When the negative and positive ion mass spectra were run using the same concentration of Na[[Rh\textsuperscript{II}(L\textsubscript{m})]\textsubscript{2}Cl], the absolute intensity (in counts) of the highest intensity signals were similar. This suggests that the species identified in the negative ion mass spectrum are not just trace species present in the Na[[Rh\textsuperscript{II}(L\textsubscript{m})]\textsubscript{2}Cl] sample.
Table 3.4: Signals observed in the high resolution negative ion mass spectrum of Na[[RhII(Lm)]2Cl], including comparison of their m/z values to calculated m/z values

<table>
<thead>
<tr>
<th>Observed m/z (charge)</th>
<th>Relative intensity</th>
<th>Calculated m/z</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1069.1395 (-1)</td>
<td>50%</td>
<td>1069.1413</td>
<td>[[RhII(Lm)]2(Cl)]</td>
</tr>
<tr>
<td>1079.1658 (-1)</td>
<td>15%</td>
<td>1079.1701</td>
<td>[[RhII(Lm)]2(CHOO)]</td>
</tr>
<tr>
<td>1101.1638 (-1)</td>
<td>20%</td>
<td>1101.1669</td>
<td>[[RhII(Lm)]2(Cl)(CH3OH)]</td>
</tr>
<tr>
<td>1105.1168 (-1)</td>
<td>100%</td>
<td>1105.1179</td>
<td>[[RhII(Lm)]2(Cl)2]2+ + H+</td>
</tr>
<tr>
<td>1115.1459 (-1)</td>
<td>85%</td>
<td>1115.1462</td>
<td>[[RhII(Lm)]2(HCOO)(Cl)]2+ + H+</td>
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<tr>
<td>1125.1728 (-1)</td>
<td>30%</td>
<td>1125.1755</td>
<td>[[RhII(Lm)]2(HCOO)2]2+ + H+</td>
</tr>
</tbody>
</table>

* These are all the major species that were identified in the negative ion mass spectrum of Na[[RhII(Lm)]2Cl] (that is, no major species other than those tabulated here were observed in the mass spectrum)

* Calibrated relative to the highest intensity signal in the mass spectrum (set to 100%).

Although a variety of axially ligated rhodium(II)-Lm species were observed in the negative ion mass spectrum of Na[[RhII(Lm)]2Cl], elemental analysis suggests that only one chloride ligand is present in the Na[[RhII(Lm)]2Cl] complex the solid state. This is because elemental analysis corresponds to a formulation of Na[[RhII(Lm)]2Cl]-2H2O. It is possible that one of the two water molecules found in the elemental analysis is present as a second axial ligand on the Na[[RhII(Lm)]2Cl] complex. Alternatively, both water molecules may be present as molecules of crystallisation. A broad and intense stretching vibration at 3466 cm⁻¹ in the ATR FTIR spectrum of the thoroughly-dried Na[[RhII(Lm)]2Cl] complex also indicates that water is present in the solid state. Despite many attempts, crystals of Na[[RhII(Lm)]2Cl] suitable for X-ray structure determination could not be obtained, even when air-free conditions were used. Therefore, it is at present unknown whether the water ligand coordinates to the second axial site. However, for simplicity, the formulation of this complex is written as Na[[RhII(Lm)]2Cl] throughout this thesis.

Sharp, non-contact shifted signals observed in the ¹H NMR spectrum of Na[[RhII(Lm)]2Cl] in methanol-d₄ indicate that the complex is diamagnetic, as would be expected based on the simplified orbital splitting diagram for this general class of dimeric metal-metal bonded complexes given in Figure 3.7. The solubility of Na[[RhII(Lm)]2Cl] is very low in deuterosolvents that are not expected to coordinate appreciably to the metal centre (and which may therefore result in cleavage of the rhodium-rhodium bond – an effect that is discussed in Chapter
5). The highest solubility of Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}Cl]] in common deutero-solvents occurs in methanol-d\textsubscript{4} (about 0.2 mg mL\textsuperscript{-1}). In this solvent, Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}Cl]] is soluble enough to obtain a \textsuperscript{1}H NMR spectrum after a large number of scans, but the signal-to-noise ratio of the \textsuperscript{13}C NMR spectrum is very low, even after a very large number of scans. Slow decomposition of Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}Cl]] in solution also prevented a good \textsuperscript{13}C NMR spectrum from being obtained. For this reason, 2D NMR techniques could not be used to assign the chemical shifts of all the \textsuperscript{1}H and \textsuperscript{13}C resonances in the Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}Cl]] complex. Reactivity studies of Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}Cl]], which are discussed in Chapter 5, also suggest that a rhodium-rhodium bond is present.

The \textsuperscript{1}H NMR spectrum of Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}Cl]] differs substantially from the \textsuperscript{1}H NMR spectra of [Ru\textsuperscript{III}(L\textsubscript{m})\textsubscript{2}][BF\textsubscript{4}]\textsubscript{2} (Sections 3.2.5) and most rhodium(II)-rhodium(II) dimers published in the literature (Section 3.1.5) in that the macrocyclic ligands are not equivalent on the NMR timescale. For [Ru\textsuperscript{III}(L\textsubscript{m})\textsubscript{2}][BF\textsubscript{4}]\textsubscript{2}, [Rh\textsuperscript{II}(porphyrin)]\textsubscript{2}, [Rh\textsuperscript{II}(phthalocyanine)]\textsubscript{2}, and [Rh\textsuperscript{II}(TMTAA)]\textsubscript{2} dimers, the two macrocyclic ligands in each complex are equivalent on the NMR timescale, and each ligand has a high degree of symmetry in the \textsuperscript{1}H NMR spectrum. As expected, in these complexes, functional groups that are oriented perpendicular to the macrocyclic ligand plane (such as the geminal-C-methyl groups of [Ru\textsuperscript{III}(L\textsubscript{m})\textsubscript{2}][BF\textsubscript{4}]\textsubscript{2}, the methylene groups of [Rh\textsuperscript{II}(OEP)]\textsubscript{2}, and the phenyl groups of [Rh\textsuperscript{II}(TPP)]\textsubscript{2}, discussed further in Sections 3.2.5 and 3.1.5) display different resonances for the protons facing towards the metal-metal bond than those facing away from the metal-metal bond.\textsuperscript{200,204,205} For [Ru\textsuperscript{III}(L\textsubscript{m})\textsubscript{2}][BF\textsubscript{4}]\textsubscript{2}, two mirror planes can be drawn through the complex shown in Figure 3.19. The vertical mirror plane drawn in this figure indicates that one “half” of each L\textsubscript{m} ligand is symmetric with the other “half” of the same L\textsubscript{m} ligand. Meanwhile, the horizontal mirror plane indicates that the two L\textsubscript{m} ligands are also related to each other by a mirror plane, either through a locked, eclipsed arrangement of the two macrocycles, or most likely through internal rotation about the metal-metal bond that is rapid on the NMR timescale. Therefore, the four “halves” of the L\textsubscript{m} ligands are related by mirror planes and so, for example, only one N-methyl signal is observed in the \textsuperscript{1}H NMR spectrum of [Ru\textsuperscript{III}(L\textsubscript{m})\textsubscript{2}][BF\textsubscript{4}]\textsubscript{2}. Figure 3.19 also illustrates why two different geminal-C-methyl signals are observed in the \textsuperscript{1}H NMR spectrum of [Ru\textsuperscript{III}(L\textsubscript{m})\textsubscript{2}][BF\textsubscript{4}]\textsubscript{2}. This is because two of these geminal-C-methyl groups point towards the metal-metal bond, while the other two point away from the metal-metal bond.
The $^1$H NMR spectrum of Na[$\text{[Rh}^{II}(L_m)\text{]}_2\text{Cl}$] differs from the $^1$H NMR spectrum of $[\text{Ru}^{III}(L_m)\text{]}_2[\text{BF}_4]_2$, because the four “halves” of the $L_m$ ligands are all inequivalent on the NMR timescale. Accordingly, four $N$-methyl singlets, four geminal-$C$-methyl singlets, eight phenyl CH multiplets, eight pyridinium ring CH doublets, and four pyridinium ring CH doublet of doublets are observed in the $^1$H NMR spectrum of Na[$\text{[Rh}^{II}(L_m)\text{]}_2\text{Cl}$], which all integrate for the expected number of protons. Therefore, the effective horizontal and vertical mirror planes that are drawn in Figure 3.19 for $[\text{Ru}^{III}(L_m)\text{]}_2[\text{BF}_4]_2$ cannot be present for Na[$\text{[Rh}^{II}(L_m)\text{]}_2\text{Cl}$].

Most of the phenyl and pyridinium CH protons are observed between 6.6 and 7.6 ppm in the $^1$H NMR spectrum of Na[$\text{[Rh}^{II}(L_m)\text{]}_2\text{Cl}$] and these signals overlap considerably in this region. Careful analysis of the splitting patterns and the signal integrations in this region indicates that all of the expected signals are present, and that there are no extra signals which could correspond to the presence of by-products. Assignment of the protons to specific positions on the $L_m$ ligands of Na[$\text{[Rh}^{II}(L_m)\text{]}_2\text{Cl}$] was not achieved because slow decomposition of the complex, low complex solubility, and the large number of overlapping signals prevented clear $^1$H-$^{13}$C 2D NMR spectra from being obtained.
Because \( \text{Na}[\text{Rh}\text{II}(\text{L}_m)\text{Cl}] \) has only one axial chloride ligand (or one axial chloride and one axial water ligand), no effective horizontal mirror plane (as drawn in Figure 3.19) is expected for this complex. This explains why the two \( \text{L}_m \) ligands are inequivalent on the NMR timescale. This does not, however, explain why there is no effective vertical mirror plane in \( \text{Na}[\text{Rh}\text{II}(\text{L}_m)\text{Cl}] \). A possible explanation for this is that there is hindered internal rotation about the rhodium-rhodium bond. For example, the \( \text{L}_m \) ligands might be rather buckled in \( \text{Na}[\text{Rh}\text{II}(\text{L}_m)\text{Cl}] \), which may restrict rotation of the two \( \text{L}_m \) ligands about the rhodium-rhodium bond. If this causes \( \text{Na}[\text{Rh}\text{II}(\text{L}_m)\text{Cl}] \) to be held in an asymmetric orientation, the symmetry about the vertical mirror plane would be broken, and so the four “halves” of the \( \text{L}_m \) ligands of \( \text{Na}[\text{Rh}\text{II}(\text{L}_m)\text{Cl}] \) would be inequivalent by \( ^1\text{H} \) NMR spectroscopy. Variable temperature NMR experiments were not attempted to determine whether the dimeric structure would become effectively more symmetric on the NMR timescale at higher temperatures, because \( \text{Na}[\text{Rh}\text{II}(\text{L}_m)\text{Cl}] \) decomposes rapidly in solution at high temperature. This decomposition is also why \( ^1\text{H} \) NMR line broadening studies were not conducted to estimate the rhodium-rhodium bond strength of \( \text{Na}[\text{Rh}\text{II}(\text{L}_m)\text{Cl}] \). Therefore, it is currently unknown how strong the rhodium-rhodium bond of \( \text{Na}[\text{Rh}\text{II}(\text{L}_m)\text{Cl}] \) is compared to similar complexes, such as \( \text{[Rh}\text{II}(\text{OEP})\text{Cl}] \) and \( \text{[Rh}\text{II}(\text{TMTAA})\text{Cl}] \). Furthermore, these reported line broadening studies have been conducted in aprotic low polarity deuterio-solvents, in which the \( \text{Na}[\text{Rh}\text{II}(\text{L}_m)\text{Cl}] \) complex has an extremely low solubility.\(^{202,208}\)

In the literature, most macrocyclic rhodium(II)-rhodium(II) complexes do not have axial ligands, and for those rhodium(II)-rhodium(II) complexes that are axially ligated, there are usually two identical axial ligands (for example, in \( \text{[Rh}\text{II}(\text{pc})(\text{py})]_2 \) – see Figure 3.12 for structure).\(^{210}\) Despite the preponderance of these complexes, a few macrocyclic rhodium(II)-rhodium(II) complexes with unsupported rhodium-rhodium bonds and a single axial ligand have been reported, such as \( \text{[Rh}\text{II}(\text{Rpc})\text{Cl}]_2(\text{PMe}_3) \) (see Section 3.1.5 for a summary of these compounds).\(^{213}\) As expected, the two macrocyclic ligands of these complexes are inequivalent by \( ^1\text{H} \) NMR spectroscopy. However, unlike \( \text{Na}[\text{Rh}\text{II}(\text{L}_m)\text{Cl}] \), each macrocyclic ligand remains symmetric on the NMR timescale in these complexes\(^{213}\) – that is, there are still effective vertical mirror plane(s) that can be drawn through these complexes, as per Figure 3.19. Unlike \( \text{Na}[\text{Rh}\text{II}(\text{L}_m)\text{Cl}] \), no macrocyclic rhodium(II)-rhodium(II) complex has been reported in the literature with anionic axial ligands. However, a few acyclic complexes with unsupported rhodium(II)-rhodium(II) bonds (such as \( \text{[Rh}\text{II}[(\text{CN}-\text{p-tolyl})_4\text{I}]_2\text{[PF}_6]_2 \); see Figure 3.13 for structure) have been reported with anionic axial ligands.\(^{186}\)
The reactivity of Na[[Rh^{II}(L_m)]_2Cl] and the ability of this complex and its dimeric and monomeric derivatives to catalyse the activation of selected small molecules is discussed in Chapter 5.

### 3.2.7 UV-visible absorption spectra of the metal-L_m complexes

UV-visible absorption spectra were recorded for all the metal-L_m complexes synthesised in this chapter (see the experimental sections in Section 3.4 for more detail), and the results are tabulated in Table 3.5. A known concentration of these complexes was dissolved in either methanol or dichloromethane (depending on the solubility of the complex), and spectra were recorded from the UV-cut-off wavelength of the solvent (where the solvent itself begins to absorb strongly) through to 900 nm.

For all the metal-L_m complexes, a significant number of strongly allowed transitions are observed in the UV region, and some of these even occur in the visible region. The broad tail of the highest wavelength peak/shoulder extends well into the visible region, and obscures the d-d transitions for each complex. These intense absorptions in the visible region also explains why all of these complexes are strongly coloured as very dilute solutions. The large number of strongly allowed transitions observed for these complexes probably arises from both charge transfer transitions, and from electronic transitions between the HOMO orbital and higher energy orbitals belonging to one ligand. Indeed, it has been shown (in Section 2.3.2) that the latter transitions are also strong in the UV-visible absorption spectra of the free ligand (H_2L_m), and that these also occur at relatively long wavelengths, with the tail end of these absorptions extending well into the visible region. Similar transitions are therefore expected in the metal complexes of ligand L_m. A significant number of strongly allowed transitions were also observed in the UV-visible absorption spectrum of the Pd^{II}(L_m) complex (Section 3.2.2), suggesting that this is common for complexes with different pyridinium amide ligands.
Table 3.5: Wavelengths and molar absorptivities of peak maxima and shoulders observed in the UV-visible absorption spectra of various metal complexes of ligand L<sub>m</sub>

<table>
<thead>
<tr>
<th></th>
<th>“Mn&lt;sup&gt;II/III&lt;/sup&gt;(L&lt;sub&gt;m&lt;/sub&gt;)”&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Fe&lt;sup&gt;III&lt;/sup&gt;(L&lt;sub&gt;m&lt;/sub&gt;)(Cl)</th>
<th>Co&lt;sup&gt;II&lt;/sup&gt;(L&lt;sub&gt;m&lt;/sub&gt;)(Br)</th>
<th>Ni&lt;sup&gt;II&lt;/sup&gt;(L&lt;sub&gt;m&lt;/sub&gt;)&lt;sup&gt;c&lt;/sup&gt;</th>
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<tbody>
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<td>λ&lt;sub&gt;max&lt;/sub&gt;</td>
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<td></td>
<td></td>
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<tr>
<td>220 (31,300)</td>
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<td>223 (30,600)</td>
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<tr>
<td>246 (20,100)&lt;sup&gt;f&lt;/sup&gt;</td>
<td>250 (22,600)&lt;sup&gt;f&lt;/sup&gt;</td>
<td>257 (14,000)&lt;sup&gt;f&lt;/sup&gt;</td>
<td>300 (12,700)&lt;sup&gt;f&lt;/sup&gt;</td>
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<tr>
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<td>Cu&lt;sup&gt;III&lt;/sup&gt;(L&lt;sub&gt;m&lt;/sub&gt;)(OH)(H&lt;sub&gt;2&lt;/sub&gt;O) c, d</td>
<td>[Ru&lt;sup&gt;III&lt;/sup&gt;(L&lt;sub&gt;m&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;][BF&lt;sub&gt;4&lt;/sub&gt;]&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Na[[Rh&lt;sup&gt;II&lt;/sup&gt;(L&lt;sub&gt;m&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Cl]&lt;sup&gt;e&lt;/sup&gt;</td>
<td>Pd&lt;sup&gt;II&lt;/sup&gt;(L&lt;sub&gt;m&lt;/sub&gt;)&lt;sup&gt;c&lt;/sup&gt;</td>
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</tbody>
</table>

<sup>a</sup> Wavelength at λ<sub>max</sub> (nm) and molar absorptivities at this wavelength (ε, in L mol<sup>-1</sup> cm<sup>-1</sup>).<br><sup>b</sup> Postulated formulation, see Section 3.2.3 for details. This compound was not purified.<br><sup>c</sup> Recorded in dichloromethane. All other spectra were recorded in methanol.<br><sup>d</sup> Postulated formulation, see Section 3.2.4 for details.<br><sup>e</sup> Postulated formulation, see Section 3.2.6 for details.<br><sup>f</sup> Observed as a shoulder rather than as a peak maximum.<br><br>The number of observed transitions and the molar absorptivity of these transitions varies for each complex, although many of the transitions observed for the Ni<sup>II</sup>(L<sub>m</sub>) complex occur at similar wavelengths and molar absorptivities to the transitions observed for the Pd<sup>II</sup>(L<sub>m</sub>) complex, as would be expected. In particular, some of the transitions for the dimeric Na[[Rh<sup>II</sup>(L<sub>m</sub>)<sub>2</sub>Cl] complex have very high molar absorptivities (up to 85,100 L mol<sup>-1</sup> cm<sup>-1</sup>). Unlike the other metal-L<sub>m</sub> complexes, the low solubility of Na[[Rh<sup>II</sup>(L<sub>m</sub>)<sub>2</sub>Cl] prevented spectra from being obtained under significantly more concentrated conditions and therefore precluded the observation of d-d transitions for this complex. The manganese complex has the largest
number of observed UV-visible transitions. This was the only complex that was not successfully purified, and the large number of transitions may reflect the presence of multiple manganese complexes in the manganese-\text{L}_m samples.

### 3.3 Conclusions and future work

Two pyridinium amide ligands, \text{L}_a and \text{L}_m, were successfully metallated with a variety of transition metals. Although a diamagnetic palladium(II) complex of the acyclic ligand (\text{L}_a) was successfully synthesised and purified, attempts to synthesise iron(III)-\text{L}_a and cobalt(III)-\text{L}_a complexes resulted in the formation of multiple products, and the isolation of a single pure product was not achieved. The macrocyclic ligand (\text{L}_m) was metallated with manganese, iron, cobalt, nickel, copper, ruthenium, rhodium, and palladium. All of these complexes were purified and characterised, except for the manganese complex, where ready inter- conversion between a Mn(II) and a Mn(III) species appeared to occur. This prevented these manganese-\text{L}_m products from being successfully separated, even after deliberate oxidation or reduction of the crude mixture. These metal-\text{L}_m complexes are the first known examples of transition metals coordinated to a macrocyclic pyridinium amide ligand, and the manganese-\text{L}_m, iron-\text{L}_m, cobalt-\text{L}_m, iron-\text{L}_a, and cobalt-\text{L}_a complexes are the first known examples of any pyridinium amide to be coordinated to manganese, iron, or cobalt metal centres. The Ni^{II}(\text{L}_m), Pd^{II}(\text{L}_m), Pd^{II}(\text{L}_a), [Ru^{III}(\text{L}_m)]_2[BF_4]_2 and Na[[Rh^{II}(\text{L}_m)]_2\text{Cl}] complexes were diamagnetic, while the iron-\text{L}_a, cobalt-\text{L}_a, manganese-\text{L}_m, Fe^{III}(\text{L}_m)\text{Cl}, Co^{III}(\text{L}_m)\text{Br}, and Cu^{III}(\text{L}_m)(\text{OH})(\text{H}_2\text{O}) complexes were paramagnetic. Spectroscopic studies suggested that the [Ru^{III}(\text{L}_m)]_2[BF_4]_2 and Na[[Rh^{II}(\text{L}_m)]_2\text{Cl}] complexes are dimeric, with direct unsupported metal-metal bonds. The asymmetry of the \text{L}_m ligands in the $^1\text{H}$ NMR spectrum of Na[[Rh^{II}(\text{L}_m)]_2\text{Cl}] was unexpected, particularly in relation to $^1\text{H}$ NMR spectra of [Ru^{III}(\text{L}_m)][BF_4]_2 and related dimeric rhodium complexes published in the literature. It was postulated that his asymmetry is due to the presence of the axial chloride ligand and hindered rotation of the \text{L}_m ligands in the Na[[Rh^{II}(\text{L}_m)]_2\text{Cl}] complex on the NMR timescale. Possible structures have been discussed to explain these observations. Unfortunately, attempts to grow X-ray quality crystals of these complexes for structure determination have so far been unsuccessful. These efforts are ongoing.
The following chapter discusses the results of dye oxidation studies with hydrogen peroxide, catalysed by the Fe$^{III}$(L$_m$)Cl and Co$^{III}$(L$_m$)Br complexes, while Chapter 5 discusses reactions relevant to small molecule activation catalysed by Na[[Rh$^{III}$(L$_m$)]$_2$Cl] and by selected monomeric and dimeric derivatives of this complex. Note that, despite the fact that they may be effective oxidation catalysts, oxidation studies with the manganese-L$_m$ complex, the iron-L$_a$ complex, and the cobalt-L$_a$ complex have not yet been studied due to time constraints, and because these complexes were not successfully purified.

3.4 Experimental

3.4.1 General procedures

See Section 2.5.1 for general synthetic and spectroscopic procedures and instrumentation.

3.4.2 Synthesis of Pd$^{II}$(L$_a$)

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure320.png}
\caption{Chemical structure of Pd$^{II}$(L$_a$)}
\end{figure}

$N^1,N^2$-bis(1-methyl-2-(p-tolylimino)-1,2-dihydropyridin-3-yl)oxalamide (H$_2$L$_a$) (0.203 g, 0.422 mmol) and palladium(II) acetate (0.095 g, 0.422 mmol) were refluxed in THF (80 mL) for 12 hours. The orange precipitate was collected by filtration and washed with THF (15 mL). The complex was purified by column chromatography on basic alumina (1:1 dichloromethane/acetonitrile). The orange band was collected and on evaporation of the solvent
under reduced pressure, a pure sample of orange PdII(La) crystallised from solution (yield: 0.104 g, 42%).

\(^1\)H NMR (300 MHz, CDCl\(_3\), \(\delta\)): 8.39 (dd, \(J_1 = 7.5\) Hz, \(J_2 = 1.5\) Hz, 2H, CH), 6.57 (d, \(J = 8.4\) Hz, 4H, CH), 6.45 (d, \(J = 8.4\) Hz, 4H, CH), 6.28 (dd, \(J_1 = 6.9\) Hz, \(J_2 = 1.5\) Hz, 2H, CH), 6.05 (dd, \(J_1 = 7.5\) Hz, \(J_2 = 6.9\) Hz, 2H, CH), 2.73 (s, 6H, N-CH\(_3\)), 2.28 (s, 6H, C-CH\(_3\)).

\(^{13}\)C NMR (75.4 MHz, CDCl\(_3\), \(\delta\)): 162.5 (C=O), 156.1 (pyridinium C-NR), 145.3 (\(p\)-toluidine C-NR), 142.2 (pyridinium C-NC(O)R), 133.4 (C-CH\(_3\)), 132.1 (pyridinium CH, ortho to N-methyl group), 129.0 (\(p\)-toluidine CH, ortho to C-methyl group), 125.2 (\(p\)-toluidine CH, meta to C-methyl group), 122.7 (pyridinium CH, para to N-methyl group), 109.6 (pyridinium CH, meta to N-methyl group), 45.4 (N-CH\(_3\)), 21.2 (C-CH\(_3\)).

IR (cm\(^{-1}\)): 3411 (m, br), 2940 (w, br), 2854 (w, br), 1727 (w), 1639 (m), 1621 (s), 1602 (s), 1542 (w), 1512 (s), 1498 (s), 1446 (m), 1416 (m), 1373 (w), 1341 (m), 1308 (m), 1208 (w), 1171 (m), 1103 (m), 1042 (m), 1019 (w), 972 (w), 862 (m), 808 (m), 762 (m), 738 (s), 637 (w), 578 (m), 521 (w), 503 (m).

ESI-MS \(m/z\): (M + H\(^+\)), calcd for C\(_{28}\)H\(_{27}\)N\(_6\)O\(_2\)Pd, 585.1235; found, 585.1241.

UV-vis (CH\(_2\)Cl\(_2\)) \(\lambda_{\text{max}}\), nm (\(\varepsilon, \text{ L mol}^{-1} \text{ cm}^{-1}\)): 251 (sh, 47,000), 314 (32,800), 359 (21,100), 437 (15,400), 471 (11,600), 751 (369)

Anal. Calcd for C\(_{28}\)H\(_{28}\)N\(_6\)O\(_2\)Pd·H\(_2\)O: C, 55.77; H, 4.68; N, 13.94. Found: C, 55.84; H, 4.96; N, 13.94.

### 3.4.3 Synthesis of iron(III) complexes of ligand La

\(N^1,N^2\)-bis(1-methyl-2-(\(p\)-tolylimino)-1,2-dihydropyridin-3-yl)oxalamide (H\(_2\)La) (0.0810 g, 0.169 mmol) and potassium tert-butoxide (0.0947 g, 0.843 mmol) were dissolved in degassed THF (20 mL) in a Schlenk tube. The reaction mixture was placed under three freeze-pump-thaw degas cycles. Anhydrous iron(II) chloride (0.0256 g, 0.202 mmol) was added to the frozen solution and the solution was placed under another freeze-pump-thaw degassing cycle. The Schlenk tube was sealed under vacuum and the solution heated to room temperature. The solution was stirred at room temperature for 1 hour and then at 50 °C for 1.5 hours, until the reaction had reached completion by TLC (alumina). The solution was cooled to room
temperature and was then neutralised with glacial acetic acid (1 M in THF). The solvent was removed under vacuum to yield a dark green solid. The complex was purified by column chromatography (silica gel, 10 x 2 cm column, 9:1 dichloromethane/methanol), collecting the green-brown band. The solvent was removed under vacuum to give a dark green-brown solid (0.0652 g), which was not purified further. See Table 3.1 for the results from the high resolution positive ion mass spectrum for this complex.

### 3.4.4 Synthesis of cobalt(III) complexes of ligand $L_a$

$N^1,N^2$-bis(1-methyl-2-(p-tolylimino)-1,2-dihydropyridin-3-yl)oxalamide (H$_2$L$_a$) (0.0784 g, 0.163 mmol) and potassium tert-butoxide (0.0915 g, 0.815 mmol) were dissolved in degassed THF (20 mL) in a Schlenk tube. The reaction mixture was placed under three freeze-pump-thaw degas cycles. Anhydrous cobalt(II) bromide (0.0428 g, 0.196 mmol) was added to the frozen solution and the solution was placed under another freeze-pump-thaw degassing cycle. The Schlenk tube was sealed under vacuum and the solution heated to room temperature. The solution was stirred at room temperature for 20 minutes and then at 50 °C for 6 hours, until the reaction had reached completion by TLC (alumina). The solution was cooled to room temperature and was then neutralised with glacial acetic acid (1 M in THF). The solvent was removed under vacuum to yield a brown solid. The residue was purified by column chromatography on silica gel (10 x 2 cm column, 4:1 dichloromethane/methanol), collecting the dark brown band. A dark brown solid was obtained after removal of the solvent under vacuum (0.0584), which was not purified further. See Table 3.2 for the results from the high resolution positive ion mass spectrum for this complex.
3.4.5 Synthesis of a manganese complex of ligand $L_m$

Figure 3.21: Chemical structure of a manganese complex of ligand $L_m$. The nature of the axial ligand(s) ($X/X'$) are currently unknown

Anhydrous manganese(II) chloride (0.0435 g, 0.346 mmol and (5E,18aE)-8,12,12,16-tetramethyl-8,10,14,16-tetrahydro-11H-benzo[e]dipyrido[3,4-b:4',3'-h][1,4,7,10]tetraazacyclotridecine-11,13(12H)-dione ($H_2L_m$) (0.103 g, 0.247 mmol) were added to dry thoroughly freeze-pump-thaw degassed methanol (25 mL) in a Schlenk tube. The solution was stirred for 5 minutes at room temperature and then sodium acetate (0.102 g, 1.24 mmol) was added and the mixture was again freeze-pump-thaw degassed. The Schlenk tube was sealed under vacuum and heated to 60 °C. After 70 hours at 60 °C, once the reaction had reached completion by TLC (alumina), the solution was cooled to room temperature and stirred in air for 2 hours. The solvent was removed under vacuum to yield a red-brown solid. Deionised water (90 mL) was added and the solution was stirred for 10 minutes at room temperature. The solution was then filtered to remove undissolved solids and sodium chloride (0.289 g, 4.94 mmol) was added. After stirring for 2 hours in air at room temperature, the solution was filtered and the filtrate was dried under vacuum. The residue was purified by column chromatography on silica gel (15 x 4 cm column, 9:1 dichloromethane/methanol), collecting the first orange-brown band. Removal of the solvent under vacuum gave a brown solid (0.083 g), which was not purified further.

IR (cm$^{-1}$): 2928 (br, m), 2860 (br, w), 1724 (m), 1609 (s), 1529 (m), 1508 (m), 1477 (s), 1448 (s), 1380 (s), 1333 (s), 1202 (m), 1176 (s), 1158 (w), 1118 (m), 994 (m), 968 (m), 860 (s), 743 (s), 687 (s), 605 (m), 559 (s), 526 (m), 488 (w), 473 (w).

ESI-MS m/z: (M – X – X'), calcd for $C_{23}H_{22}MnN_6O_2$, 469.1179; found, 469.1164 (100%, z = +1).

UV-vis ($CH_3OH$) $\lambda_{max}$, nm ($\epsilon$, L mol$^{-1}$ cm$^{-1}$): 220 (31,300), 246 (sh, 20,100), 274 (sh, 14,600), 296 (13,600), 319 (14,400), 382 (12,900), 393 (13,200), 485 (sh, 1,300).
3.4.6 Synthesis of Fe\textsuperscript{III}(L\textsubscript{m})Cl

Anhydrous iron(III) chloride (0.0623 g, 0.384 mmol) and (5\textit{E},18\textit{a}E)-8,12,16-tetramethyl-8,10,14,16-tetrahydro-11\textit{H}-benzo[\textit{e}]dipyrido[3,4-\textit{b}:4',3'-\textit{h}][1,4,7,10]tetraazacyclotridecine-11,13(12\textit{H})-dione (H\textsubscript{2}L\textsubscript{m}) (0.114 g, 0.274 mmol) were added to dry thoroughly freeze-pump-thaw degassed methanol (25 mL) in a Schlenk tube. The solution was stirred for 5 minutes at room temperature and then sodium acetate (0.113 g, 1.38 mmol) was added and the mixture was again freeze-pump-thaw degassed. The Schlenk tube was sealed under vacuum and was heated to 60 °C. After 25 hours at 60 °C, once the reaction had reached completion by TLC (alumina), the solution was cooled to room temperature and exposed to air. Methanol (150 mL) was added and the solution was filtered to remove undissolved solids. Sodium chloride (0.750 g, 12.8 mmol) was added and the solution was stirred in air at room temperature for 2 hours. The solvent was removed under vacuum and the brown solid was purified by column chromatography on neutral alumina (15 x 4.5 cm column, 19:1 dichloromethane/methanol), collecting the orange-brown band. Upon evaporation of the solvent under reduced pressure, the pure Fe\textsuperscript{III}(L\textsubscript{m})Cl complex crystallised from solution (yield: 0.080 g, 58%).

IR (cm\textsuperscript{-1}): 2936 (br, w), 1719 (w), 1603 (s), 1528 (m), 1473 (s), 1449 (m), 1382 (s), 1339 (s), 1287 (m), 1260 (w), 1204 (w), 1177 (m), 1120 (m), 997 (m), 968 (m), 857 (s), 788 (m), 740 (s), 691 (s), 613 (w), 562 (m), 526 (w), 492 (w), 473 (w).

ESI-MS m/z: (M – Cl\textsuperscript{-}), calcd for C\textsubscript{23}H\textsubscript{22}FeN\textsubscript{6}O\textsubscript{2}, 470.1148; found, 470.1143 (100%, z = +1).

UV-vis (CH\textsubscript{3}OH) $\lambda_{\text{max}}$, nm (\(\varepsilon\), L mol\textsuperscript{-1} cm\textsuperscript{-1}): 221 (35,400), 250 (sh, 22,600), 314 (23,000), 358 (sh, 17,500), 435 (sh, 6,200).

Anal. Calcd for C\textsubscript{23}H\textsubscript{22}ClFeN\textsubscript{6}O\textsubscript{2}·H\textsubscript{2}O: C, 52.74; H, 4.62; N, 16.05. Found: C, 52.74; H, 4.41; N, 15.89.
3.4.7 Synthesis of Co\textsuperscript{III}(L\textsubscript{m})Br

![Figure 3.23: Chemical structure of Co\textsuperscript{III}(L\textsubscript{m})Br](image)

Anhydrous cobalt(II) bromide (0.0799 g, 0.365 mmol) and \((5E,18aE)-8,12,12,16\)-tetramethyl-8,10,14,16-tetrahydro-11\texttextit{H}-benzo[\texttextit{e}]dipyrido[3,4-\texttextit{b}:4',3'-\texttextit{h}][1,4,7,10]tetraazacyclotridecine-11,13(12\texttextit{H})-dione (H\texttextsubscript{2}L\textsubscript{m}) (0.109 g, 0.261 mmol) were added to dry thoroughly freeze-pump-thaw degassed methanol (25 mL) in a Schlenk tube. The solution was stirred for 5 minutes at room temperature and the sodium acetate (0.107 g, 1.30 mmol) was added and the solution was again freeze-pump-thaw degassed. The Schlenk tube was sealed under vacuum and was heated to 60 °C. After 26 hours at 60 °C, once the reaction had reached completion by TLC (alumina), the solution was cooled to room temperature and was then stirred in air for 45 minutes. Methanol (100 mL) was added and the solution was stirred in air at room temperature for 15 minutes. The solution was filtered to remove undissolved solids and was washed with methanol (250 mL). Sodium bromide (1.50 g, 14.6 mmol) was added and the solution was stirred in air at room temperature for 2 hours. The solution was filtered to remove undissolved solids and was washed with methanol (100 mL). The solvent was removed under vacuum and the brown solid was purified by column chromatography on neutral alumina (15 x 4.5 cm column, 19:1 to 9:1 dichloromethane/methanol), collecting the yellow-brown band. Upon evaporation of the solvent under reduced pressure, a pure sample of Co\textsuperscript{III}(L\textsubscript{m})Br crystallised from solution as a brown solid (yield: 0.077 g, 53%).

IR (cm\textsuperscript{-1}): 2927 (br, m), 1724 (m), 1599 (s), 1529 (m), 1500 (w), 1474 (m), 1448 (m), 1385 (s), 1334 (s), 1283 (s), 1206 (m), 1173 (m), 1154 (w), 1117 (m), 965 (m), 907 (w), 859 (m), 831 (w), 782 (s), 735 (s), 692 (m), 612 (m), 560 (m), 527 (w), 491 (w), 408 (w).

ESI-MS m/z: (M – Cl\textsuperscript{-}), calcd for C\textsubscript{23}H\textsubscript{22}CoN\textsubscript{6}O\textsubscript{2}, 473.1131; found, 473.1130 (100%, \(z = +1\)).

UV-vis (CH\textsubscript{3}OH) \(\lambda_{\text{max}}, \) nm (\(\varepsilon, \) L mol\textsuperscript{-1} cm\textsuperscript{-1}): 223 (30,600), 257 (sh, 14,000), 297 (sh, 7,900), 378 (15,100), 395 (15,200), 420 (14,100), 444 (sh, 10,300).

3.4.8 Synthesis of Ni$^{II}$(L$_m$)

![Figure 3.24: Chemical structure of Ni$^{II}$(L$_m$)](image)

Ni(OAc)$_2$.4H$_2$O (0.0546 g, 0.219 mmol) was added to a suspension of (5E,18aE)-8,12,12,16-tetramethyl-8,10,14,16-tetrahydro-11H-benzo[e]dipyrido[3,4-b:4’,3”-h][1,4,7,10]tetraazacyclotridecine-11,13(12H)-dione (H$_2$L$_m$) (0.0762 g, 0.183 mmol) in methanol (12.5 mL). Sodium acetate (0.0750 g, 0.914 mmol) was added and the yellow-orange suspension was heated to reflux. After 20 hours under reflux, the solution was cooled to room temperature. The orange precipitate was collected by filtration and was washed with methanol (7.5 mL). The solid was purified by column chromatography on silica gel (14 x 2 cm column, 9:1 dichloromethane/methanol), collecting the orange band. Upon evaporating the solvent under reduced pressure, the pure Ni$^{II}$(L$_m$) complex precipitated as an orange solid (yield: 0.0605 g, 70%).

$^1$H NMR (400 MHz, DMSO-$d_6$, $\delta$): 9.19 (d, $J = 2.0$ Hz, 2H, CH), 7.65 (dd, $J_1 = 7.2$ Hz, $J_2 = 2.0$ Hz, 2H, CH), 7.57-7.60 (m, 2H, phenyl CH), 7.31 (d, $J = 7.2$ Hz, 2H, CH), 6.85-6.87 (m, 2H, phenyl CH), 3.81 (s, 6H, N-CH$_3$), 1.42 (s, 6H, C-CH$_3$).

$^{13}$C NMR (100.6 MHz, DMSO-$d_6$, $\delta$): 179.4 (C=O), 152.4 (pyridinium C=NR), 144.5 (phenyl C), 144.4 (pyridinium C-NR), 135.7 (pyridinium CH), 129.5 (pyridinium CH), 120.9 (phenyl CH), 117.0 (phenyl CH), 105.2 (pyridinium CH), 54.3 (C-CH$_3$), 44.3 (N-CH$_3$), 28.4 (C-CH$_3$).

IR (cm$^{-1}$): 3461 (br, s), 3142 (w), 2939 (w), 2869 (w), 2717 (w), 1613 (s), 1593 (s), 1510 (s), 1474 (m), 1447 (m), 1386 (m), 1357 (w), 1305 (m), 1258 (m), 1203 (w), 1176 (m), 1138 (w),
1050 (w), 1006 (m), 968 (w), 909 (w), 863 (m), 767 (m), 728 (s), 694 (s), 614 (m), 556 (m), 526 (w), 503 (w), 447 (w).

ESI-MS m/z: (M + H\(^{+}\)), calcd for C\(_{23}\)H\(_{23}\)N\(_{6}\)NiO\(_{2}\), 473.1230; found, 473.1239 (42%, z = +1). (M + Na\(^{+}\)), calcd for C\(_{23}\)H\(_{22}\)N\(_{6}\)NaNiO\(_{2}\), 495.1050; found, 495.1061 (100%, z = +1). (M + K\(^{+}\)), calcd for C\(_{23}\)H\(_{22}\)KN\(_{6}\)NiO\(_{2}\), 511.0789; found, 511.0804 (13%, z = +1).

UV-vis (CH\(_{2}\)Cl\(_{2}\)) \(\lambda_{\text{max}}\), nm (\(\varepsilon\)), L mol\(^{-1}\) cm\(^{-1}\)): 269 (27,200), 300 (sh, 12,700), 338 (18,300), 400 (32,500), 426 (34,200), 450 (sh, 24,000).

Anal. Calcd for C\(_{23}\)H\(_{22}\)N\(_{6}\)NiO\(_{2}\)·H\(_{2}\)O: C, 56.24; H, 4.93; N, 17.11. Found: C, 56.73; H, 4.78; N, 17.42.

### 3.4.9 Synthesis of Cu\textsuperscript{III}(L\textsubscript{m})(OH)(H\(_{2}\)O)

![Chemical structure of Cu\textsuperscript{III}(L\textsubscript{m})(OH)(H\(_{2}\)O)](image)

**Figure 3.25: Chemical structure of Cu\textsuperscript{III}(L\textsubscript{m})(OH)(H\(_{2}\)O)**

Copper(II) chloride (0.0411 g, 0.306 mmol) was added to a suspension of (5\textit{E},18\textit{aE})-8,12,12,16-tetramethyl-8,10,14,16-tetrahydro-11\textit{H}-benzo[\textit{e}]dipyrido[3,4-\textit{b}:4'\textit{,3'-\textit{h}]1,4,7,10\textit{tetraazacyclotridecine-11,13(12\textit{H})-dione (H\(_{2}\)L\textsubscript{m}) (0.106 g, 0.255 mmol) in methanol (40 mL). Sodium acetate (0.104 g, 1.27 mmol) was then added and the orange-brown suspension was stirred at room temperature for 26 hours. The red-orange precipitate was collected by filtration and was washed with methanol (9 mL). The solid was purified by column chromatography on silica gel (18 x 5 cm column, 9:1 dichloromethane/methanol), collecting the red-orange band. The solvent was then evaporated under reduced pressure and pure Cu\textsuperscript{III}(L\textsubscript{m})(OH)(H\(_{2}\)O) precipitated from solution as a red-orange solid (yield: 0.102 g, 78%). As discussed further in Section 3.2.4, this complex appears to have a structure of Cu\textsuperscript{III}(L\textsubscript{m})(OH)(H\(_{2}\)O) in solution and Cu\textsuperscript{III}(L\textsubscript{m})(OH) in the solid state, although a formulation of Cu\textsuperscript{II}(L\textsubscript{m})(H\(_{2}\)O) has not been ruled out. Hence, the
characterisation data below is quoted for the former complex in solution (ESI-MS and UV-vis results) and the latter complex in the solid state (IR and elemental analysis).

IR (cm\(^{-1}\)): 3435 (br, w), 2937 (br, m), 1616 (m), 1589 (s), 1517 (s), 1474 (m), 1451 (m), 1386 (s), 1343 (m), 1304 (s), 1255 (w), 1189 (s), 1162 (w), 1131 (w), 955 (m), 899 (w), 855 (m), 792 (m), 733 (s), 683 (s), 604 (w), 560 (m), 527 (m), 502 (w), 466 (w).

ESI-MS \( m/z \): (M – OH – H\(_2\)O), calcd for C\(_{23}\)H\(_{22}\)CuN\(_6\)O\(_2\), 477.1095; found, 477.1110 (100%, \( z = +1 \)).

UV-vis (CH\(_2\)Cl\(_2\)) \( \lambda_{max} \), nm (\( \epsilon, \text{ L mol}^{-1} \text{ cm}^{-1} \)): 279 (23,500), 358 (46,400), 392 (36,100), 409 (sh, 34,700).

Anal. Calcd for C\(_{23}\)H\(_{23}\)CuN\(_6\)O\(_3\): C, 55.81; H, 4.68; N, 16.98. Found: C, 55.98; H, 4.74; N, 16.77.

3.4.10 Synthesis of [Ru\(^{III}\)(L\(_m\))\(_2\)][BF\(_4\)]\(_2\)

![Figure 3.26: Chemical structure of [Rh\(^{III}\)(L\(_m\))\(_2\)][BF\(_4\)]\(_2\). The ruthenium-ruthenium bond has been lengthened considerably in this figure to clearly show the two ligands](image)

RuCl\(_3\).3H\(_2\)O (0.147 g, 0.562 mmol) was added to a suspension of (5E,18aE)-8,12,12-tetramethyl-8,10,14,16-tetrahydro-11H-benzo[e]dipyrido[3,4-b:4',3'-h][1,4,7,10]tetraazacyclotridecine-11,13(12\(H\))-dione (H\(_2\)L\(_m\)) (0.147 g, 0.353 mmol) in 2-methoxyethanol (50 mL). Sodium carbonate (0.187 g, 1.76 mmol) was added and the brown solution was heated under reflux for 18 hours. The solution was cooled to room temperature and filtered. The filtrate was
dried under vacuum at 100 °C for five hours. After cooling to room temperature, deionised water (175 mL) was added. The solution was stirred for 15 minutes and was then filtered to remove undissolved solids and the solid was washed with deionised water (150 mL). Sodium tetrafluoroborate (0.969 g, 8.83 mmol, dissolved in 20 mL deionised water) was added and the solution was stirred for one hour at room temperature. The product was extracted with dichloromethane (5 x 200 mL) and the combined dichloromethane extracts were filtered through filter paper. The solvent was removed under vacuum and the dark brown residue was purified by column chromatography (alumina, 39:1 to 19:1 dichloromethane/methanol) and the purple-brown band was collected. The pure [Ru^{III}(L_m)]_2[BF_4]_2 complex precipitated as a dark purple-brown solid upon evaporation of the solvent under reduced pressure, and was collected by filtration (yield: 0.125 g, 59%).

^1^H NMR (500 MHz, DMSO-d_6, δ): 9.02 (d, J = 0.9 Hz, 4H, pyridinium CH), 8.26 (dd, J_1 = 6.9 Hz, J_2 = 0.9 Hz, 4H, pyridinium CH), 8.16 (d, J = 6.9 Hz, 4H, pyridinium CH), 7.84-7.85 (m, 4H, phenyl CH), 7.11-7.13 (m, 4H, phenyl CH), 4.14 (s, 12H, N-CH_3), 1.32 (s, 6H, C-CH_3), 1.24 (s, 6H, C-CH_3).

^1^3^C NMR (125.7 MHz, DMSO-d_6, δ): 181.1 (C=O), 153.2 (pyridinium C=NR), 146.0 (phenyl C), 143.9 (pyridinium C-NC(O)R), 138.6 (pyridinium CH), 136.8 (pyridinium CH), 124.0 (phenyl CH), 119.3 (phenyl CH), 110.2 (pyridinium CH), 55.1 (C-CH_3), 45.8 (N-CH_3), 29.7 (C-CH_3), 25.3 (C-CH_3).

IR (cm⁻¹): 3364 (br, s), 2962 (m), 2034 (w), 1911 (br, w), 1609 (s), 1543 (m), 1489 (s), 1449 (s), 1382 (w), 1360 (w), 1316 (m), 1280 (s), 1259 (m), 1210 (w), 1174 (m), 1090 (s), 1019 (s), 965 (w), 867 (m), 796 (s), 746 (m), 689 (w), 617 (w), 570 (w), 524 (w), 503 (w).

ESI-MS m/z: (M^2+), calcd for C_{46}H_{44}N_{12}O_{14}Ru_2, 516.0844; found, 516.0884 (100%, z = +2).

UV-vis (CH_3OH) λ_{max}, nm (ε, L mol⁻¹ cm⁻¹): 218 (37,200), 254 (sh, 21,900), 319 (23,400), 364 (sh, 16,100), 463 (7,700), 539 (sh, 4,600).

Anal. Calcd for C_{46}H_{44}B_{2}F_{8}N_{12}O_{14}Ru_2: C, 45.86; H, 3.68; N, 13.95. Found: C, 45.62; H, 3.72; N, 13.82.
3.4.11 Synthesis of Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}Cl]

Figure 3.27: Chemical structure of Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}Cl]. The rhodium-rhodium and rhodium-chlorine bonds have been lengthened considerably in this figure to show the L\textsubscript{m} ligands more clearly.

RhCl\textsubscript{3}·xH\textsubscript{2}O (0.281 g, 1.07 mmol, assuming x = 3) was added to a suspension of (5E,18aE)-8,12,12,16-tetramethyl-8,10,14,16-tetrahydro-11\textit{H}-benzo[e]dipyrido[3,4-\textit{b}:4',3'-\textit{h}][1,4,7,10]-tetraazacyclotridecine-11,13(12\textit{H})-dione (H\textsubscript{2}L\textsubscript{m}) (0.296 g, 0.711 mmol) in methanol (50 mL). Sodium acetate (0.292 g, 3.56 mmol) was then added and the brown suspension was heated to reflux. After 6 hours under reflux, the solution was cooled to room temperature. The orange precipitate was collected by filtration and was washed with ice-cold methanol (30 mL). Yield: 0.177 g (47%).

Note that \textsuperscript{13}C NMR signals are not listed in the characterisation data below, because Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}Cl] has a very low solubility (less than 0.2 mg mL\textsuperscript{-1}) in methanol-\textit{d}\textsubscript{4} and decomposes slowly in solution over long scan times. \textsuperscript{1}H NMR coupling constants are not given below due to the significant overlapping of signals in the aromatic region and low signal-to-noise ratios. The term \textit{d\textsubscript{fine}} denotes a finely-coupled (<2 Hz) doublet signal.

\textsuperscript{1}H NMR (500 MHz, methanol-\textit{d}_{4}, \delta): 9.40 (d\textsubscript{fine}, 1H), 9.25 (d\textsubscript{fine}, 1H), 7.59 (dd, 1H), 7.49 (dd, 1H), 7.47 (dd, 1H), 7.37 (d, 1H), 7.36 (d, 1H), 7.34 (d, 1H), 7.33 (d, 1H), 7.32 (dd, 1H), 7.27 (d,
1H), 7.26 (d, 2H), 7.24 (d<sub>fine</sub>, 1H), 7.20 (d, 1H), 6.93 (t, 1H), 6.88 (t, 1H), 6.76 (d<sub>fine</sub>, 1H), 6.74 (t, 1H), 6.64 (t, 1H), 3.97 (s, 3H), 3.91 (s, 3H), 3.77 (s, 3H), 3.55 (s, 3H), 1.67 (s, 3H), 1.60 (s, 3H), 1.19 (s, 3H), 0.88 (s, 3H).

IR (cm<sup>-1</sup>): 3466 (br, m), 2935 (w), 1707 (w), 1667 (m), 1625 (m), 1611 (m), 1577 (s), 1473 (w), 1462 (w), 1431 (m), 1375 (s), 1336 (m), 1268 (w), 1246 (m), 1193 (s), 1173 (s), 1035 (m), 1001 (m), 844 (s), 785 (s), 754 (m), 737 (s), 695 (m), 681 (s), 614 (m), 512 (s), 470 (m).

UV-vis (CH<sub>3</sub>OH) λ<sub>max</sub>, nm (ε<sub>cm</sub>-1: 213 (89,900), 258 (sh, 46,800), 336 (sh, 27,600), 421 (52,600), 464 (sh, 27,100).

ESI-MS m/z (positive ion mode): (M<sup>-</sup> – Cl<sup>-</sup> + H<sup>+</sup>) calcd for C<sub>46</sub>H<sub>45</sub>N<sub>12</sub>O<sub>4</sub>Rh<sub>2</sub>, 1035.1791; found, 1035.1815 (100%, z = +1). ([Rh<sup>III</sup>(L<sub>m</sub>)<sup>+</sup>]<sup>+</sup>) calcd for C<sub>23</sub>H<sub>22</sub>N<sub>6</sub>O<sub>2</sub>Rh, 517.0854; found, 517.0867 (85%, z = +1).

ESI-MS m/z (negative ion mode): (M<sup>-</sup> + Cl<sup>-</sup> + H<sup>+</sup>) calcd for C<sub>46</sub>H<sub>46</sub>Cl<sub>2</sub>N<sub>12</sub>O<sub>4</sub>Rh<sub>2</sub>, 1105.1179; found, 1105.1168 (100%, z = -1). (M<sup>-</sup> + HCOO<sup>-</sup> + H<sup>+</sup>) calcd for C<sub>47</sub>H<sub>46</sub>ClN<sub>12</sub>O<sub>5</sub>Rh<sub>2</sub>, 1115.1462; found, 1115.1459 (85%, z = -1). (M<sup>-</sup>) calcd for C<sub>46</sub>H<sub>46</sub>ClN<sub>12</sub>O<sub>4</sub>Rh<sub>2</sub>, 1069.1413; found, 1069.1395 (50%, z = -1). (M<sup>-</sup> – Cl<sup>-</sup> + 2HCOO<sup>-</sup> + H<sup>+</sup>) calcd for C<sub>48</sub>H<sub>47</sub>N<sub>12</sub>O<sub>5</sub>Rh<sub>2</sub>, 1125.1755; found, 1125.1728 (30%, z = -1). (M<sup>-</sup> + CH<sub>3</sub>OH) calcd for C<sub>47</sub>H<sub>48</sub>ClN<sub>12</sub>O<sub>5</sub>Rh<sub>2</sub>, 1101.1669; found, 1101.1638 (20%, z = -1). (M<sup>-</sup> – Cl<sup>-</sup> + HCOO<sup>-</sup>) calcd for C<sub>47</sub>H<sub>45</sub>N<sub>12</sub>O<sub>6</sub>Rh<sub>2</sub>, 1079.1701; found, 1079.1658 (15%, z = -1).


### 3.4.12 Synthesis of Pd<sup>II</sup>(L<sub>m</sub>)

![Figure 3.28: Chemical structure of Pd<sup>II</sup>(L<sub>m</sub>)](image-url)

Figure 3.28: Chemical structure of Pd<sup>II</sup>(L<sub>m</sub>)
Palladium(II) acetate (0.103 g, 0.459 mmol) was added to a suspension of (5E,18aE)-8,12,16-tetramethyl-10,14,16-tetrahydro-11H-benzo[e]dipyrido[3,4-b:4',3'-h][1,4,7,10]tetraazacyclotridecine-11,13(12H)-dione (H2Lm) (0.144 g, 0.346 mmol) in methanol (40 mL). Sodium acetate (0.142 g, 1.73 mmol) was added and the green suspension was heated to reflux. After 28 hours under reflux, the solution was cooled to room temperature and the green precipitate was collected by filtration and washed with methanol (3 mL). The solid was purified by column chromatography on silica gel (16 x 5 cm column, 9:1 dichloromethane/methanol), collecting the bright yellow band. Upon evaporation of the solvent under reduced pressure, the yellow PdII(Lm) complex precipitated from solution and was collected by filtration (yield: 0.143 g, 79%).

1H NMR (400 MHz, DMSO-d6, δ): 9.01 (d, J = 2.0 Hz, 2H, CH), 7.71 (dd, J1 = 7.6 Hz, J2 = 2.0 Hz, 2H, CH), 7.64-7.66 (m, 2H, phenyl CH), 7.34 (d, J = 7.6 Hz, 2H, CH), 6.94-6.96 (m, 2H, phenyl CH), 3.84 (s, 6H, N-CH3), 1.47 (s, 6H, C-CH3).

13C NMR (100.6 MHz, DMSO-d6, δ): 178.4 (C=O), 152.5 (pyridinium C=NR), 145.3 (phenyl C), 145.2 (pyridinium C-NR), 135.9 (pyridinium CH), 130.9 (pyridinium CH), 121.5 (phenyl CH), 119.0 (phenyl CH), 106.6 (pyridinium CH), 59.1 (C-CH3), 44.2 (N-CH3), 28.6 (C-CH3).

IR (cm⁻¹): 3429 (br, s), 2938 (br, w), 1612 (m), 1584 (m), 1506 (s), 1466 (s), 1436 (s), 1376 (s), 1341 (m), 1299 (m), 1254 (w), 1180 (s), 1049 (w), 1006 (m), 959 (m), 895 (w), 865 (w), 770 (m), 734 (m), 686 (s), 610 (m), 553 (m), 518 (w), 495 (w).

ESI-MS m/z: (M + H⁺), calcd for C23H23N6O2Pd, 521.0921; found, 521.0918 (z = +1, 35%). (M + Na⁺), calcd for C23H22N6NaO2Pd, 543.0731; found, 543.0752 (z = +1, 100%).

UV-vis (CH2Cl2) λmax, nm (ε, L mol⁻¹ cm⁻¹): 259 (26,600), 318 (13,000), 359 (sh, 18,600), 382 (27,000), 395 (30,300), 425 (39,300), 449 (33,700).

Anal. Calcd for C23H22N6O2Pd·0.5H2O: C, 52.16; H, 4.38; Cl, 3.14; N, 15.86. Found: C, 52.16; H, 4.47; Cl, 3.05; N, 15.79.
Chapter 4: Oxidation of Dye Substrates by Hydrogen Peroxide, Catalysed by the New Metal-Pyridinium Amide Complexes

4.1 Introduction

This chapter describes investigations into the oxidation of dye substrates by hydrogen peroxide, catalysed by the iron (Fe\textsuperscript{III}(L\textsubscript{m})Cl) and cobalt (Co\textsuperscript{III}(L\textsubscript{m})Br) complexes of the new macrocyclic pyridinium amide ligand (L\textsubscript{m}). Comparisons are made between these reactions and Fe(III)-TAML and Co(III)-TAML catalysed oxidations under similar conditions. As described in more detail in Section 1.6.3, Fe(III)-TAML and Co(III)-TAML complexes are highly efficient catalysts for the selective oxidation of a diverse range of substrates by hydrogen peroxide.\textsuperscript{93,107-116} Their effectiveness as oxidation catalysts stems in part from: 1) the strongly donating TAML ligand, which enables the formation of highly reactive Fe(V)-oxo active catalyst species and 2) the resilience of the TAML ligand to oxidative degradation by the active catalyst species.\textsuperscript{17,105} Because the L\textsubscript{m} ligand is also expected to act as a strong donor to metal centres, and because the Fe\textsuperscript{III}(L\textsubscript{m})Cl and Co\textsuperscript{III}(L\textsubscript{m})Br complexes are similar in structure to the [NEt\textsubscript{4}][Fe\textsuperscript{III}(B*)(H\textsubscript{2}O)] and [NEt\textsubscript{4}][Co\textsuperscript{III}(B*)] TAML complexes, it was anticipated that the Fe\textsuperscript{III}(L\textsubscript{m})Cl and Co\textsuperscript{III}(L\textsubscript{m})Br complexes may also be effective catalysts for the oxidation of dye substrates by hydrogen peroxide. Little is known about the oxidative resistances of pyridinium amide functional groups. Studying the behaviour of the Fe\textsuperscript{III}(L\textsubscript{m})Cl and Co\textsuperscript{III}(L\textsubscript{m})Br complexes as oxidation catalysts may therefore also aid in understanding the oxidative resistance of pyridinium amide functional groups.

When designing catalysts for substrate oxidations with hydrogen peroxide, it is desirable to maximise the peroxidase-like activity (where the catalyst activates hydrogen peroxide to form high oxidation state metal-oxo complexes, which then oxidise the substrate catalytically), and to minimise both hydrogen peroxide disproportionation and Fenton-like chemistry. The latter two processes waste hydrogen peroxide by converting it to dioxygen and water (in the hydrogen peroxide disproportionation reaction), or to highly reactive but unselective hydroxyl radicals (in Fenton-like reactions). In contrast, the activation of hydrogen peroxide via peroxidase-like activity leads to the efficient and selective oxidation of substrates. Section 1.6.2.5 describes
these processes in more detail.\cite{17,105} Fe(III)-TAML and Co(III)-TAMLs have indeed been shown to behave as excellent peroxidase-like catalysts with minimal hydrogen peroxide disproportionation. Furthermore, the formation of hydroxyl radicals via Fenton-like chemistry has not been observed in these systems.\cite{80,93,96}

The remainder of this introduction section discusses some of the key results for the Fe(III)-TAML- and Co(III)-TAML-catalysed oxidation of dye substrates by hydrogen peroxide. Following this introduction section, the results for the Fe\textsuperscript{III}(L\textsubscript{m})Cl- and Co\textsuperscript{III}(L\textsubscript{m})Br-catalysed oxidation of dye substrates with hydrogen peroxide are described and discussed in Sections 4.2 and 4.3, and these results are compared to Fe(III)-TAML- and Co(III)-TAML-catalysed dye oxidation studies.

### 4.1.1 Oxidation of dye substrates with hydrogen peroxide, catalysed by Fe(III)-TAMLs

Fe(III)-TAMLs have been extensively studied as catalysts for substrate oxidations with hydrogen peroxide.\cite{93,96,107-116} The most commonly studied substrates are water-soluble organic dyes, such as Orange II, Safranine O, and Pinacyanol chloride (see Figure 1.28 for the structures of these dyes). These dyes are convenient for studying the kinetics and mechanisms of Fe(III)-TAML-catalysed substrate oxidations by hydrogen peroxide, because they are oxidised to colourless products. Substrate oxidation can therefore be monitored using UV-visible absorption spectroscopy, by measuring the absorbance at $\lambda_{\text{max}}$ in the visible region as a function of time. The initial rate method is then used to determine the initial rate of dye oxidation. In this method, the slope of the line for the first 10% of the decrease in the absorbance versus time plots is divided by the molar absorptivity of the dye at $\lambda_{\text{max}}$. Thus, initial rates are obtained in units of mol L\textsuperscript{-1} s\textsuperscript{-1} and are the average of at least three concordant runs.\cite{93,96} The absorbance versus time plots are interpreted using the initial rate method because the dye concentration has not changed significantly compared to the initial dye concentration. Moreover, the initial part of the absorbance versus time plot is easier to interpret because it is approximately linear, and there is minimal interference by the colourless dye oxidation products, which may undergo further oxidation or coordination to the catalyst.\cite{93}
Changes to the initial rate of dye oxidation with changing reagent concentrations, solution pH, temperature, the particular Fe(III)-TAML catalyst used, the dye employed, and the types and concentrations of the buffers have been used to deduce the catalytic properties for the Fe(III)-TAML-catalysed oxidation of dye substrates with hydrogen peroxide. Some of the key results of these studies are summarised in this section.

4.1.1.1 Experimental conditions

Dye oxidation experiments with Fe(III)-TAMLs are usually conducted by dissolving a known concentration of the dye and a known concentration of the Fe(III)-TAML in a buffered aqueous solution inside a cuvette. The cuvette is then placed inside a temperature-controlled cell holder. After equilibration of the solution temperature, an aliquot of hydrogen peroxide with a known concentration is added, and the absorbance is monitored as a function of time. The initial rate method described above is then used to calculate the initial rate of dye oxidation. The dye is usually added to the solution prior to the addition of hydrogen peroxide, because Fe(III)-TAMLs are known to catalyse hydrogen peroxide disproportionation in the absence of substrates and also decompose slowly in the absence of substrates. However, in the presence of suitable dye substrates, hydrogen peroxide disproportionation is minimal compared to the peroxidase-like activity, and the dye is oxidised in preference to oxidative destruction of the catalyst. Depending on the pH of the solution, either phosphate or carbonate buffers are used because these are not expected to interfere significantly with the catalyst via coordination to the metal centre. Buffer concentrations of 0.01 to 0.1 mol L\(^{-1}\) are usually chosen. These buffer concentrations are high enough that they buffer the solution effectively (and therefore are significantly higher than the concentration of the reagents), but are not so high that they interfere significantly with the performance of the catalyst. Dye concentrations of around 5-100 \(\mu\)mol L\(^{-1}\) are used so that the initial absorbances are between about 0.1 and 2. Low catalyst concentrations (usually 0.1-5 \(\mu\)mol L\(^{-1}\)) are commonly used to minimise intermolecular catalyst decomposition. To ensure that catalytic amounts of the Fe(III)-TAML complex are used, the dye concentration is always greater than the catalyst concentration. A large excess of hydrogen peroxide is used (normally about 0.1 to 10 mmol L\(^{-1}\)) so that appreciable turnover rates are obtained, and so that the concentration of hydrogen peroxide effectively remains constant during the reaction. Blank experiments are run under the same conditions but without the addition of a Fe(III)-TAML, because hydrogen peroxide itself will very slowly oxidise the dye.
4.1.1.2 Changes in the initial rate of dye oxidation with changing pH

The initial rate of dye oxidation for Fe(III)-TAMLs is highly pH-dependent. Bell-shaped curves are typically observed when the initial rate of dye oxidation is plotted as a function of pH. The maximum initial rate of dye oxidation usually occurs somewhere between pH 9 and 10.5, and this value depends on the particular Fe(III)-TAML catalyst used. Basic conditions are therefore required for optimum rates of catalytic oxidation. Fe(III)-TAMLs decompose in acidic solutions, although for later generations of TAML ligands (see Figure 1.27), this decomposition is very slow under mildly acidic conditions.

4.1.1.3 Approximate values for the initial rate of dye oxidation, compared to blank samples

Orange II is the most common dye used to study the behaviour of Fe(III)-TAMLs as catalysts for oxidations with hydrogen peroxide. Orange II is reasonably easy to oxidise by activated Fe(III)-TAMLs, and kinetic data from these experiments are usually relatively easy to interpret. This is partly due to the clean oxidation of Orange II to colourless products. On the other hand, the reaction kinetics for the Fe(III)-TAML-catalysed oxidation of many other easily-oxidised dye substrates (such as Pinacyanol chloride) are more complex and are harder to interpret. Spectroscopic and computational studies suggest that this is due to the coordination of Pinacyanol chloride and its decomposition products to the Fe(III)-TAML metal centre. In contrast, spectroscopic and computational studies suggest that the coordination of Orange II and its decomposition products to Fe(III)-TAMLs is negligible. Another advantage of Orange II is that the wavelength and molar absorptivity at $\lambda_{\text{max}}$ in the visible region changes only slightly over a wide pH range.

The initial rates of Orange II oxidation have been reported for the Li[Fe$^{\text{III}}$](B*)(H$_2$O)], Li[Fe$^{\text{III}}$(BF$_2$)(H$_2$O)] and Na[Fe$^{\text{III}}$(D*(NO$_2$)$_2$)(H$_2$O)] catalyst systems under a variety of conditions (see Figure 1.27 for the structures of these TAML ligands). For example, at 25 °C, 1 mmol L$^{-1}$ hydrogen peroxide, 45 µmol L$^{-1}$ Orange II, and 0.25 µmol L$^{-1}$ catalyst, the initial rate of dye oxidation was approximately $1.0 \times 10^{-7}$ mol L$^{-1}$ s$^{-1}$ for Li[Fe$^{\text{III}}$(B*)(H$_2$O)] and $1.3 \times 10^{-7}$ mol L$^{-1}$ s$^{-1}$ for Li[Fe$^{\text{III}}$(BF$_2$)(H$_2$O)]. These were measured at pH 11, which is close to the optimum pH of 10.8 and 10.2 for Li[Fe$^{\text{III}}$(B*)(H$_2$O)] and Li[Fe$^{\text{III}}$(BF$_2$)(H$_2$O)], respectively. Dye bleaching is usually complete after about 10 minutes under these conditions. In comparison, under the same concentration and temperature conditions, the initial rate of dye oxidation for
Na[Fe\textsuperscript{III}(D*(NO\textsubscript{2})\textsubscript{2})(H\textsubscript{2}O)] measured at the optimum pH (9.0) was about $2.5 \times 10^{-6}$ mol L\textsuperscript{-1} s\textsuperscript{-1}.\textsuperscript{92} All these initial rate values were obtained in 0.01 mol L\textsuperscript{-1} phosphate buffer solutions.\textsuperscript{92,96} For comparison, the initial rate of dye oxidation was approximately $9.2 \times 10^{-9}$ mol L\textsuperscript{-1} s\textsuperscript{-1} for a blank run under similar conditions (25 °C, 2 mmol L\textsuperscript{-1} hydrogen peroxide and 45 μmol L\textsuperscript{-1} Orange II, in 0.01 mol L\textsuperscript{-1} phosphate buffer at pH 10.4).\textsuperscript{106} Fe(III)-TAMLs therefore catalyse Orange II dye oxidation with hydrogen peroxide several orders of magnitude faster than dye oxidation by hydrogen peroxide on its own. Increasing the temperature increases the initial rate of dye oxidation for both the Fe(III)-catalysed runs and the blank runs.\textsuperscript{80,106,135}

4.1.1.4 Turnover numbers (TONs) and turnover frequencies (TOFs)

Turnover numbers (TONs) for Fe(III)-TAMLs indicate the approximate number of substrate molecules oxidised per Fe(III)-TAML catalyst molecule, before the catalyst becomes inactivated. They have been estimated by continually adding aliquots of the dye to the reaction until dye bleaching no longer reaches completion. The ratio of the total dye concentration to the catalyst concentration at this point provides an estimate of the minimum TON. In calculating the TON, it is assumed that one Fe(III)-TAML molecule oxidises one dye molecule per turnover of the catalyst cycle. These TON estimation experiments are conducted in the presence of a large excess of hydrogen peroxide to ensure that hydrogen peroxide does not become a limiting reagent. TOFs can be determined from the TONs and the rate of dye oxidation. The calculated TON and TOF values for a particular catalyst depend on the reaction conditions, such as the reagent concentrations, the pH, the temperature, and the dye substrate used. For Orange II dye, TONs of at least 3000 have been estimated with Li[Fe\textsuperscript{III}(B*)(H\textsubscript{2}O)] and [NEt\textsubscript{4}]\textsubscript{2}[Fe\textsuperscript{III}(B\textsuperscript{J})Cl] at 25 °C, pH 10.0, and 1 mmol L\textsuperscript{-1} hydrogen peroxide, and TOFs are on the order of thousands per minute. Safranine O dye is more resistant to oxidation by the active iron-TAML complexes than Orange II, and TONs have been estimated to be about 210 for Li[Fe\textsuperscript{III}(B*)(H\textsubscript{2}O)] and 160 for [NEt\textsubscript{4}]\textsubscript{2}[Fe\textsuperscript{III}(B\textsuperscript{J})Cl] at pH 9.0, 40 °C, and 1 mmol L\textsuperscript{-1} hydrogen peroxide. TOFs are on the order of tens per minute under these conditions.\textsuperscript{93,97,135}

4.1.1.5 Kinetics and postulated mechanism of substrate oxidation

Kinetic data obtained from the aforementioned dye oxidation studies have been used to propose a mechanism for the Fe(III)-TAML-catalysed oxidation of dye substrates by hydrogen peroxide
(Figure 4.1). In this model, activation of the resting Fe(III)-TAML catalyst with hydrogen peroxide leads to the formation of an active catalyst, which is probably a Fe(V)(=O)-TAML species (as discussed in further detail in Section 1.6.3.2). The rate for this step has been given the symbol \( k_I \), and the rate for the reverse of this step has been given the symbol \( k_{-I} \). Kinetic studies have shown that the rate of the \( k_I \) step is negligible compared to the \( k_{-I} \) step, and therefore can be effectively ignored in the kinetic analyses. In the next step of the reaction, the active catalyst oxidises the dye substrate, with a rate of \( k_{II} \). The active catalyst can also oxidise itself via intramolecular oxidative degradation, with a rate of \( k_{i} \). Although the active catalyst may also undergo intermolecular oxidative degradation by reacting with another active or resting catalyst molecule, this degradation pathway is minimal under the low catalyst concentrations used in these studies and can effectively be ignored. Medium-induced degradation of the resting catalyst may also occur, but this too is minimal under the experimental conditions.\(^{80,93,96}\)

![Figure 4.1: Proposed mechanism for the oxidation of dye substrates with hydrogen peroxide, catalysed by Fe(III)-TAMLs](image)

Using the proposed mechanism shown in Figure 4.1, the values of \( k_I, k_{II}, \) and \( k_i \) can be calculated by determining the change in the initial rate of dye oxidation with changing reaction conditions (such as substrate concentrations), and by applying rate equations and kinetic models to these data. These methods and the calculated values of \( k_I, k_{II}, \) and \( k_i \) will not be described in this section. However, the key results are that \( k_i \) and \( k_{II} \) can be determined under conditions where \( k_i[H_2O_2] > k_{II}[dye] \) (where \( k_i \) and \( k_{II} \) become rate-determining), whereas \( k_I \) can be determined under conditions where \( k_I[H_2O_2] < k_{II}[dye] \) (where \( k_I \) becomes rate-determining). Because \( k_i[H_2O_2] \) and \( k_{II}[dye] \) are similar in this system, the former occurs when high hydrogen peroxide concentrations and difficult to oxidise dyes (such as Safranine O) are used, whereas the latter occurs when low hydrogen peroxide concentrations and easy to oxidise dyes (such as Orange II and Pinacyanol chloride) are used.\(^{80,93,96}\)
4.1.2 Oxidation of dye substrates with hydrogen peroxide, catalysed by Co(III)-TAMLs

Although Co(III)-TAMLs have been less extensively studied than Fe(III)-TAMLs as catalysts for the oxidation of dye substrates by hydrogen peroxide, they are still effective oxidation catalysts. Results have shown that the initial rate for the [NEt₄][Co^{III}(B¹)]-catalysed oxidation of Orange II dye by hydrogen peroxide is about 10 times greater than the same reaction catalysed by [NEt₄][Fe^{III}(B¹)(Cl)] when the same reaction conditions are used. However, catalyst self-oxidation also seems to be much more prevalent for [NEt₄][Co^{III}(B¹)] than [NEt₄][Fe^{III}(B¹)(Cl)], and so turnover numbers are about 30 times lower for the former complex. For example, using 1 mmol L⁻¹ hydrogen peroxide, 45 µmol L⁻¹ Orange II, and 0.25 µmol L⁻¹ catalyst at 25 °C, the initial rate of dye oxidation was found to be about 1.0 x 10⁻⁷ mol L⁻¹ s⁻¹ for [NEt₄][Fe^{III}(B¹)(Cl)] and about 1.2 x 10⁻⁶ mol L⁻¹ s⁻¹ for [NEt₄][Co^{III}(B¹)]. These were recorded in 0.01 mol L⁻¹ carbonate buffers at the optimum pH values of 9.0 and 10.0, respectively. Under the same conditions, a minimum TON of 2900 was found for [NEt₄][Fe^{III}(B¹)(Cl)] and a minimum TON of 90 was found for [NEt₄][Co^{III}(B¹)]. These TONs were calculated assuming that one M^{III}-TAML molecule oxidises one dye molecule per turnover of the catalyst cycle. The mechanism of Co(III)-TAML-catalysed dye oxidation with hydrogen peroxide is currently under investigation in our laboratory.

4.2 Oxidation of Orange II dye by hydrogen peroxide, catalysed by Fe^{III}(L_m)Cl

4.2.1 Preliminary investigations

Preliminary investigations for the oxidation of dye substrates with hydrogen peroxide, catalysed by the new Fe^{III}(L_m)Cl complex were conducted under similar conditions to those used in the Fe(III)-TAML-catalysed dye oxidation studies (Section 4.1.1). Therefore, using the method described in Sections 4.1.1.1 and 4.5.6, the initial conditions used were: 25 °C, 45 µmol L⁻¹ Orange II dye, 0.25 µmol L⁻¹ Fe^{III}(L_m)Cl, and 1 mmol L⁻¹ hydrogen peroxide. Because the optimum pH was unknown at this stage, experiments were conducted at pH 7.5, 9.0, 10.0, and 10.8. A phosphate buffer (0.01 mol L⁻¹) was used at pH 7.5 and carbonate buffers were used at
pH 9.0, 10.0, and 10.8. Although phosphate buffers are used over this entire pH range in most Fe(III)-TAML dye oxidation studies, a few Fe(III)-TAMLs (for example, [NEt₄]₂[Fe⁺⁺⁺(B⁺)(Cl)] have been investigated using carbonate buffers between pH 9 and 11, and phosphate buffers outside of this range. Blank experiments were also run under the same conditions, in which no catalyst was added to the solution. At each pH value used, the initial rate of dye oxidation for the runs with the Fe³⁺(L₃)Cl complex present were almost identical to the initial rate of dye oxidation for the corresponding blank. This suggests that Fe³⁺(L₃)Cl is not catalysing dye oxidation under these conditions. This contrasts with Fe(III)-TAMLs under the same conditions, where the initial rate of Fe(III)-catalysed dye oxidation is several orders of magnitude greater than the initial rate of dye oxidation for the corresponding blank. Therefore, the Fe³⁺(L₃)Cl concentration was increased significantly to see whether dye oxidation would occur. A Fe³⁺(L₃)Cl concentration of 10 µmol L⁻¹ (about 22 mol%) was selected, which is much higher than the concentration used in the preliminary experiments, but not so high that the concentration of the catalyst is close to or greater than the concentration of the Orange II dye. Thus, if dye oxidation proceeds at a significantly faster rate than the blank reaction under these conditions, it would indicate that the reaction is catalytic.

At each pH value used, the initial rate of dye oxidation in the presence Fe³⁺(L₃)Cl was compared to the initial rate of dye oxidation of the corresponding blank (Table 4.1). At pH 7.5, the initial rate of dye oxidation was about four times greater for the run with Fe³⁺(L₃)Cl present than for the blank. This suggests that under these conditions, dye oxidation is catalytic. Therefore, Fe³⁺(L₃)Cl appears to catalyse peroxidase-like activity at pH 7.5, albeit very slowly. In contrast, for the experiments at pH 9.0, 10.0, and 10.8, the initial rate of dye oxidation with Fe³⁺(L₃)Cl present was actually slightly lower than for the corresponding blank, and the difference became larger with increasing pH. Peroxide test strips were used to check the approximate amount of hydrogen peroxide left once the dye absorbance no longer decreased (that is, once the absorbance versus time curves plateaued). At pH 7.5, about 0.5 mmol L⁻¹ hydrogen peroxide was left, whereas at pH 9.0-10.8, no hydrogen peroxide was left, even though a large excess of hydrogen peroxide was used relative to the amounts of Fe³⁺(L₃)Cl and the dye. For reference, about 0.75-1 mmol L⁻¹ hydrogen peroxide was left for the blank runs at each pH used. Copious dioxygen bubble evolution was also observed for the runs with the catalyst present at pH 9.0-10.8, but not for the corresponding blanks. These results suggest that Fe³⁺(L₃)Cl is catalysing the disproportionation of hydrogen peroxide to water and dioxygen. Assuming that the rate of dye oxidation is proportional to the hydrogen peroxide concentration, the lower initial rate of dye oxidation for the runs with Fe³⁺(L₃)Cl present than for the blank runs is probably due to
Fe\textsuperscript{III}(L\textsubscript{m})Cl-catalysed hydrogen peroxide disproportionation, which causes a rapid decrease in hydrogen peroxide concentration during the reaction.

Table 4.1: Initial rates of Orange II dye oxidation with hydrogen peroxide at 25 °C, catalysed by Fe\textsuperscript{III}(L\textsubscript{m})Cl

<table>
<thead>
<tr>
<th>Conditions</th>
<th>7.5</th>
<th>9.0</th>
<th>10.0</th>
<th>10.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>With Fe\textsuperscript{III}(L\textsubscript{m})Cl present (^b)</td>
<td>4.2 x 10(^{-9})</td>
<td>2.9 x 10(^{-9})</td>
<td>1.9 x 10(^{-9})</td>
<td>1.5 x 10(^{-9}) (^d)</td>
</tr>
<tr>
<td>Blank (^c)</td>
<td>1.1 x 10(^{-9})</td>
<td>4.0 x 10(^{-9})</td>
<td>5.2 x 10(^{-9})</td>
<td>6.1 x 10(^{-9})</td>
</tr>
</tbody>
</table>

\(^a\) Values are the average of at least three concordant runs.

\(^b\) General conditions: 25 °C, 45 \(\mu\)mol L\(^{-1}\) Orange II dye, 10 \(\mu\)mol L\(^{-1}\) Fe\textsuperscript{III}(L\textsubscript{m})Cl, and 1 mmol L\(^{-1}\) hydrogen peroxide in 0.01 mol L\(^{-1}\) carbonate (pH 9.0-10.8 runs) or phosphate (pH 7.5 runs) buffers.

\(^c\) Same as the conditions for point \(^b\), but without any Fe\textsuperscript{III}(L\textsubscript{m})Cl added.

\(^d\) Precipitation of the Fe\textsuperscript{III}(L\textsubscript{m})Cl complex occurs at this pH.

Unlike the experiments at pH 7.5, it is difficult to tell whether any peroxidase-like activity is occurring at pH 9.0-10.8, because any peroxidase-like activity would be masked by the rapid decrease in hydrogen peroxide concentration that is caused by the Fe\textsuperscript{III}(L\textsubscript{m})Cl-catalysed disproportionation of hydrogen peroxide. Dye oxidation by either unactivated hydrogen peroxide on its own, or by Fe\textsuperscript{III}(L\textsubscript{m})Cl-catalysed peroxidase-like activity is expected to decrease in rate with decreasing hydrogen peroxide concentration. This would explain the observation that the initial rate of dye oxidation becomes lower for the runs with Fe\textsuperscript{III}(L\textsubscript{m})Cl present than for the corresponding blanks in the experiments at pH 9.0-10.8. In summary, reduction in the initial rate of dye oxidation suggests that the Fe\textsuperscript{III}(L\textsubscript{m})Cl complex catalyses hydrogen peroxide disproportionation to such a great extent that it dominates any peroxidase-like activity that might occur.

Analysis of the extent of dye oxidation showed that, as expected, dye oxidation reaches completion at pH 7.5, but is incomplete at pH 9.0-10.8. The extent of bleaching also decreased with increasing pH. In contrast, dye oxidation reached completion for each blank. This makes sense, because the increase in hydrogen peroxide disproportionation with increasing pH removes hydrogen peroxide more rapidly from the system, before the active Fe-L\textsubscript{m} catalyst (or unactivated hydrogen peroxide alone) has an opportunity to oxidise the dye substrate. The
Fe$^{III}$(L$_m$)Cl catalyst itself, however, seems to be rather robust, because dye oxidation resumes after the addition of another aliquot of hydrogen peroxide to the reaction, even after the solution has been left overnight at room temperature. The initial rate of dye oxidation following the addition of this second aliquot of hydrogen peroxide is similar to the initial rate of dye oxidation observed after addition of the initial hydrogen peroxide aliquot. This suggests that minimal catalyst inactivation occurs after Fe$^{III}$(L$_m$)Cl sits overnight in solution. With the addition of sequential aliquots of hydrogen peroxide, dye oxidation eventually reaches completion. This also occurs at pH 7.5 if another aliquot of Orange II dye is added, followed by another aliquot of hydrogen peroxide. The system is therefore catalytic, with excess Orange II being oxidised relative to the amount of Fe$^{III}$(L$_m$)Cl (Orange II : Fe$^{III}$(L$_m$)Cl mole ratio >9 : 1 at pH 7.5), at a rate that is significantly faster than the blank. However, the exact ratio of dye oxidised by the catalyst versus that oxidised by unactivated hydrogen peroxide was not determined in these experiments. In contrast to these results, the initial rate of dye oxidation for Fe(III)-TAMLs under similar conditions is several orders of magnitude greater than for the blank, indicating that in these cases, dye oxidation by unactivated hydrogen peroxide alone is negligible compared to peroxidase-like dye oxidation by the activated catalyst.$^{93}$

Minimum turnover numbers (TONs) for Fe(III)-TAMLs are usually estimated by determining the molar ratio of the dye substrate to the catalyst at the point where dye bleaching just becomes incomplete (see Section 4.1.1.4 for more detail).$^{93}$ For Fe(III)-TAMLs, oxidation of the dye by unactivated hydrogen peroxide alone is negligible compared to dye oxidation by the active catalyst. Therefore, TONs represent dye oxidation by the active catalyst only. At the optimum pH, TONs of several thousand have been found for the Fe(III)-TAML-catalysed oxidation of Orange II with hydrogen peroxide (see Section 4.1.1.4 for actual values).$^{93,97}$ Fe$^{III}$(L$_m$)Cl, on the other hand, is a poor peroxidase-like catalyst, and dye oxidation by unactivated hydrogen peroxide alone cannot be ignored under the experimental conditions. Furthermore, the rapid disproportionation of hydrogen peroxide changes the concentration of hydrogen peroxide in solution rapidly, further complicating the analysis of the initial rate data. Therefore, TONs estimated using the same method as for Fe(III)-TAMLs will be a combination of dye oxidation by Fe$^{III}$(L$_m$)Cl-catalysed peroxidase-like activity and dye oxidation by unactivated hydrogen peroxide. Additionally, these TON measurements would be affected by the rapid disproportionation of hydrogen peroxide catalysed by the Fe$^{III}$(L$_m$)Cl complex. Without further experiments, TONs for the peroxidase-like activity alone could not be determined from the aforementioned experiments.
4.2.2 Effect of tert-butanol cosolvent on the initial rate of dye oxidation

In the aforementioned experiments, the results at pH 10.8 were complicated by the incomplete solubility of the Fe\(^{III}\)(L\(_m\))Cl complex in the carbonate buffer. This also occurs in pH 10.8 phosphate buffered solutions. In contrast, the complex remains fully soluble at pH 7.5-10.0. In pH neutral aqueous solutions, EPR studies have suggested that Fe(III)-TAMLs become six-coordinate, with two axial water ligands. The Fe\(^{III}\)(L\(_m\))Cl complex may also form a bis(aquo) [Fe\(^{III}\)(L\(_m\))(H\(_2\)O)\(_2\)]\(^+\) resting catalyst species in neutral aqueous solutions. Above the pK\(_a\) for this complex (which is probably somewhere between pH 10.0 and 10.8), one of the water ligands may be deprotonated, forming a neutral Fe\(^{III}\)(L\(_m\))(H\(_2\)O)(OH) complex which precipitates out of solution. It is also possible that a low-solubility neutral Fe\(^{III}\)(L\(_m\))(H\(_2\)O)(OOH) complex forms once hydrogen peroxide is added to the solution. High resolution positive ion mass spectrometry of the collected precipitate that formed in the pH 10.8 solution prior to hydrogen peroxide addition showed only one major species, which corresponded to a formulation of [Fe\(^{III}\)(L\(_m\))]\(^+\), where any axial ligands present on this complex are presumably lost in the electrospray ionisation process. Therefore, this precipitate is indeed a Fe\(^{III}\)-L\(_m\) complex. Removal of the Fe\(^{III}\)-L\(_m\) complex from solution by precipitation should decrease both the rate of peroxidase-like activity and the rate of hydrogen peroxide disproportionation, because it is unlikely that either of these processes is catalysed heterogeneously by the precipitate.

To investigate the effects of precipitation on the initial rate of dye oxidation at pH 10.8, a cosolvent was added to the reaction to keep the Fe\(^{III}\)(L\(_m\))Cl complex fully dissolved. The experiment outlined in Table 4.1 was therefore repeated, but was modified so that the Fe\(^{III}\)(L\(_m\))Cl complex was fully dissolved in a small amount of tert-butanol prior to the addition of the pH 10.8 aqueous buffer solution. The relative volume of tert-butanol was kept low (about 1% v/v) relative to volume of the buffer solution in order to minimise interference of the tert-butanol solvent on the oxidation results. The Fe\(^{III}\)(L\(_m\))Cl complex remained fully dissolved throughout the experiment. Tert-butanol (1% v/v) was also added to the blank. The initial rate of dye oxidation for the blank (6.3 x 10\(^{-9}\) mol L\(^{-1}\) s\(^{-1}\)) was virtually unchanged (within experimental error) from the blank run without tert-butanol. However, for the run with Fe\(^{III}\)(L\(_m\))Cl present, the initial rate of dye oxidation was somewhat higher in the presence of tert-butanol (2.3 x 10\(^{-9}\) mol L\(^{-1}\) s\(^{-1}\)) than in the absence of tert-butanol (1.5 x 10\(^{-9}\) mol L\(^{-1}\) s\(^{-1}\)). This suggests that the rate of peroxidase-like activity increases slightly relative to the rate of hydrogen peroxide disproportionation once the complex is fully dissolved. At pH 7.5-10.0, the initial rate of dye oxidation for the runs with Fe\(^{III}\)(L\(_m\))Cl present and for the blanks were virtually unchanged in...
the presence of tert-butanol compared to the initial rate of dye oxidation in the absence of tert-butanol. This suggests that tert-butanol does not interfere significantly with the dye oxidation experiments, and also suggests that the increase in initial rate of dye oxidation for the Fe$^{III}$(L$_m$)Cl-catalysed run at pH 10.8 upon tert-butanol addition is due to the increase in solubility of the Fe$^{III}$(L$_m$)Cl complex.

4.2.3 Effect of temperature on the initial rate of dye oxidation

Because the Fe$^{III}$(L$_m$)Cl complex appears to catalyse both peroxidase-like activity and hydrogen peroxide disproportionation, experiments were repeated at higher temperature to see whether the rate of peroxidase-like activity would increase relative to the rate of hydrogen peroxide disproportionation. Since it is possible that more than one peroxidase-like dye oxidation mechanism may be operating in these systems, a different dye oxidation mechanism may become important at higher reaction temperatures, and so the rate of peroxidase-like activity may increase relative to the rate of hydrogen peroxide disproportionation. The experimental conditions used in Section 4.2.1 and given in Table 4.1 were repeated here, except that a reaction temperature of 50 °C was used instead of 25 °C. Although the initial rate of dye oxidation increased for both the Fe$^{III}$(L$_m$)Cl-catalysed runs and the blank runs (Table 4.2), the relative difference between the Fe$^{III}$(L$_m$)Cl-catalysed runs and the blank runs did not change significantly as the temperature increased. This suggests that the rate of hydrogen peroxide disproportionation and the rate of peroxidase-like activity increases by a similar amount with increasing temperature. Like the experiments at 25 °C, peroxide test strips suggested that a small amount of hydrogen peroxide was left after the Fe$^{III}$(L$_m$)Cl-catalysed pH 7.5 run had reached completion, but no hydrogen peroxide was left after the pH 9.0-10.8 runs had reached completion. This indicates that at pH 9.0-10.8, hydrogen peroxide completely disproportionates before the dye has completely bleached.
Table 4.2: Initial rates of Orange II dye oxidation with hydrogen peroxide at 50 °C, catalysed by Fe$^{III}$(L$_m$)Cl

<table>
<thead>
<tr>
<th>Conditions</th>
<th>7.5 (mol L$^{-1}$ s$^{-1}$)</th>
<th>9.0</th>
<th>10.0</th>
<th>10.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>With Fe$^{III}$(L$_m$)Cl present $^b$</td>
<td>3.9 x 10$^{-8}$</td>
<td>2.4 x 10$^{-8}$</td>
<td>1.6 x 10$^{-8}$</td>
<td>1.5 x 10$^{-8}$ $^d$</td>
</tr>
<tr>
<td>Blank $^c$</td>
<td>9.1 x 10$^{-9}$</td>
<td>3.0 x 10$^{-8}$</td>
<td>4.9 x 10$^{-8}$</td>
<td>5.7 x 10$^{-8}$</td>
</tr>
</tbody>
</table>

$a$ Values are the average of at least three concordant runs.

$b$ General conditions: 50 °C, 45 μmol L$^{-1}$ Orange II dye, 10 μmol L$^{-1}$ Fe$^{III}$(L$_m$)Cl, and 1 mmol L$^{-1}$ hydrogen peroxide in 0.01 mol L$^{-1}$ carbonate (pH 9.0-10.8 runs) or phosphate (pH 7.5 runs) buffers.

$c$ Same as the conditions for point $b$, but without any Fe$^{III}$(L$_m$)Cl added.

$d$ Precipitation of the Fe$^{III}$(L$_m$)Cl complex occurs at this pH.

### 4.2.4 Effect of buffers on the initial rate of dye oxidation

The results given in Table 4.1 and Table 4.2 suggest that some peroxidase-like activity indeed occurs at pH 7.5, but little or no peroxidase-like activity occurs at pH 9.0-10.8. It is possible that the buffers interfered with these results, because a phosphate buffer was used at pH 7.5, whereas carbonate buffers were used at pH 9.0-10.8. Dye oxidation experiments (as per the conditions given in Table 4.1) were therefore conducted at pH 10.0 in 0.01 mol L$^{-1}$ carbonate buffer, in 0.01 mol L$^{-1}$ phosphate buffer, and in unbuffered aqueous sodium hydroxide (1 x 10$^{-4}$ mol L$^{-1}$).

The initial rates of dye oxidation in the carbonate buffered solutions were similar to the initial rates of dye oxidation in the phosphate buffered solutions (Table 4.3). This suggests that the carbonate buffer does not impede catalyst performance significantly compared to the phosphate buffer. In contrast, it appears that the initial rate of dye oxidation for the blank is somewhat higher in the phosphate buffered solution than in the carbonate buffered solution. Therefore, the blank outperforms the Fe$^{III}$(L$_m$)Cl-catalysed run to a greater extent in the phosphate buffered solution than in the carbonate buffered solution. This suggests that there is a minor increase in the rate of hydrogen peroxide disproportionation relative to the rate of peroxidase-like activity when the reaction is carried out in phosphate buffers, compared to the reaction carried out in carbonate buffer.

The initial rate of dye oxidation for the blank that was run in unbuffered sodium hydroxide (at 1 x 10$^{-4}$ mol L$^{-1}$) was higher than for the blanks that were run in the carbonate and the phosphate
buffers (Table 4.3). This may be due to drifting of the pH during the experiment. In contrast to the blank, the initial rate of dye oxidation for the Fe\textsuperscript{III}(L\textsubscript{m})Cl-catalysed run in sodium hydroxide is lower than for the initial rate of dye oxidation for the Fe\textsuperscript{III}(L\textsubscript{m})Cl-catalysed runs in carbonate and phosphate buffered solutions. As described in Section 4.5.6, all these dye oxidation experiments were conducted by preparing enough Orange II plus Fe\textsuperscript{III}(L\textsubscript{m})Cl stock solution to enable triplicate runs. These are run sequentially by addition of an aliquot of hydrogen peroxide to a portion of this stock solution. The Fe\textsuperscript{III}(L\textsubscript{m})Cl complex therefore sits for longer in the stock solution with each successive run. Unlike any of the experiments in the carbonate and phosphate buffered solutions, each successive Fe\textsuperscript{III}(L\textsubscript{m})Cl-catalysed run in the unbuffered sodium hydroxide experiments showed a substantial increase in the initial rate of dye oxidation, until in the final run, the initial rate of dye oxidation is similar to the blank. Peroxide test strips for the first run showed that no hydrogen peroxide was left, whereas for the last run, the amount of hydrogen peroxide left (about 0.75 mmol L\textsuperscript{-1}) was similar to the amount left after the blank run. This suggests that by the final run, Fe\textsuperscript{III}(L\textsubscript{m})Cl is catalysing neither peroxidase-like activity nor hydrogen peroxide disproportionation. This is probably due to inactivation of the Fe\textsuperscript{III}(L\textsubscript{m})Cl complex by sodium hydroxide over extended periods of time. Furthermore, a small amount of a fine brown precipitate formed in the Fe\textsuperscript{III}(L\textsubscript{m})Cl-catalysed runs in sodium hydroxide, which appeared to increase slightly in amount with each successive run. This is perhaps due to the formation of a water-insoluble Fe\textsuperscript{III}(L\textsubscript{m})OH complex, which catalyses neither peroxidase-like activity nor hydrogen peroxide disproportionation. The value quoted for the Fe\textsuperscript{III}(L\textsubscript{m})Cl-catalysed run in aqueous sodium hydroxide in Table 4.3 is for the first run only.

Table 4.3: Initial rates of Orange II dye oxidation with hydrogen peroxide at 25 °C, catalysed by Fe\textsuperscript{III}(L\textsubscript{m})Cl in different buffer solutions

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Carbonate buffer (d)</th>
<th>Phosphate buffer (d)</th>
<th>NaOH (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>With Fe\textsuperscript{III}(L\textsubscript{m})Cl present (b)</td>
<td>1.9 x 10(^{-9})</td>
<td>2.1 x 10(^{-9})</td>
<td>1.6 x 10(^{-9}) (f)</td>
</tr>
<tr>
<td>Blank (c)</td>
<td>5.2 x 10(^{-9})</td>
<td>8.3 x 10(^{-9})</td>
<td>1.8 x 10(^{-8})</td>
</tr>
</tbody>
</table>

\(a\) Values are the average of at least three concordant runs.

\(b\) General conditions: 25 °C, 45 µmol L\textsuperscript{-1} Orange II dye, 10 µmol L\textsuperscript{-1} Fe\textsuperscript{III}(L\textsubscript{m})Cl, and 1 mmol L\textsuperscript{-1} hydrogen peroxide.

\(c\) Same as the conditions for point \(b\), but without any Fe\textsuperscript{III}(L\textsubscript{m})Cl added.

\(d\) In 0.01 mol L\textsuperscript{-1} carbonate or phosphate buffers.

\(e\) In 1.0 x 10\(^{-4}\) mol L\textsuperscript{-1} sodium hydroxide.

\(f\) Initial rate of dye oxidation is given for the first run only.
Even though many attempts were made to enhance the peroxidase-like activity of Fe\textsuperscript{III}(L\textsubscript{m})Cl by varying the reaction conditions, the Fe\textsuperscript{III}(L\textsubscript{m})Cl complex is a very poor catalyst for the oxidation of Orange II dye by hydrogen peroxide, especially when compared to the very high peroxidase-like activities of Fe(III)-TAMLs. For example, at the optimum pH, the initial rate of Fe(III)-TAML-catalysed oxidation of Orange II dye is usually around 10\textsuperscript{-7} to 10\textsuperscript{-6} mol L\textsuperscript{-1} s\textsuperscript{-1} at 25 °C, whereas a maximum initial rate of dye oxidation of 4.2 x 10\textsuperscript{-9} mol L\textsuperscript{-1} s\textsuperscript{-1} was measured for Fe\textsuperscript{III}(L\textsubscript{m})Cl at 25 °C (pH 7.5). Moreover, a catalyst concentration of 0.25 μmol L\textsuperscript{-1} was used for the Fe(III)-TAML experiments, compared to a catalyst concentration of 10 μmol L\textsuperscript{-1} for the Fe\textsuperscript{III}(L\textsubscript{m})Cl experiments. Because the initial rate of dye oxidation is usually proportional to the Fe(III)-TAML concentration, the initial rate of dye oxidation at 10 μmol L\textsuperscript{-1} Fe(III)-TAML is expected to be much higher again than the 10\textsuperscript{-7} to 10\textsuperscript{-6} mol L\textsuperscript{-1} s\textsuperscript{-1} measured at a Fe(III)-TAML concentration of 0.25 μmol L\textsuperscript{-1}.\textsuperscript{92,93,96,135} Unlike Fe(III)-TAMLs, Fe\textsuperscript{III}(L\textsubscript{m})Cl seems to catalyse hydrogen peroxide disproportionation to a greater extent than it catalyses peroxidase-like activity in the presence of Orange II. Also unlike Fe(III)-TAMLs, the initial rates of dye oxidation in the presence and absence of the Fe\textsuperscript{III}(L\textsubscript{m})Cl complex were similar, which suggests that dye oxidation by unactivated hydrogen peroxide alone plays a significant role under these experimental conditions. Because these results indicate that Fe\textsuperscript{III}(L\textsubscript{m})Cl is a very poor peroxidase-like catalyst compared to Fe(III)-TAMLs, Fe\textsuperscript{III}(L\textsubscript{m})Cl was not investigated further as a potential dye oxidation catalyst. The following section describes investigations into the ability of Co\textsuperscript{III}(L\textsubscript{m})Br to act as a catalyst for the oxidation of Orange II by hydrogen peroxide.

### 4.3 Oxidation of Orange II dye by hydrogen peroxide, catalysed by Co\textsuperscript{III}(L\textsubscript{m})Br

#### 4.3.1 Preliminary investigations

To investigate the ability of Co\textsuperscript{III}(L\textsubscript{m})Br to catalyse the oxidation of Orange II dye by hydrogen peroxide, initial conditions were selected that were similar to those used in Co(III)-TAML-catalysed dye oxidation studies (Section 4.1.2).\textsuperscript{106} These conditions were also similar to the preliminary conditions used in the Fe\textsuperscript{III}(L\textsubscript{m})Cl-catalysed dye oxidation studies (Section 4.2.1). Initial conditions of 25 °C, 45 μmol L\textsuperscript{-1} Orange II, 1 mmol L\textsuperscript{-1} hydrogen peroxide, and 0.25 μmol L\textsuperscript{-1} Co\textsuperscript{III}(L\textsubscript{m})Br in 0.01 mol L\textsuperscript{-1} carbonate (pH 9.0-10.8) or phosphate (pH 7.5) buffered
solutions were therefore chosen. Like the \( \text{Fe}^{\text{III}}(\text{L}_m)\text{Cl} \) complex (Section 4.2.1) under these conditions, the initial rate of dye oxidation in the presence of \( \text{Co}^{\text{III}}(\text{L}_m)\text{Br} \) was almost identical to the initial rate of dye oxidation for the corresponding blanks at pH 7.5, 9.0, 10.0, and 10.8. This suggests that \( \text{Co}^{\text{III}}(\text{L}_m)\text{Br} \) is not catalysing Orange II dye oxidation with hydrogen peroxide under these conditions. Therefore, as for the \( \text{Fe}^{\text{III}}(\text{L}_m)\text{Cl} \) complex, the experiments were repeated using a much higher \( \text{Co}^{\text{III}}(\text{L}_m)\text{Br} \) concentration (10 \( \mu \text{mol L}^{-1} \), or about 22 mol%). Thus, if dye oxidation proceeds at significantly faster rate than the blank reaction under these conditions, it would indicate that the reaction is catalytic. The results are summarised in Table 4.4.

Table 4.4: Initial rates of Orange II dye oxidation with hydrogen peroxide at 25 °C, catalysed by \( \text{Co}^{\text{III}}(\text{L}_m)\text{Br} \)

<table>
<thead>
<tr>
<th>Conditions</th>
<th>pH: 7.5</th>
<th>9.0</th>
<th>10.0</th>
<th>10.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>With ( \text{Co}^{\text{III}}(\text{L}_m)\text{Br} ) present</td>
<td>( 6.0 \times 10^{-10} )</td>
<td>( 1.1 \times 10^{-8} )</td>
<td>( 3.3 \times 10^{-8} )</td>
<td>( 5.2 \times 10^{-8} )</td>
</tr>
<tr>
<td>Blank</td>
<td>( 1.1 \times 10^{-9} )</td>
<td>( 4.0 \times 10^{-9} )</td>
<td>( 5.2 \times 10^{-9} )</td>
<td>( 6.1 \times 10^{-9} )</td>
</tr>
</tbody>
</table>

\( a \) Values are the average of at least three concordant runs.

\( b \) General conditions: 25 °C, 45 \( \mu \text{mol L}^{-1} \) Orange II dye, 10 \( \mu \text{mol L}^{-1} \) \( \text{Co}^{\text{III}}(\text{L}_m)\text{Br} \), and 1 mmol L\(^{-1} \) hydrogen peroxide in 0.01 mol L\(^{-1} \) carbonate (pH 9.0-10.8 runs) or phosphate (pH 7.5 runs) buffers.

\( c \) Same as the conditions for point \( b \), but without any \( \text{Co}^{\text{III}}(\text{L}_m)\text{Br} \) added.

\( d \) An orange precipitate forms at this pH.

In contrast to the \( \text{Fe}^{\text{III}}(\text{L}_m)\text{Cl} \) complex, \( \text{Co}^{\text{III}}(\text{L}_m)\text{Br} \) remained fully soluble at pH 9.0-10.8. However, at pH 7.5, an orange precipitate formed about five minutes after the addition of Orange II and \( \text{Co}^{\text{III}}(\text{L}_m)\text{Br} \) to the buffered solution. This precipitate formed prior to the addition of hydrogen peroxide, and the orange colour of the solution became significantly less intense after precipitate formation. High resolution positive and negative ion mass spectrometries of the isolated precipitate suggested that the formulation of this species is \( [\text{Co}^{\text{III}}(\text{L}_m)]^+\text{[Orange II]}^- \). This is because the only major signals that were observed in the positive and negative ion mass spectra of this precipitate corresponded to formulations of \( [\text{Co}^{\text{III}}(\text{L}_m)]^+ \) and \( \text{[Orange II]}^- \), respectively. Both spectra were run using the same concentration of \( [\text{Co}^{\text{III}}(\text{L}_m)]^+\text{[Orange II]}^- \) in methanol. The similarity in the absolute intensities (in counts) of the highest intensity signals observed in both spectra suggests that these major signals are not due to the presence of trace charged species in the sample solution. The \( [\text{Co}^{\text{III}}(\text{L}_m)]^+\text{[Orange II]}^- \) complex probably forms
via exchange of the bromide axial ligand or counteranion of Co\(^{\text{III}}\)(L\(_m\))Br for the anionic Orange II molecule.

In the pH 7.5 aqueous solution, the axial bromide ligand of Co\(^{\text{III}}\)(L\(_m\))Br may be exchanged for an axial water ligand to form a [Co\(^{\text{III}}\)(L\(_m\))(H\(_2\)O)\(_n\)]\(^+\)[Br\(^-\)] complex (n = 1 or 2). Upon addition of Na[Orange II], the bromide counteranion may then exchange for an Orange II counteranion, forming the water-insoluble [Co\(^{\text{III}}\)(L\(_m\))(H\(_2\)O)\(_n\)]\(^+\)[Orange II\(^-\)] complex (n = 0 to 2). Although axial water ligand(s) were not observed in the high resolution positive ion mass spectrum of the latter complex, these are expected to be readily lost in the electrospray ionisation process. This would be consistent with many other metal-L\(_m\) complexes described in the followed sections, where axial ligands that were expected to be present on these complexes were often not observed by mass spectrometry, presumably because the strongly donating L\(_m\) ligand labilises axial ligands to a significant extent. The reason that an orange precipitate was not observed at pH 9.0-10.8 is perhaps because an axial water ligand on the [Co\(^{\text{III}}\)(L\(_m\))(H\(_2\)O)\(_n\)]\(^+\)[Br\(^-\)] complex speciates to form a hydroxide axial ligand, producing a water-soluble charge-neutral Co\(^{\text{III}}\)(L\(_m\))(OH)(H\(_2\)O)\(_n\) (n = 0 or 1) complex. In contrast, an orange precipitate was not observed at pH 7.5 in analogous reactions with the Fe\(^{\text{III}}\)(L\(_m\))Cl complex, even though a charged complex (such as [Fe\(^{\text{III}}\)(L\(_m\))(H\(_2\)O)\(_n\)]\(^+\)[Cl\(^-\)], where n = 1 or 2) may be formed in solution at this pH. Fe\(^{\text{III}}\)(L\(_m\))Cl also differs from the Co\(^{\text{III}}\)(L\(_m\))Br complex in that the former precipitates out of solution above pH 10.0, while the latter remains fully soluble at pH 9.0-10.8. Although both complexes are expected to form neutral species at these basic pH values (probably M\(^{\text{III}}\)(L\(_m\))(OH)(H\(_2\)O)\(_n\) species, where n = 0 or 1), the Co\(^{\text{III}}\)(L\(_m\))(OH)(H\(_2\)O)\(_n\) complex seems to be much higher in solubility under these conditions than the Fe\(^{\text{III}}\)(L\(_m\))(OH)(H\(_2\)O)\(_n\) complex.

Alternatively, the [Co\(^{\text{III}}\)(L\(_m\))]\(^+\)[Orange II\(^-\)] complex observed in the mass spectrum of the orange precipitate formed at pH 7.5 could be due to axial ligation of the Co\(^{\text{III}}\)(L\(_m\))Br complex by Orange II, forming a charge-neutral Co\(^{\text{III}}\)(L\(_m\))(Orange II)(H\(_2\)O)\(_n\) complex (n = 0 or 1). To be consistent with the mass spectrometry results, the Orange II axial ligand would have to be lost readily during the electrospray ionisation process, because neither a Co\(^{\text{III}}\)(L\(_m\))(Orange II)(H\(_2\)O)\(_n\) + H\(^+\) species nor a Co\(^{\text{III}}\)(L\(_m\))(Orange II)(H\(_2\)O)\(_n\) + Na\(^+\) species was observed in the positive ion mass spectrum. If the orange precipitate observed at pH 7.5 is indeed due to the formation of a water-insoluble Co\(^{\text{III}}\)(L\(_m\))(Orange II)(H\(_2\)O)\(_n\) complex containing an axial Orange II ligand, the absence of an orange precipitate at pH 9.0-10.8 could be due to displacement of the axial Orange II
ligand by an axial hydroxide ligand to form a water-soluble Co\textsuperscript{III}(L\textsubscript{m})(OH)(H\textsubscript{2}O)\textsubscript{n} complex (n = 0 or 1).

Although the initial rate of dye oxidation is significantly lower for the Co\textsuperscript{III}(L\textsubscript{m})Br-catalysed run than for the blank at pH 7.5 (Table 4.4), at pH 9.0-10.8 the initial rate of dye oxidation is noticeably higher for the Co\textsuperscript{III}(L\textsubscript{m})Br-catalysed runs than the corresponding blanks, and the difference increases with increasing pH. This suggests that Co\textsuperscript{III}(L\textsubscript{m})Br may indeed be catalysing peroxidase-like activity above pH 7.5. Because the initial rate of dye oxidation for the Co\textsuperscript{III}(L\textsubscript{m})Br-catalysed runs at pH 9.0-10.8 are not dramatically greater than the corresponding blank runs, dye oxidation under these conditions is expected to be a combination of oxidation by the active Co-L\textsubscript{m} catalyst (peroxidase-like activity) and oxidation by unactivated hydrogen peroxide on its own. Similar observations were made for the Fe\textsuperscript{III}(L\textsubscript{m})Cl system in Section 4.2.1.

In contrast, for Co(III)-TAMLs, dye oxidation by unactivated hydrogen peroxide alone is negligible compared to dye oxidation by the active catalyst, because the initial rate of dye oxidation is much greater for the Co(III)-TAML-catalysed runs than for the corresponding blanks.

Even though appreciable peroxidase-like activity appears to be occurring at pH 9.0-10.8 for the Co\textsuperscript{III}(L\textsubscript{m})Br complex, the initial rate of dye oxidation in the presence of Co\textsuperscript{III}(L\textsubscript{m})Br is several orders of magnitude lower than for Fe(III)-TAML- and Co(III)-TAML-catalysed dye oxidations run under similar conditions.\textsuperscript{93,106} For example, at 25 °C, 0.25 μmol L\textsuperscript{-1} catalyst, 45 μmol L\textsuperscript{-1} Orange II, and 1 mmol L\textsuperscript{-1} hydrogen peroxide, initial rates of dye oxidation are on the order of 10\textsuperscript{-7} to 10\textsuperscript{-6} mol L\textsuperscript{-1} s\textsuperscript{-1} for Fe(III)-TAMLs and around 10\textsuperscript{-6} mol L\textsuperscript{-1} s\textsuperscript{-1} for Co(III)-TAMLs. In contrast, the maximum observed initial rate of dye oxidation was 5.2 x 10\textsuperscript{-8} mol L\textsuperscript{-1} s\textsuperscript{-1} for Co\textsuperscript{III}(L\textsubscript{m})Br (pH 10.8) and 4.2 x 10\textsuperscript{-9} mol L\textsuperscript{-1} s\textsuperscript{-1} for Fe\textsuperscript{III}(L\textsubscript{m})Cl (pH 7.5). These were measured at 10 μmol L\textsuperscript{-1} M\textsuperscript{III}-L\textsubscript{m} complex, whereas a catalyst concentration of 0.25 μmol L\textsuperscript{-1} was used in the M\textsuperscript{III}-TAML systems. Because the initial rate of dye oxidation for M\textsuperscript{III}-TAMLs is usually proportional to the catalyst concentration, at 10 μmol L\textsuperscript{-1} M\textsuperscript{III}-TAML the initial rate of dye oxidation would be considerably higher again than the initial rates of 10\textsuperscript{-7} to 10\textsuperscript{-6} mol L\textsuperscript{-1} s\textsuperscript{-1} that were measured at 0.25 μmol L\textsuperscript{-1} M\textsuperscript{III}-TAML, making the difference between the initial rates of the M\textsuperscript{III}-TAML-catalysed systems and the M\textsuperscript{III}(L\textsubscript{m})(X)-catalysed systems even greater.\textsuperscript{80,92,93,106}
Like Fe\textsuperscript{III}(L\textsubscript{m})Cl, Co\textsuperscript{III}(L\textsubscript{m})Br also seems to catalyse hydrogen peroxide disproportionation to a significant extent. This is because peroxide test strips showed that no peroxide was left after dye oxidation had finished at each pH. For reference, about 0.75-1 mmol L\textsuperscript{-1} hydrogen peroxide was left in the corresponding blanks at each pH. Further evidence of hydrogen peroxide disproportionation was demonstrated by the formation of dioxygen bubbles in Co\textsuperscript{III}(L\textsubscript{m})Br-catalysed runs, and by the incomplete dye oxidation once dye oxidation has finished. The latter observation suggests that the reactions run out of hydrogen peroxide before there is a chance to oxidise all of the Orange II dye. This contrasts with the blank runs, where no dioxygen bubbles were observed and dye oxidation reaches completion. Similar effects were observed in the Fe\textsuperscript{III}(L\textsubscript{m})Cl-catalysed dye oxidation experiments (Section 4.2.1). However, unlike the Fe\textsuperscript{III}(L\textsubscript{m})Cl system, analysis of the initial rates of dye oxidation for the Co\textsuperscript{III}(L\textsubscript{m})Br system suggests that peroxidase-like activity becomes significant at pH 9.0-10.8. When more hydrogen peroxide was added to the Co\textsuperscript{III}(L\textsubscript{m})Br system, Orange II dye bleaching eventually reached completion at all the pH values used. After the addition of a second aliquot of Orange II dye, followed by more aliquots of hydrogen peroxide, dye oxidation again reached completion. This suggests that Co\textsuperscript{III}(L\textsubscript{m})Br is indeed catalytically activating hydrogen peroxide towards substrate oxidation (via peroxidase-like activity), albeit rather poorly and in competition with the Co\textsuperscript{III}(L\textsubscript{m})Br-catalysed hydrogen peroxide disproportionation. Even after leaving an incompletely-bleached solution overnight at room temperature, dye oxidation resumes after the addition of another aliquot of hydrogen peroxide. The initial rate of dye oxidation under these conditions is similar to the initial rate of dye oxidation after the first aliquot of hydrogen peroxide was added. This suggests that, like Fe\textsuperscript{III}(L\textsubscript{m})Cl complex, the Co\textsuperscript{III}(L\textsubscript{m})Br complex is robust under the experimental conditions, and does not decompose appreciably in solution overnight.

Turnover numbers (TONs) and turnover frequencies (TOFs) were not determined for the Co\textsuperscript{III}(L\textsubscript{m})Br catalyst system because dye oxidation is a combination of oxidation by the active Co\textsuperscript{III}-L\textsubscript{m} catalyst and oxidation by unactivated hydrogen peroxide on its own. Determination of TONs for the peroxidase-like activity alone is difficult under these conditions, because of interference from Co\textsuperscript{III}(L\textsubscript{m})Br-catalysed hydrogen peroxide disproportionation and from oxidation of the dye by unactivated hydrogen peroxide. Without further experiments, the TONs for the peroxidase-like activity alone could not be determined from the aforementioned experiments. In contrast, for Co(III)-TAMLs, hydrogen peroxide disproportionation and dye oxidation by unactivated hydrogen peroxide are negligible compared to peroxidase-like activity,
and so TONs and TOFs reflect only the peroxidase-like activity of the catalyst system.\textsuperscript{106}

At pH 7.5, although the initial rate of dye oxidation was slightly lower for the Co\textsuperscript{III}(L\textsubscript{m})Br-catalysed run than for the blank run (Table 4.4), peroxidase-like activity may become dominant over hydrogen peroxide disproportionation if dye precipitation can be avoided. This is because the initial rate of dye oxidation might be proportional to the Orange II concentration. Removal of the dye by precipitation would therefore decrease the observed initial rate of dye oxidation in the Co\textsuperscript{III}(L\textsubscript{m})Br-catalysed run. Using a cationic dye that is relatively easy to oxidise (such as Pinacyanol chloride) may mitigate this problem, and would avoid the issues associated with the scattering of light off the precipitate observed at pH 7.5 in the Co\textsuperscript{III}(L\textsubscript{m})Br-catalysed runs.

Like the Fe\textsuperscript{III}(L\textsubscript{m})Cl complex, the effect of increasing the reaction temperature and changing the buffers was explored for the Co\textsuperscript{III}(L\textsubscript{m})Br system. As for the Fe\textsuperscript{III}(L\textsubscript{m})Cl complex, increasing the reaction temperature from 25 °C to 50 °C increased the initial rate of dye oxidation for both the Co\textsuperscript{III}(L\textsubscript{m})Br-catalysed runs and for the blank runs, but the relative ratio between these rates did not change significantly. This suggests that the rate of peroxidase-like activity and the rate of hydrogen peroxide disproportionation increase to a similar extent with increasing reaction temperature. Also like the Fe\textsuperscript{III}(L\textsubscript{m})Cl system, changing the buffers from carbonate to phosphate had only a small effect on the relative difference between the initial rate of dye oxidation for the Co\textsuperscript{III}(L\textsubscript{m})Br-catalysed runs compared to the blank runs. The use of sodium hydroxide instead of carbonate or phosphate buffers appeared to lead to inactivation of the Co\textsuperscript{III}(L\textsubscript{m})Br complex.

4.3.2 Effect of variation in hydrogen peroxide concentration

It was shown in the Co\textsuperscript{III}(L\textsubscript{m})Br-catalysed dye oxidation experiments (Section 4.3.1) that the addition of sequential aliquots of 1 mmol L\textsuperscript{-1} hydrogen peroxide eventually enabled dye oxidation to reach completion. These experiments were repeated with a single larger excess of hydrogen peroxide, to see whether the reaction would reach completion under these conditions at a rate that is significantly faster than the blank. It was speculated that increasing the hydrogen peroxide concentration might favourably alter the relative rate of the peroxidase-like reaction compared to the rate of the hydrogen peroxide disproportionation reaction. A pH of 10.8 was used for these experiments because the ratio between the initial rate of dye oxidation for the
Co\textsuperscript{III}(L\textsubscript{m})Br-catalysed run and the initial rate of dye oxidation for the blank run was higher at this pH than for any of the other pH values studied (see Table 4.4).

The extent of dye bleaching was found to increase with increasing initial hydrogen peroxide concentration (Table 4.5), and reached completion using an initial hydrogen peroxide concentration somewhere between 1 mmol L\textsuperscript{-1} and 5 mmol L\textsuperscript{-1} hydrogen peroxide. Peroxide test strips showed that no hydrogen peroxide remained after bleaching had finished for the runs at initial hydrogen peroxide concentrations of 0.1 to 5 mmol L\textsuperscript{-1}. However, using an initial hydrogen peroxide concentration of 10 mmol L\textsuperscript{-1}, about 0.5 mmol L\textsuperscript{-1} hydrogen peroxide remained after bleaching had reached completion. Although the initial rate of dye oxidation increased with increasing hydrogen peroxide concentration, this increase was small. For example, with a 100-fold increase in initial hydrogen peroxide concentration (from 0.1 to 10 mmol L\textsuperscript{-1}), a three-fold increase in the initial rate of dye oxidation was observed. This is probably because the rate of dye oxidation (which is a combination of oxidation by activated hydrogen peroxide and oxidation by unactivated hydrogen peroxide) increases with increasing initial hydrogen peroxide concentration, but at the same time, the rate of hydrogen peroxide disproportionation increases with increasing initial hydrogen peroxide concentration. Therefore, the actual amount of hydrogen peroxide in solution is decreasing more rapidly as the initial hydrogen peroxide concentration increases.

Table 4.5: Initial rates and extents of Co\textsuperscript{III}(L\textsubscript{m})Br-catalysed Orange II dye bleaching at pH 10.8, using different initial hydrogen peroxide concentrations

<table>
<thead>
<tr>
<th>Initial H\textsubscript{2}O\textsubscript{2} concentration (mmol L\textsuperscript{-1}) \textsuperscript{a}</th>
<th>Initial rate of dye oxidation (mol L\textsuperscript{-1} s\textsuperscript{-1}) \textsuperscript{b}</th>
<th>Extent of dye bleaching \textsuperscript{c}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>3.6 x 10\textsuperscript{-8}</td>
<td>3%</td>
</tr>
<tr>
<td>0.5</td>
<td>4.9 x 10\textsuperscript{-8}</td>
<td>15%</td>
</tr>
<tr>
<td>1.0</td>
<td>5.5 x 10\textsuperscript{-8}</td>
<td>21%</td>
</tr>
<tr>
<td>5.0</td>
<td>7.8 x 10\textsuperscript{-8}</td>
<td>100%</td>
</tr>
<tr>
<td>10.0</td>
<td>1.1 x 10\textsuperscript{-7}</td>
<td>100%</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Initial concentration of hydrogen peroxide added to the solution (mmol L\textsuperscript{-1}).

\textsuperscript{b} General conditions: 25 °C, 45 µmol L\textsuperscript{-1} Orange II dye and 10 µmol L\textsuperscript{-1} Co\textsuperscript{III}(L\textsubscript{m})Br in 0.01 mol L\textsuperscript{-1} carbonate buffer (pH 10.8). Values are the average of at least three concordant runs.

\textsuperscript{c} Calculated using: [(initial absorbance – final absorbance) ÷ (initial absorbance)] x 100.
Using an initial hydrogen peroxide concentration of 5 mmol L$^{-1}$ at pH 10.8, dye oxidation just reached completion and peroxide test strips indicated that no hydrogen peroxide remained at the end of the reaction. In contrast, peroxide test strips showed that a small amount of hydrogen peroxide remained at the end of the reaction when an initial concentration of 10 mmol L$^{-1}$ hydrogen peroxide was used. Therefore, it can tentatively be said that under these conditions, the Co$^{III}$(L$_m$)Br catalyst has undergone approximately 4.5 turnovers of dye oxidation and approximately 500 turnovers of the hydrogen peroxide disproportionation reaction. The former is calculated by the molar ratio of Orange II to Co$^{III}$(L$_m$)Br at which dye oxidation just reaches completion, while the latter is calculated from the molar ratio of hydrogen peroxide to Co$^{III}$(L$_m$)Br at which hydrogen peroxide disproportionation just reaches completion. These results assume that that one Co$^{III}$(L$_m$)Br molecule oxidises one dye molecule per turnover of the catalytic cycle for the peroxidase-like activity, and that one Co$^{III}$(L$_m$)Br molecule disproportionates one hydrogen peroxide molecule per turnover of the catalytic cycle for hydrogen peroxide disproportionation reaction. This is at best a rough estimate, because the peroxidase-like activity, hydrogen peroxide disproportionation, and dye oxidation by unactivated hydrogen peroxide all compete with each other, and the rates of each process will change as the concentration of hydrogen peroxide decreases. The main point, however, is that there are significantly more turnovers for the hydrogen peroxide disproportionation reaction than for the peroxidase-like reaction, indicating that Co$^{III}$(L$_m$)Br is much better at catalysing hydrogen peroxide disproportionation than it is at catalysing dye oxidation. The dominance of hydrogen peroxide disproportionation over the peroxidase-like activity is expected to be even greater for the Fe$^{III}$(L$_m$)Cl complex, where the initial rates of the Fe$^{III}$(L$_m$)Cl-catalysed dye oxidation runs were even lower compared to the corresponding blanks. This contrasts with Fe(III)-TAMLs and Co(III)-TAMLs, where minimal hydrogen peroxide disproportionation occurs in the presence of oxidisable substrates, and hundreds to thousands of dye oxidation turnovers occur using very small amounts of catalyst.$^{80,93,106,135}$

Because of the very poor peroxidase-like catalytic performance of the Co$^{III}$(L$_m$)Br and Fe$^{III}$(L$_m$)Cl complexes, these were not investigated further as dye oxidation catalysts. Possible mechanisms of dye oxidation also were not investigated, due to competition between hydrogen peroxide disproportionation, peroxidase-like activity, and dye oxidation by unactivated hydrogen peroxide.
4.4 Conclusions and future work

Although both Fe\textsuperscript{III}(L\textsubscript{m})Cl and Co\textsuperscript{III}(L\textsubscript{m})Br catalysed the oxidation of dye substrates with hydrogen peroxide very slowly under the conditions used in the experiments described in chapter, they appeared to be much better at catalysing the disproportionation of hydrogen peroxide. The rates of Fe\textsuperscript{III}(L\textsubscript{m})Cl- and Co\textsuperscript{III}(L\textsubscript{m})Br-catalysed peroxidase-like activity were very low compared to the rates of Fe(III)-TAML- and Co(III)-TAML-catalysed peroxidase-like activity when measured under similar conditions. Furthermore, the latter complexes are excellent peroxidase-like catalysts with minimal hydrogen peroxide disproportionation. Despite their poor behaviour as oxidation catalysts, Fe\textsuperscript{III}(L\textsubscript{m})Cl and Co\textsuperscript{III}(L\textsubscript{m})Br seemed to be rather robust under the conditions used in the dye oxidation experiments, and did not decompose readily between pH 7.5 and 10.8. This suggests that the pyridinium amide moieties of the L\textsubscript{m} ligand are robust towards hydrolysis and oxidation by the active catalyst.

The slow rates of Fe\textsuperscript{III}(L\textsubscript{m})Cl- and Co\textsuperscript{III}(L\textsubscript{m})Br-catalysed dye oxidation meant that oxidation of the dye by unactivated hydrogen peroxide played a significant role in the overall dye oxidation process, and must be accounted for in the analysis of the kinetic data. Competition between these two processes, combined with Fe\textsuperscript{III}(L\textsubscript{m})Cl- and Co\textsuperscript{III}(L\textsubscript{m})Br-catalysed hydrogen peroxide disproportionation made determination of the ability of these complexes to act as peroxidase-like oxidation catalysts difficult to quantify. However, the results obtained suggested that the amount of catalytic dye oxidation increased relative to catalytic hydrogen peroxide disproportionation at less basic pH values (around pH 7.5) for Fe\textsuperscript{III}(L\textsubscript{m})Cl and at more basic pH values (around pH 10.8) for Co\textsuperscript{III}(L\textsubscript{m})Br.

Although precipitation of Fe\textsuperscript{III}(L\textsubscript{m})Cl at high pH values became problematic, the complex was successfully solubilised using 1% v/v tert-butanol as a cosolvent. This cosolvent did not appear to interfere noticeably with the dye oxidation results. Substitution of carbonate buffers for phosphate buffers also did not affect the catalytic performance of Fe\textsuperscript{III}(L\textsubscript{m})Cl and Co\textsuperscript{III}(L\textsubscript{m})Br greatly. Increasing the reaction temperature for the Fe\textsuperscript{III}(L\textsubscript{m})Cl-catalysed and Co\textsuperscript{III}(L\textsubscript{m})Br-catalysed experiments did not significantly change the rate of peroxidase-like activity relative to the rate of hydrogen peroxide disproportionation. Furthermore, increasing the initial hydrogen peroxide concentration in the Co\textsuperscript{III}(L\textsubscript{m})Br-catalysed experiments at pH 10.8 appeared to increase the contribution of the peroxidase-like activity very slightly relative to the hydrogen peroxide...
disproportionation reaction, although the latter reaction still remained dominant. At less basic pH values (below pH 9.0), Co$^{III}$(L$_m$)Br precipitated out of solution as a product that was formulated as [Co$^{III}$(L$_m$)][Orange II]. The use of cationic dyes that are relatively easy to oxidise, such as Pinacyanol chloride, may mitigate this problem.

Even though Fe$^{III}$(L$_m$)Cl and Co$^{III}$(L$_m$)Br were poor oxidation catalysts, they seemed to be good hydrogen peroxide disproportionation catalysts, and they could be useful in applications where hydrogen peroxide removal is desired (for example, in the sterilisation of dairy products and in the removal of hydrogen peroxide left over from textile bleaching processes), where they would be cheaper alternatives to the catalase enzymes that are normally used to destroy hydrogen peroxide in these processes.

Due to the very poor performance of the Fe$^{III}$(L$_m$)Cl and the Co$^{III}$(L$_m$)Br complexes as oxidation catalysts, dye oxidation studies with these complexes were not investigated further. Possible mechanisms for the Fe$^{III}$(L$_m$)Cl-catalysed and Co$^{III}$(L$_m$)Br-catalysed oxidation of Orange II dye by hydrogen peroxide also were not investigated, because of the similarity in rates between the hydrogen peroxide disproportionation reaction, the peroxidase-like oxidation reaction, and dye oxidation by unactivated hydrogen peroxide alone. The competition between these three processes makes the measurement of any one activity difficult to determine from the kinetic data.

It is possible that better catalytic performance may be obtained for the Fe$^{III}$(L$_m$)Cl and Co$^{III}$(L$_m$)Br complexes at pH values that are outside of the pH range used in these studies. For example, these complexes may be effective peroxidase-like catalysts under slightly acidic conditions. Measuring the stability of the Fe$^{III}$(L$_m$)Cl and Co$^{III}$(L$_m$)Br complexes under these acidic conditions will be useful for determining whether catalytic studies will be feasible at low pH.

Structural modifications to the L$_m$ ligands of Fe$^{III}$(L$_m$)Cl and Co$^{III}$(L$_m$)Br may lead to complexes with superior peroxidase-like activities and minimal hydrogen peroxide disproportionation activity. For example, introducing substituents on the phenylenediamine aromatic ring or on the pyridinium amide rings, or replacing the geminal-C-methyl groups with other functionalities.
may increase the rate of peroxidase-like activity relative to the rate of hydrogen peroxide disproportionation. If this can be achieved, TONs for the peroxidase-like activity in these systems could be determined because hydrogen peroxide disproportionation and oxidation of the dye substrate by hydrogen peroxide alone would be minimal compared to the peroxidase-like activity. Therefore, unlike in the experiments with the Fe$^{III}$($L_{m}$)Cl and Co$^{III}$($L_{m}$)Br complexes described in Sections 4.2 and 4.3, measured TON values would reflect only the peroxidase-like activity in these systems. The low rates of catalytic dye oxidation observed for these Fe$^{III}$($L_{m}$)Cl and Co$^{III}$($L_{m}$)Br complexes suggests that the pyridinium amide moieties have a dramatic effect on the catalytic oxidation properties of the Fe$^{III}$($L_{m}$)Cl and Co$^{III}$($L_{m}$)Br complexes, compared to those of the structurally-related [Fe$^{III}$($B^{*}$)(H$_{2}$O)]$^{+}$ and [Co$^{III}$($B^{*}$)]$^{-}$ TAML complexes. This structural modification alters the catalytic properties of the Fe$^{III}$($L_{m}$)Cl and Co$^{III}$($L_{m}$)Br complexes, so that instead of behaving as excellent peroxidase-like catalysts with minimal catalysis of the hydrogen peroxide disproportionation reaction (as occurs in the M$^{III}$-TAML systems), they become complexes that catalyse hydrogen peroxide disproportionation much better than they catalyse peroxidase-like activity.

Once a system is found where the rate of peroxidase-like activity is significantly higher than the rate of hydrogen peroxide disproportionation, the products formed from the oxidative degradation of these catalysts may be useful for finding the most vulnerable site of the ligand system so that more robust ligands can be synthesised. For metal-TAMLs, repeating this process has led to the development of steadily more robust TAML ligands.$^{17}$

In Chapter 3, the synthesis and characterisation of a variety of other metal-$L_{m}$ complexes were described, as were iron and cobalt complexes of ligand $L_{a}$. Once the manganese-$L_{m}$, iron-$L_{a}$, and cobalt-$L_{a}$ complexes have been purified, these too will be investigated as potential catalysts for the oxidation of dye substrates by hydrogen peroxide.

Fe$^{III}$($L_{m}$)Cl and Co$^{III}$($L_{m}$)Br might be much better oxidation catalysts if an organic peroxide (such as tert-butyl hydroperoxide) is used instead of hydrogen peroxide. These organic peroxides are unlikely to undergo disproportionation, and may enable determination of the oxidation activity for these catalysts. This will be investigated in the near future. However, if the peroxidase-like activity remains low, dye oxidation by the organic peroxide alone may still be significant. Because tert-butyl hydroperoxide is soluble in many non-aqueous solvents, dye
oxidation studies could even be conducted in solvents other than water, and this may prevent precipitation of the Fe\textsuperscript{III}(L\textsubscript{m})Cl and Co\textsuperscript{III}(L\textsubscript{m})Br complexes. Another future direction is to investigate the oxidation of dye substrates which are easier and faster to oxidise than Orange II (such as Pinacyanol chloride). With faster to oxidise dyes, the rate of dye oxidation is expected to increase relative to the rate of hydrogen peroxide disproportionation.

Yet another area of future research is to investigate the ability of Fe\textsuperscript{III}(L\textsubscript{m})Cl and Co\textsuperscript{III}(L\textsubscript{m})Br to catalyse the oxidation of substrates other than dyes. Although Fe\textsuperscript{III}(L\textsubscript{m})Cl and Co\textsuperscript{III}(L\textsubscript{m})Br are poor catalysts for the oxidation of Orange II by hydrogen peroxide, they may be effective catalysts for reactions such as alkene epoxidations, particularly if oxidants other than hydrogen peroxide are used.

Despite the poor performance of the Fe\textsuperscript{III}(L\textsubscript{m})Cl and Co\textsuperscript{III}(L\textsubscript{m})Br complexes as dye oxidation catalysts with hydrogen peroxide, the Na[[Rh\textsuperscript{II}(L\textsubscript{m})]\textsubscript{2}Cl] complex that was described in Section 3.2.6 and derivatives of this rhodium complex may be effective catalysts for the activation of various small molecules. This was therefore investigated, and the results of these studies are reported in the following chapter.

4.5 Experimental

4.5.1 General procedures

All chemicals were used as received from commercial suppliers unless otherwise stated. Peroxide test strips were obtained from Merck and used according to the supplier’s instructions.

4.5.2 Preparation of buffer solutions

Carbonate and phosphate buffer solutions (0.01 mol L\textsuperscript{-1}) were prepared according to standard procedures.\textsuperscript{217,218} After heating each buffer solution to the appropriate temperature, the pH was
determining using a TPS Labchem pH meter equipped with a Sartorius pH/ATC electrode. The pH meter was first calibrated with pH 4.00, 6.88, and 9.18 standard buffer solutions.

### 4.5.3 Standardisation of hydrogen peroxide

Stock solutions of hydrogen peroxide (approximately 1% w/v) were prepared by diluting reagent grade hydrogen peroxide (approximately 30% w/v) with deionised water inside a volumetric flask (250 mL). The volumetric flask was wrapped in aluminium foil to prevent photo-induced degradation. Stock solutions were standardised daily by UV-visible absorption readings and the thiosulfate titration method (see Sections 4.5.3.1, 4.5.3.2, and 4.5.3.3 below).

#### 4.5.3.1 Standardisation of hydrogen peroxide by UV-visible absorption spectroscopy

An aliquot of the hydrogen peroxide stock solution (1 mL, approximately 1% w/v) was diluted to 20 mL with deionised water inside a volumetric flask. The absorbance was measured at 230 nm ($\varepsilon = 63 \text{ mol}^{-1} \text{L cm}^{-1}$),\textsuperscript{219} using a PerkinElmer 35 UV-visible double beam spectrometer (10 nm slit width; 480 nm min$^{-1}$ scan speed) and quartz cuvettes. Standardisations were obtained in triplicate and the values were averaged to determine the hydrogen peroxide concentration.

#### 4.5.3.2 Standardisation of sodium thiosulfate with potassium iodate

Sodium thiosulfate was standardised according to a literature method.\textsuperscript{220} Thus, five drops of a saturated aqueous ammonium molybdate solution was added to a solution that contained potassium iodate (5.0 mL of a 0.0355 mol L$^{-1}$ aqueous stock solution), potassium iodide (5.0 mL of a 0.50 mol L$^{-1}$ aqueous stock solution), and sulfuric acid (5.0 mL of a 2.0 mol L$^{-1}$ aqueous stock solution) in deionised water (30.0 mL), inside a 100 mL conical flask. An orange-brown solution formed after stirring for about 10 seconds, which was then carefully titrated against a solution of sodium thiosulfate decahydrate (15 g dissolved in deionised water in a 500 mL volumetric flask, and then added to a 50 mL burette) until the solution became very pale yellow. Starch (about 10 mg) was then added, forming a blue-black solution. More sodium thiosulfate decahydrate was carefully added dropwise until the colourless endpoint was reached. The
sodium thiosulfate concentration was calculated from the average of triplicate runs (average: 0.118 mol L\(^{-1}\)).

4.5.3.3 Standardisation of hydrogen peroxide with sodium thiosulfate

A standard literature method was used to standardise hydrogen peroxide with sodium thiosulfate.\(^{221}\) Thus, a saturated aqueous solution of ammonium molybdate (5 drops) was added to a solution that contained potassium iodide (10.0 mL of a 0.0158 mol L\(^{-1}\) aqueous stock solution) and sulfuric acid (5.0 mL of a 2.0 mol L\(^{-1}\) aqueous stock solution) in deionised water (30.0 mL) inside a 100 mL conical flask. Hydrogen peroxide (2.0 mL of an approximately 1 mol L\(^{-1}\) aqueous stock solution) was added, and the solution was stirred for 2 minutes until the solution became orange-brown. This solution was then titrated against the sodium thiosulfate solution that was standardised in Section 4.5.3.2 (0.118 mol L\(^{-1}\)) until the solution became very pale yellow. Starch (about 10 mg) was added, causing the solution to become blue-black. More sodium thiosulfate was then added carefully dropwise until the colourless endpoint was reached. The hydrogen peroxide concentration was calculated from the average of triplicate runs (0.249 mol L\(^{-1}\)).

4.5.4 Preparation of Orange II dye stock solutions

Orange II dye was purified by column chromatography on C18 reverse-phase silica (1:9 methanol/water).\(^{96}\) The orange band was collected and the solvent was removed under vacuum. Stock solutions of Orange II dye were prepared in deionised water using volumetric flasks.

4.5.5 Preparation of catalyst stock solutions

Stock solutions of the catalysts were prepared by dissolving the appropriate metal complex in 0.01 mol L\(^{-1}\) carbonate or phosphate buffer solutions (with brief sonication when necessary) to a concentration of about 1 mmol L\(^{-1}\), using volumetric flasks.
4.5.6 General procedure for determination of the initial rate of dye oxidation by hydrogen peroxide, catalysed by various metal complexes

Aliquots of Orange II dye (0.229 mL of a 1.965 mmol L\(^{-1}\) aqueous stock solution) and the appropriate metal complex (97.83 µL of a 0.9783 mmol L\(^{-1}\) aqueous stock solution) were added to a 10 mL volumetric flask and the solutions were diluted to 10 mL with 0.01 mol L\(^{-1}\) aqueous buffer solution. This gave a final concentration of 45 µmol L\(^{-1}\) Orange II and 10 µmol L\(^{-1}\) of the metal complex. An aliquot of this solution (3.0 mL) was added to a quartz cuvette (1.0 cm pathlength) and a 5 mm Teflon magnetic stirrer bar was added. The cuvette was placed in a temperature-controlled holder heated to the appropriate temperature, controlled to within ± 0.01 °C with a Quantum Northwest TC125 temperature control unit. The cuvette was left to equilibrate over five to ten minutes and then an aliquot of hydrogen peroxide (12 µL of a 0.249 mol L\(^{-1}\) aqueous stock solution; 1 mmol L\(^{-1}\) final concentration) was added to the cuvette. The absorbance at 483 nm was measured every 0.5 seconds using an Ocean Optics LS-1 tungsten halogen lamp and a USB2000-VIS-NIR detector operating between 350 and 1000 nm. Results were obtained as the average of concordant triplicate runs. The initial rate of Orange II dye oxidation was obtained from the slope of the absorbance versus time plots over the first 10% of the decrease in absorbance, and this value was divided by the molar absorptivity of Orange II dye at each pH (17,800 L mol\(^{-1}\) cm\(^{-1}\) at pH 7.5, 23,000 L mol\(^{-1}\) cm\(^{-1}\) at pH 9.0-10.0; and 19,400 L mol\(^{-1}\) cm\(^{-1}\) at pH 10.8),\(^{96}\) to give the initial rate of dye oxidation in units of mol L\(^{-1}\) s\(^{-1}\). The first 5 seconds of data were discarded to allow enough time for the hydrogen peroxide to mix. Initial rates were calculated using SigmaPlot for Windows, version 11.

Blank experiments were repeated as above, without any metal complex added.
Chapter 5: Reactivity of Rhodium-Pyridinium Amide Macrocyclic Complexes and Catalysis of Reactions Relevant to Small Molecule Activation

5.1 Introduction

In this chapter, reactions of the new dimeric rhodium complex, Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}]Cl], with a variety of substrates are discussed, and investigations of the structural and spectroscopic properties of the products are described. As explained in Chapter 3, the characterisation data strongly suggests that Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}]Cl] has a direct rhodium-rhodium bond and a chloride axial ligand. The reactions of Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}]Cl] described in this chapter are carried out in alcohol solvents, because of the low solubility of Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}]Cl] in other solvents. This contrasts with the reactions of [Rh\textsuperscript{II}(porphyrin)]\textsubscript{2} and [Rh\textsuperscript{II}(TMTAA)]\textsubscript{2} with various substrates published in the literature, which are usually carried out in low polarity aprotic solvents.\textsuperscript{208}

As discussed in Section 1.7, small molecule activation involves the activation (often catalytically) of otherwise rather inert chemicals to produce organic products. These small molecules (for example, dihydrogen, carbon monoxide, acetylene, and carbon dioxide) are relatively cheap and abundant feedstocks, and some of these are greener alternatives to many petrochemical-derived reagents that are currently used to synthesise commodity and fine chemicals.\textsuperscript{117} Because some of the reported [Rh\textsuperscript{II}(porphyrin)]\textsubscript{2} and [Rh\textsuperscript{II}(TMTAA)]\textsubscript{2} dimers have shown promise as catalysts for the activation of small molecules (such as dihydrogen, acetylene and carbon monoxide),\textsuperscript{222-224} the ability of the related complex, Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}]Cl], and selected derivatives of this complex to behave as catalysts for these reactions were investigated, and the results are reported in this chapter.
5.1.1 General reactivity of complexes with direct unsupported rhodium-rhodium bonds

A handful of complexes that contain direct unsupported rhodium-rhodium bonds and macrocyclic ligands have been published in the literature. These complexes are discussed in Section 3.1.5. Three main types of macrocyclic ligands are known to form dimeric rhodium-rhodium bonded complexes: porphyrins, TMTAAs, and phthalocyanines (see Figure 3.5 and Figure 3.12 for the general structures of these ligands). These dimeric rhodium-rhodium complexes react with a wide variety of substrates to produce either dimeric or monomeric products. These reactions can be divided into three main classes: 1) reactions where the rhodium-rhodium bond remains intact; 2) reactions where the rhodium-rhodium bond cleaves heterolytically to give monomeric products; and 3) reactions where the rhodium-rhodium bond cleaves homolytically to give monomeric products. Because these reactions are highly relevant to the research discussed in this chapter, they are summarised in Sections 5.1.1.1 to 5.1.1.3 below.

5.1.1.1 Reactions where the rhodium-rhodium bond remains intact

It is rare for rhodium-rhodium bonded dimers to react with substrates to produce complexes where the rhodium-rhodium bond remains intact. As discussed in Section 3.1.5, the rhodium-rhodium bonds of [Rh\(^{II}\)(porphyrin)]\(_2\) and [Rh\(^{II}\)(TMTAA)]\(_2\) dimers are rather weak (17 to 22 kcal mol\(^{-1}\)) and these bonds usually break in the presence of reagents such as pyridine to form monomeric products.\(^{208}\) However, [Rh\(^{II}\)(phthalocyanine)]\(_2\) dimers (discussed further in Section 3.1.5) often react with substrates such as pyridines and imidazoles to form [Rh\(^{II}\)(phthalocyanine)(L')]\(_2\) adducts (L' = donor ligand), where the rhodium-rhodium bond remains intact. This has been attributed to the stronger rhodium-rhodium bonds in [Rh\(^{II}\)(phthalocyanine)]\(_2\) dimers than in most [Rh\(^{II}\)(porphyrin)]\(_2\) and [Rh\(^{II}\)(TMTAA)]\(_2\) dimers.\(^{210,211}\) Furthermore, it has been shown that the phthalocyanine complex, [Rh\(^{II}\)(Rpc)]\(_2\) (see Figure 3.12 forRpc ligand structure), reacts with stoichiometric amounts of trimethylphosphine to form [Rh\(^{II}\)(Rpc)]\(_2\)(PMe\(_3\)) and [Rh\(^{II}\)(Rpc)]\(_2\)(PMe\(_3\))\(_2\) adducts. However, the addition of excess trimethylphosphine to [Rh\(^{II}\)(Rpc)]\(_2\) was shown to break the rhodium-rhodium bond to form a monomeric complex, Rh\(^{III}\)(Rpc\(^-\))(PMe\(_3\))\(_2\).\(^{211}\)
5.1.1.2 Reactions where the rhodium-rhodium bond cleaves heterolytically

The weak rhodium-rhodium bond of most rhodium(II) dimers cleaves readily in the presence of a wide range of substrates, forming monomeric products. These reactions can be divided into two main classes: those where the rhodium-rhodium bond breaks heterolytically, and those where the rhodium-rhodium bond breaks homolytically. When the rhodium-rhodium bond breaks heterolytically, a rhodium(I) complex and a rhodium(III) complex are formed (Figure 5.1). Spectroscopic studies have indicated that rhodium(I)-porphyrin and rhodium(I)-TMTAA complexes are usually four-coordinate, and it has been postulated that this is due to the filled $d_{z^2}$ orbital in these complexes. In contrast, the rhodium(III) complexes formed via heterolytic cleavage of these rhodium(II) dimers are usually six-coordinate, with two axial ligands. For example, the rhodium-rhodium bond of $\text{[Rh}^{\text{II}}(\text{OEP})\text{]}_2$ (OEP = octaethylporphyrin; see Figure 3.10 for ligand structure) has been shown to cleave heterolytically in the presence of pyridine-$d_5$ (py) to form a 1:1 mixture of $\text{[Rh}^{\text{I}}(\text{OEP})\text{]}^+$ and $\text{[Rh}^{\text{III}}(\text{OEP})(\text{py})_2\text{]}^+$. These monomeric products have also been shown to react further in the presence of another reagent. For instance, $\text{[Rh}^{\text{II}}(\text{OEP})\text{]}_2$ in the presence of pyridine has been shown to react heterolytically with carbon monoxide and dihydrogen to form the metalloformyl complex, $\text{Rh}^{\text{III}}(\text{OEP})(\text{CHO})(\text{py})$. Heterolytic cleavage mechanisms are discussed in more detail in Section 5.1.7.

$$\begin{array}{c}
\text{(L)Rh}^{\text{II}} \quad \text{Rh}^{\text{II}}(\text{L}) \\
\xrightarrow{2 \text{L}'} \\
\text{[Rh}^{\text{I}}(\text{L})]^+ + \text{[Rh}^{\text{III}}(\text{L})(\text{L}')_2]^+
\end{array}$$

**Figure 5.1:** General reaction for the heterolytic cleavage of rhodium(II)-rhodium(II) dimers in the presence of a substrate (L’)

5.1.1.3 Reactions where the rhodium-rhodium bond cleaves homolytically

If the rhodium-rhodium bond of the rhodium(II) dimer ($\text{[Rh}^{\text{II}}(\text{L})\text{]}_2$) cleaves homolytically in the presence of a substrate, two equivalents of the highly reactive rhodium(II) radical species, ($\text{[Rh}^{\text{II}}(\text{L})\text{]}^+$), are formed. These rhodium(II) radicals can then abstract a radical from the substrate to form monomeric rhodium(III) species (Figure 5.2). The products formed depend on the substrate. Some substrates result in the formation of two monomeric rhodium(III) products. For example, when $\text{[Rh}^{\text{II}}(\text{OEP})\text{]}_2$ reacts with benzyl bromide, a bromide radical is first abstracted by one of the $\text{[Rh}^{\text{II}}(\text{OEP})\text{]}^+$ radicals to form $\text{Rh}^{\text{III}}(\text{OEP})(\text{Br})$, and the benzyl radical then reacts with the second $\text{[Rh}^{\text{II}}(\text{OEP})\text{]}^+$ radical to form $\text{Rh}^{\text{III}}(\text{OEP})(\text{CH}_2\text{Ph})$ (Figure 5.3). Other substrates react
with rhodium(II) dimers to form products with ligands that are bridged between two rhodium(III) metal centres. For instance, terminal alkynes have been shown to react with $\text{[Rh}^{\text{II}}(\text{OEP})_2$) to form the product, $\text{trans-}(\text{OEP})\text{Rh}^{\text{III}}\text{-CH=CR-Rh}^{\text{III}}(\text{OEP})$ (Figure 5.3). This is an example of a radical chain transfer reaction, where one of the $\text{[Rh}^{\text{II}}(\text{OEP})\text{]}^\cdot$ radicals reacts with one of the alkyne carbon atoms, followed by transfer of the radical to the terminal end of the coordinated alkyne and subsequent reaction with the second $\text{[Rh}^{\text{II}}(\text{OEP})\text{]}^\cdot$ radical. Yet other substrates form single rhodium(III) products when they react with rhodium(II) dimers. For example, allylic compounds (such as allylbenzene, allyl cyanide, or hex-1-ene) react with $\text{[Rh}^{\text{II}}(\text{OEP})_2$) to form the products, $\text{Rh}^{\text{III}}(\text{OEP})(\text{CH}_2\text{CH=CHR})$ (Figure 5.3). In the postulated mechanism for this reaction, the $\text{[Rh}^{\text{II}}(\text{OEP})\text{]}^\cdot$ radical reacts with the terminal carbon of the alkene, followed by migration of the double bond to the terminal end of the axial ligand. It has been proposed that only one product forms in this reaction because the terminal hydrogen atom is then lost as a hydrogen radical, and two of these radicals then combine to form dihydrogen gas. Homolytic rhodium-rhodium bond cleavage tends to be favoured in low polarity solvents (such as benzene or toluene) and heterolytic bond cleavage tends to be favoured in high polarity solvent (such as pyridine). It is believed that this is because high polarity solvents support ionic reaction pathways, which lowers the energy of heterolytic reaction pathways relative to homolytic reaction pathways.$^{24,226}$

![Figure 5.2: General reaction for the homolytic cleavage of rhodium(II)-rhodium(II) dimers, followed by reaction with a substrate (RX)](image)

![Figure 5.3: Examples of reactions of rhodium(II) dimers that are believed to occur via homolytic cleavage of the rhodium-rhodium bond](image)
The rest of this introduction section discusses the reactivity of rhodium dimers with various substrates, focusing on those substrates that will be used for the activation of small molecules with Na[[Rh\(^{\text{III}}\)(L\(_m\))]\(_2\)Cl].

### 5.1.2 Reactions of rhodium-rhodium dimers with dihydrogen

The reaction of rhodium–rhodium dimers with dihydrogen gas usually forms the corresponding monomeric rhodium(III)-hydride complex (Figure 5.4). These are equilibrium reactions, and are believed to occur via homolytic rhodium-rhodium bond cleavage in low polarity solvents (such as benzene), or via heterolytic rhodium-rhodium bond cleavage in high polarity solvents (such as pyridine). The differences between these two mechanisms are discussed further in Section 5.1.7. If dihydrogen gas is removed from the reaction in low polarity solvents, the [Rh\(^{\text{III}}\)(L)]\(_2\) dimer reforms, whereas if dihydrogen gas is removed from the reaction in pyridine, a 1:1 mixture of [Rh\(^{\text{II}}\)(L)]\(^+\) and [Rh\(^{\text{III}}\)(L)(py)]\(^+\) forms. Dihydrogen overpressures of at least 0.25 atmospheres are therefore required to minimise reversion back to the dimer. It has been found that when low dihydrogen overpressures are used in low polarity deuterio-solvents, the \(^1\)H NMR signals of Rh\(^{\text{III}}\)(L)H broaden due to partial formation of a [Rh\(^{\text{II}}\)(L)]\(^•\) radical from the small amount of [Rh\(^{\text{II}}\)(L)]\(_2\) present in the solution.

The \(^1\)H NMR spectra of Rh\(^{\text{III}}\)(porphyrin)H and Rh\(^{\text{III}}\)(TMTAA)H complexes show distinctive upfield-shifted hydride signals, which are split into doublets by \(^1\)H–\(^{103}\)Rh coupling. For example, the hydride ligand of Rh\(^{\text{III}}\)(OEP)H was observed as a doublet at -41.28 ppm (\(J_{\text{1H-103Rh}} = 44\) Hz) in benzene-\(d_6\) at room temperature, and this hydride signal shifted slightly on changing the solution temperature. The chemical shifts of the OEP ligand protons were consistent with a diamagnetic rhodium(III) complex, as expected.\(^{226,227}\) The hydride ligand resonance occurred at similar \(^1\)H NMR chemical shifts for other Rh\(^{\text{III}}\)(porphyrin)H complexes in benzene-\(d_6\), for example, at -40.19 ppm (\(J_{\text{1H-103Rh}} = 43\) Hz) for Rh\(^{\text{III}}\)(TPP)H and at -40.18 ppm (\(J_{\text{1H-103Rh}} = 43\) Hz) for Rh\(^{\text{III}}\)(TTP)H (note: TPP = tetraphenylporphyrin; TTP = tetra-\(p\)-tolylporphyrin; see Figure 3.10 for the structure of these ligands).\(^{204}\) For the Rh\(^{\text{III}}\)(TMTAA)H complex, the hydride signal was observed at -20.2 ppm (\(J_{\text{1H-103Rh}} = 47.6\) Hz) in THF-\(d_8\) and at -24.1 ppm (\(J_{\text{1H-103Rh}} = 58.3\) Hz) in toluene-\(d_8\). The upfield shift of the hydride ligand in the Rh\(^{\text{III}}\)(porphyrin)H complexes compared to the Rh\(^{\text{III}}\)(TMTAA)H complex was attributed to the ring-current effect of the porphyrin ligands.\(^{15,24}\)
Rh\textsuperscript{III}(OEP)\textsubscript{2}H \rightleftharpoons 2 \text{Rh}\textsuperscript{III}(L)H

**Figure 5.4: Synthesis of Rh(III)-hydride complexes from rhodium(II) dimers (L = porphyrin or TMTAA)**

Rh\textsuperscript{III}(OEP)\textsubscript{2}H has also been characterised by \textsuperscript{1}H NMR spectroscopy in CD\textsubscript{2}Cl\textsubscript{2}. The hydride chemical shift and coupling constant in CD\textsubscript{2}Cl\textsubscript{2} (-41.61 ppm, \textit{J}_{\text{IH-103Rh}} = 44 \text{ Hz}) was similar to the hydride signal of Rh\textsuperscript{III}(OEP)\textsubscript{2}H in benzene-\textit{d}_6 (-41.28 ppm, \textit{J}_{\text{IH-103Rh}} = 44 \text{ Hz}). However, unlike the spectrum of Rh\textsuperscript{III}(OEP)\textsubscript{2}H in benzene-\textit{d}_6, the hydride signal of Rh\textsuperscript{III}(OEP)\textsubscript{2}H in CD\textsubscript{2}Cl\textsubscript{2} remained sharp in the absence of a dihydrogen atmosphere and no [Rh\textsuperscript{II}(OEP)]\textsubscript{2} was observed. However, a small amount of Rh\textsuperscript{III}(OEP)Cl was observed in the \textsuperscript{1}H NMR spectrum of Rh\textsuperscript{III}(OEP)\textsubscript{2}H in CD\textsubscript{2}Cl\textsubscript{2}, which was attributed to abstraction of a chlorine radical from the CD\textsubscript{2}Cl\textsubscript{2} solvent by a [Rh\textsuperscript{II}(OEP)]\textsuperscript{•} radical. This removed the [Rh\textsuperscript{II}(OEP)]\textsubscript{2} and [Rh\textsuperscript{II}(OEP)]\textsuperscript{•} species from solution and therefore prevented \textsuperscript{1}H NMR line broadening.\textsuperscript{228}

Other methods have also been used to synthesise Rh\textsuperscript{III}(porphyrin)\textsubscript{2}H complexes. For example, Rh\textsuperscript{III}(porphyrin)\textsubscript{2}H complexes have been synthesised by reducing the corresponding Rh\textsuperscript{III}(porphyrin)X complex (X = halide) with sodium borohydride in a 14:1 mixture of ethanol and 0.5 mol L\textsuperscript{-1} aqueous sodium hydroxide, followed by the addition of glacial acetic acid and removal of the solvent under a stream of nitrogen.\textsuperscript{200}

### 5.1.3 Reactions of rhodium-rhodium dimers with phosphines

A few papers that describe the reaction of rhodium(II) dimers with phosphines have been published. For example, as discussed in Section 3.1.5, [Rh\textsuperscript{II}(Rpc)]\textsubscript{2} was shown to react with trimethylphosphine to form a variety of products, depending on the reaction stoichiometry. Therefore, when one equivalent of trimethylphosphine was added per equivalent of [Rh\textsuperscript{II}(Rpc)]\textsubscript{2}, the mono-axially ligated [Rh\textsuperscript{II}(Rpc)]\textsubscript{2}(PMe\textsubscript{3}) adduct was synthesised, whereas two equivalents of trimethylphosphine gave the bis-axially ligated [Rh\textsuperscript{II}(Rpc)]\textsubscript{2}(PMe\textsubscript{3})\textsubscript{2} adduct, and four equivalents of trimethylphosphine gave the monomeric complex, Rh\textsuperscript{III}(Rpc•-)\textsubscript{2}(PMe\textsubscript{3})\textsubscript{2}. The latter complex was paramagnetic, and it was concluded that the Rpc ligand exists as a singly-reduced \(\pi\)-radical anion species (Rpc•).\textsuperscript{211}
Some interesting differences have been observed between the reactions of rhodium-OEP and rhodium-TPP complexes with excess triethylphosphine. Thus, the reaction of [Rh\textsuperscript{II}(OEP)\textsubscript{2}] or Rh\textsuperscript{III}(OEP)H with excess triethylphosphine has been shown to form a mono-axially ligated complex, Rh\textsuperscript{III}(OEP\textsuperscript{•})(PEt\textsubscript{3}), whereas the reaction of Rh\textsuperscript{III}(TPP)H with excess triethylphosphine formed a bis-axially ligated complex, Rh\textsuperscript{III}(TPP\textsuperscript{•})(PEt\textsubscript{3})\textsubscript{2}. These reactions were carried out in benzene or toluene under stringently air- and water-free conditions. Even when neat triethylphosphine was used, only the mono-phosphine complex, Rh\textsuperscript{III}(OEP\textsuperscript{•})(PEt\textsubscript{3}), was synthesised. Both phosphine complexes were paramagnetic, with broad contact-shifted NMR spectra. In the presence of air, Rh\textsuperscript{III}(OEP\textsuperscript{•})(PEt\textsubscript{3}) oxidised to a diamagnetic (PEt\textsubscript{3})(OEP)Rh\textsuperscript{III}-O-O-Rh\textsuperscript{III}(OEP)(PEt\textsubscript{3}) peroxo dimer and Rh\textsuperscript{III}(TPP\textsuperscript{•})(PEt\textsubscript{3})\textsubscript{2} oxidised to a diamagnetic [Rh\textsuperscript{III}(TPP)(PEt\textsubscript{3})\textsubscript{2}]\textsuperscript{+} complex.\textsuperscript{229} A stable bis-axially ligated triphenylphosphine complex, [Rh\textsuperscript{III}(TPP)(PPh\textsubscript{3})\textsubscript{2}]\textsuperscript{+}, has been synthesised under similar conditions.\textsuperscript{230}

Rhodium(III)-corrole complexes have also been synthesised with axial phosphine ligands. These complexes are neutral, diamagnetic, and air-stable, with one phosphine ligand per metal centre. They are usually synthesised from the free H\textsubscript{3}corrole ligand, a rhodium source (such as RhCl\textsubscript{3}·xH\textsubscript{2}O or [Rh(CO)\textsubscript{2}Cl\textsubscript{2}] and a mild base (such as potassium carbonate or sodium acetate) in the presence of excess phosphine and air. A few of these complexes have also been characterised by X-ray crystallography. Some examples of these complexes include Rh\textsuperscript{III}(tpfc)(PPh\textsubscript{3}), Rh\textsuperscript{III}(omc)(PPh\textsubscript{3}), Rh\textsuperscript{III}(omc)(PPh\textsubscript{2}Me), and Rh\textsuperscript{III}(tdcc)(PPh\textsubscript{3}), where tpfc = 5,10,15-tris(pentafluorobenzene)corrole, omc = 2,3,7,8,12,13,17,18-octamethylcorrole, and tdcc = 5,10,15-tris(2,6-dichlorophenyl)corrole.\textsuperscript{222-224}

5.1.4 Reduction of rhodium-rhodium dimers and derivatives to rhodium(I) complexes and subsequent reactions with electrophiles

Monomeric rhodium(I)-porphyrin and rhodium(I)-TMTAA complexes have been synthesised by reducing the corresponding rhodium(II) dimers or rhodium(III)-halide monomers using sodium borohydride, dissolved in a 14:1 mixture of ethanol and 0.5 mol L\textsuperscript{-1} aqueous sodium hydroxide. These reactions are usually performed under an argon or nitrogen atmosphere because the rhodium(I) complex rapidly oxidises upon exposure to air.\textsuperscript{15,231} These rhodium(I) complexes are usually four-coordinate and do not have axial ligands, which has been attributed to the filled \textit{d}_{z^2} orbital in these complexes.\textsuperscript{225} Proton NMR spectra of Na[Rh\textsuperscript{I}(TPP)],
Na[Rh\textsuperscript{I}(TTP)], \text{ and } \text{Na}[\text{Rh}^{\text{I}}(\text{OETAP})] \text{ have been obtained in degassed benzene-}d_6 \text{ (note that OETAP } = \text{ octaethyltetraazaporphyrin). This was achieved by reacting the corresponding \text{Rh}^{\text{III}}(\text{porphyrin})\text{Cl or Rh}^{\text{III}}(\text{porphyrin})\text{I complex with sodium borohydride in basic ethanol under stringently air-free conditions inside an NMR tube, followed by removal of the solvent under vacuum and introduction of degassed benzene-}d_6. \text{ The } ^1\text{H NMR signals of the porphyrin ligands in these Na[Rh}^{\text{I}}(\text{porphyrin})\text{] complexes are shifted considerably upfield compared to the spectra of the corresponding \text{Rh}^{\text{III}}(\text{porphyrin})\text{Cl complexes, as would be expected.}^{204,232}

The rhodium(I) centre of the Na[Rh\text{I}(\text{L})] complexes is nucleophilic, and has been shown to react with various electrophiles to give organometallic rhodium(III) complexes. These reactions are usually conducted by adding an electrophile \textit{in situ} to the Na[Rh\text{I}(\text{L})] complex generated from sodium borohydride in basic ethanol. Examples of these reactions include the synthesis of \text{Rh}^{\text{III}}(\text{L})(\text{alkyl}) complexes from alkyl halides, \text{Rh}^{\text{III}}(\text{OEP})(\text{CH}_2\text{CH}_2\text{CN}) \text{ from acrylonitrile, } \text{Rh}^{\text{III}}(\text{OEP})(\text{CH}=\text{CHR}) \text{ complexes from alkynes, } \text{Rh}^{\text{III}}(\text{TXP})(\text{C(O)Me}) \text{ from acetyl chloride, } \text{Rh}^{\text{III}}(\text{TTP})(\text{CH}_2\text{CH}_2)\text{Rh}^{\text{III}}(\text{TTP}) \text{ from 1,2-bromoethane, and } \text{Rh}^{\text{III}}(\text{porphyrin})\text{H complexes from dihydrogen (Section 5.1.2).}^{15,200,204,231,233} \text{ In contrast to these nucleophilic rhodium(I) complexes, the rhodium centres of most rhodium(III)-porphyrin complexes are electrophilic, and are known to react with various nucleophiles.}^{226} \text{ In the remainder of this section, the structural and spectroscopic properties of Rh}^{\text{III}}(\text{L})(\text{alkyl}) \text{ complexes (alkyl } = \text{ Me, Et, Bn) is discussed, so that they can be compared to similar Rh}^{\text{III}}(\text{L}_m)(\text{alkyl}) \text{ complexes discussed in Section 5.2.5.}

The methyl ligands of \text{Rh}^{\text{III}}(\text{L})\text{Me complexes are typically observed as upfield-shifted doublet resonances in the } ^1\text{H NMR spectra. For example, the methyl ligand of } \text{Rh}^{\text{III}}(\text{TMP})\text{Me (TMP } = \text{ tetramesitylporphyrin) was observed at -5.25 ppm (}J_{1\text{H}^{\text{I}},103\text{Rh}} = 2.9 \text{ Hz),}^{205} \text{ and similar values have been observed for other Rh}^{\text{III}}(\text{porphyrin})\text{Me complexes, such as } \text{Rh}^{\text{III}}(\text{OETAP})\text{Me (-6.16 ppm, }J_{1\text{H}^{\text{I}},103\text{Rh}} = 2.9 \text{ Hz).}^{232} \text{ For } \text{Rh}^{\text{III}}(\text{OEP})\text{Me,}^{232} \text{ Rh}^{\text{III}}(\text{TXP})\text{Me,}^{233} \text{ and } \text{Rh}^{\text{III}}(\text{TPP})\text{Me,}^{204} \text{ methyl proton doublets were observed at -6.02, -5.56, and -5.51 ppm, respectively, but } ^1\text{H}^{103}\text{Rh coupling constants were not reported for these complexes. These } ^1\text{H NMR spectra were all recorded in benzene-}d_6. \text{ Positive ion FAB mass spectrometry of various Rh}^{\text{III}}(\text{porphyrin})\text{Me complexes were also consistent with their expected formulations,}^{205,232} \text{ and X-ray crystal structures have been obtained for a few of these complexes.}^{232} \text{ Although the } ^1\text{H}^{103}\text{Rh coupling constant of the methyl ligand of the related complex, } \text{Rh}^{\text{III}}(\text{TMTAA})\text{Me, (3.6 Hz) was similar to the reported Rh}^{\text{III}}(\text{porphyrin})\text{Me complexes, the chemical shift of this methyl ligand (2.20
ppm) was significantly downfield from Rh\textsuperscript{III}(porphyrin)Me complexes, due to the absence of a porphyrin ring-current effect.\textsuperscript{15}

Rh\textsuperscript{II}(L)Et complexes (L = porphyrin or TMTAA) have also been synthesised, and the ethyl ligands of these complexes have been identified by upfield methylene quartets of doublets and upfield methyl triplet of doublets in their \(^1\text{H}\) NMR spectra. Because the methyl group is farther from the rhodium centre than the methylene group, \(^1\text{H}\)-\(103\text{Rh}\) coupling constants were found to be smaller for the methyl group protons than for the methylene group protons. For example, the methylene group of Rh\textsuperscript{III}(TMTAA)Et was observed at 3.08 ppm (\(J_{1\text{H}-103\text{Rh}} = 3.4\) Hz), and the methyl group was observed at 0.75 ppm (\(J_{1\text{H}-103\text{Rh}} = 2.5\) Hz) in benzene-\(d_6\).\textsuperscript{15} Although the chemical shifts of the methylene (-4.40 ppm) and methyl (-4.18 ppm) protons were quoted for Rh\textsuperscript{III}(TPP)Et, \(^1\text{H}\)-\(103\text{Rh}\) coupling constants were not given. The methylene group was probably upfield of the methyl group in Rh\textsuperscript{III}(TPP)Et, due to its closer proximity to the porphyrin ring-current.\textsuperscript{204} Only slight differences in the \(^1\text{H}\) NMR chemical shifts (less than 0.05 ppm) of the macrocyclic L ligands have been observed between the Rh\textsuperscript{III}(L)Et complexes and the corresponding Rh\textsuperscript{III}(L)Me complexes for the same L ligand.\textsuperscript{15,234}

A Rh\textsuperscript{III}(TMP)Bn complex has been synthesised by the reaction of benzyl bromide with Na[Rh\textsuperscript{I}(TMP)]. In benzene-\(d_6\), the methylene protons of the benzyl ligand appeared as a doublet at -3.15 ppm (\(J_{1\text{H}-103\text{Rh}} = 3.7\) Hz), and the phenyl ring protons of the benzyl ligand were observed at 3.66 ppm (ortho-H), 5.78 ppm (meta-H), and 6.24 ppm (para-H). These benzyl ligand protons were shifted considerably upfield relative to free benzyl bromide, which was due in part to the ring-current effect of the TMP porphyrin ligand.\textsuperscript{205}

Rh\textsuperscript{II}(L)Me complexes have also been synthesised by adding methyl iodide to various [Rh\textsuperscript{III}(L)]\textsubscript{2} dimers (for example, L = OETAP or TMTAA) to give 1:1 mixtures of Rh\textsuperscript{III}(L)Me and Rh\textsuperscript{III}(L)I. These two products can then separated by column chromatography.\textsuperscript{15,232} Various Rh\textsuperscript{III}(porphyrin)Me complexes have also be synthesised by heating the corresponding Rh\textsuperscript{III}(porphyrin)Cl complex in degassed methanol with excess potassium carbonate for 24 hours at 150 °C inside sealed vessels.\textsuperscript{235}
5.1.5 Reactions of rhodium-rhodium dimers with carbon monoxide

Rhodium(II) dimers are known to react with carbon monoxide to form several products, including [Rh\textsuperscript{II}(L)]\textsubscript{2}(CO) carbonyl adducts, (L)Rh\textsuperscript{III}-C(\textequiv O)-Rh\textsuperscript{III}(L) dimetal ketones, (L)Rh\textsuperscript{III}-C(\textequiv O)-C(\textequiv O)-Rh\textsuperscript{III}(L) dimetal diketones, and Rh\textsuperscript{III}(L)(CHO) formyl complexes. Furthermore, if ethanol is added to the reaction used to synthesise the Rh\textsuperscript{III}(L)(CHO) complex, metalloester complexes (Rh\textsuperscript{III}(L)(C(\textequiv O)OEt)) can be synthesised. The next section discusses each of these complexes and describes the general conditions for their formation. Except for the metalloester complexes, these complexes are usually only observed in situ in dry, degassed solutions and are unstable in the absence of an atmosphere of carbon monoxide.\textsuperscript{228}

5.1.5.1 Formation of [Rh\textsuperscript{II}(L)]\textsubscript{2}(CO), (L)Rh\textsuperscript{III}-C(\textequiv O)-Rh\textsuperscript{III}(L), and (L)Rh\textsuperscript{III}-C(\textequiv O)-C(\textequiv O)-Rh\textsuperscript{III}(L) complexes

Proton NMR experiments have shown that [Rh\textsuperscript{II}(L)]\textsubscript{2}(CO), (L)Rh\textsuperscript{III}-C(\textequiv O)-Rh\textsuperscript{III}(L) and (L)Rh\textsuperscript{III}-C(\textequiv O)-C(\textequiv O)-Rh\textsuperscript{III}(L) complexes (L = porphyrin or TMTAA) can be synthesised by reacting the corresponding [Rh\textsuperscript{II}(L)]\textsubscript{2} dimers with carbon monoxide in inert deutero-solvents (such as toluene-\textit{d8}) under air- and water-free conditions inside sealed NMR tubes (Figure 5.5). These three classes of complexes have been referred to in the literature as carbon monoxide adducts, dimetal ketones, and dimetal diketones, respectively. Dimetal ketones and dimetal diketones arise from reductive coupling of carbon monoxide to the rhodium centres. The ratio of the three products depends on the reaction conditions used and the steric bulk of the macrocyclic ligands. In many reactions, one product is formed exclusively.\textsuperscript{236,237}
Figure 5.5: Equilibrium reactions involved in the formation of carbonyl adducts, dimetal ketones, and dimetal diketones from the reaction of Rh(II)-porphyrin and Rh(II)-TMTAA dimers with carbon monoxide in dry degassed toluene-$d_8$

At room temperature, the reaction of $[\text{Rh}^{II}(\text{OEP})]_2$ with carbon monoxide in dry degassed toluene-$d_8$ gave a mixture of the $[\text{Rh}^{II}(\text{L})]_2(\text{CO})$ adduct and the $(\text{OEP})\text{Rh}^{III}-\text{C}(-\text{O})-\text{Rh}^{III}(\text{OEP})$ dimetal ketone. A dimetal diketone was not observed in this reaction. The ratio of the $(\text{OEP})\text{Rh}^{III}-\text{C}(-\text{O})-\text{Rh}^{III}(\text{OEP})$ dimetal ketone to the $[\text{Rh}^{II}(\text{OEP})]_2(\text{CO})$ adduct increased with increasing carbon monoxide pressure, reaching an upper limit of about 2.2:1 at carbon monoxide pressures above 13 atmospheres. $[\text{Rh}^{II}(\text{OEP})]_2(\text{CO})$ and $(\text{OEP})\text{Rh}^{III}-\text{C}(-\text{O})-\text{Rh}^{III}(\text{OEP})$ were only stable under an atmosphere of carbon monoxide, and completely reverted to $[\text{Rh}^{II}(\text{OEP})]_2$ after removing the carbon monoxide atmosphere via freeze-pump-thaw degassing.$^{236}$

The structures of $[\text{Rh}^{II}(\text{OEP})]_2(\text{CO})$ and $(\text{OEP})\text{Rh}^{III}-\text{C}(-\text{O})-\text{Rh}^{III}(\text{OEP})$ were determined by NMR and IR spectroscopies. For both complexes, the methylene protons for the OEP ethyl groups were diastereotopic by $^1\text{H}$ NMR spectroscopy, confirming that both complexes are dimeric. The carbonyl carbon of $[\text{Rh}^{II}(\text{OEP})]_2(\text{CO})$ was observed as a broad peak at 180 ppm by $^{13}\text{C}$ NMR spectroscopy. Peak broadening was attributed to exchange of the carbonyl ligand with free carbon monoxide. A carbonyl stretching frequency of 2094 cm$^{-1}$ in dry degassed benzene confirmed that a carbonyl ligand was indeed coordinated to $[\text{Rh}^{II}(\text{OEP})]_2(\text{CO})$. Meanwhile, $(\text{OEP})\text{Rh}^{III}-\text{C}(-\text{O})-\text{Rh}^{III}(\text{OEP})$ was identified by a triplet in the $^{13}\text{C}$ NMR spectrum at 116 ppm ($J_{13\text{C}-103\text{Rh}} = 44$ Hz), which is consistent with a carbonyl group coordinated to two $^{103}\text{Rh}$ centres through the carbonyl carbon atom. The carbonyl stretching frequency of $(\text{OEP})\text{Rh}^{III}-\text{C}(-\text{O})-\text{Rh}^{III}(\text{OEP})$ was identified at 1733 cm$^{-1}$. Because this stretching frequency is similar to organic ketones, and because the bulky porphyrin ligands are expected to stabilise the Rh-C-Rh bond in an approximately linear geometry, it was concluded that the -C(=O)- group of
(OEP)Rh$_{III}^{II}$-C(=O)-Rh$_{III}^{II}$(OEP) is best described as a dimetal ketone, with a sp$^2$-hybridised carbon atom and normal rhodium-carbon covalent bonds. The dimetal ketone therefore formed via reductive coupling of carbon monoxide ligands to two rhodium centres. This reaction is rare in organometallic chemistry. Thermodynamic studies have suggested that this reaction is facilitated by the weak rhodium-rhodium bond of [Rh$_{II}^{II}$(OEP)]$_2$ and the relatively strong rhodium-carbon bonds of the dimetal ketone.$^{236}$

When the reaction of [Rh$_{II}^{II}$(OEP)]$_2$ with carbon monoxide in dry degassed toluene-$d_6$ was repeated at temperatures significantly below room temperature using carbon monoxide pressures above 12 atmospheres, a (OEP)Rh$_{III}^{III}$-C(=O)-C(=O)-Rh$_{III}^{II}$(OEP) dimetal diketone was observed as a mixture with [Rh$_{II}^{II}$(OEP)]$_2$(CO) and (OEP)Rh$_{III}^{III}$-C(=O)-Rh$_{III}^{II}$(OEP). Like [Rh$_{II}^{II}$(L)]$_2$(CO) and (OEP)Rh$_{III}^{III}$-C(=O)-Rh$_{III}^{II}$(OEP), the methylene protons of (OEP)Rh$_{III}^{III}$-C(=O)-C(=O)-Rh$_{III}^{II}$(OEP) were diastereotopic by $^1$H NMR spectroscopy, suggesting that this complex still contains two rhodium centres in close proximity. The difference in chemical shift between the two methylene proton signals decreased from [Rh$_{II}^{II}$(OEP)]$_2$(CO) to (OEP)Rh$_{III}^{III}$-C(=O)-Rh$_{III}^{II}$(OEP) to (OEP)Rh$_{III}^{III}$-C(=O)-C(=O)-Rh$_{III}^{II}$(OEP). This was ascribed to the decreasing interaction between the two OEP ligands as the distance between these ligands increased. When 99.3% $^{13}$CO was used as the carbon monoxide source, (OEP)Rh$_{III}^{III}$-$^{13}$C(=O)-$^{13}$C(=O)-Rh$_{III}^{II}$(OEP) was identified by the presence of a sharp AA’XX’-type multiplet in the $^{13}$C NMR spectrum at 165.7 ppm, indicating that the $^{13}$C and $^{103}$Rh atoms are chemically equivalent but magnetically inequivalent. Simulation of this multiplet was used to calculate the following coupling constants: $^1J_{13C-103Rh} = 40$ Hz, $^1J_{13C-13C} = 20$ Hz, $^2J_{13C-103Rh} = 9$ Hz and $^3J_{103Rh-103Rh} = 4$ Hz. When 30% $^{13}$CO was used as the carbon monoxide source, the dimetal diketone was observed as a sharp doublet of doublets at 165.7 ppm ($^1J_{13C-103Rh} = 40$ Hz, $^2J_{13C-103Rh} = 9$ Hz) because this complex was predominantly in the (OEP)Rh$_{III}^{III}$-$^{13}$C(=O)-$^{13}$C(=O)-Rh$_{III}^{II}$(OEP) isotope form. As expected, the $^1J_{13C-103Rh}$ coupling constants of (OEP)Rh$_{III}^{III}$-C(=O)-C(=O)-Rh$_{III}^{II}$(OEP) (40 Hz) and (OEP)Rh$_{III}^{III}$-C(=O)-Rh$_{III}^{II}$(OEP) (44 Hz) were similar. Carbonyl stretching vibrations were not identified for the dimetal diketone by solution IR spectroscopy because they overlapped significantly with the dimetal ketone carbonyl stretching vibrations, and because the solubility of the dimetal diketone was low.$^{236}$

Unlike the reaction of [Rh$_{II}^{II}$(OEP)]$_2$ with carbon monoxide, the reaction of [Rh$_{II}^{II}$(TMTAA)]$_2$ with carbon monoxide (0.8-20 atmospheres) in dry degassed benzene-$d_6$ formed only the dimetal ketone complex at room temperature. NMR and IR spectroscopies of this complex were
similar to the OEP dimetal ketone. For example, the -C(=O)- carbon was observed as a triplet at 159.2 ppm \((J_{13C\cdot103Rh} = 45 \text{ Hz})\) by \(^{13}\text{C}\) NMR spectroscopy, with a carbonyl stretching frequency of 1726 cm\(^{-1}\).\(^{237}\)

Although the rhodium-rhodium bond is slightly stronger in \([\text{Rh}^{\text{II}}(\text{TMTAA})]_2\) than in \([\text{Rh}^{\text{II}}(\text{OEP})]_2\), thermodynamic studies suggested that inserting carbon monoxide into the rhodium-rhodium bond is more energetically favoured for \([\text{Rh}^{\text{II}}(\text{TMTAA})]_2\). This is because the rhodium-carbon bond was found to be significantly stronger for (TMTAA)Rh\(^{\text{III}}\)-C(=O)-Rh\(^{\text{III}}\)(TMTAA) than for (OEP)Rh\(^{\text{III}}\)-C(=O)-Rh\(^{\text{III}}\)(OEP). It has been speculated that this is because the TMTAA ligand is more flexible than the OEP ligand, which decreases steric repulsion between the TMTAA ligands. The reason that a dimetal diketone was observed in the OEP system and not in the TMTAA system is believed to be because the TMTAA system relieves steric strain via ligand distortions, whereas the more rigid OEP system relieves strain by reacting with a second carbon monoxide molecule to increase the distance between the two OEP ligands.\(^{209}\) Thermodynamic studies have suggested that insertion of a second C(=O) group into (OEP)Rh\(^{\text{III}}\)-C(=O)-Rh\(^{\text{II}}\)(OEP) is favoured by an increase in rhodium-carbon bond energy of about 5 kcal mol\(^{-1}\).\(^{217}\)

Based on the aforementioned observations, further studies were conducted using more sterically bulky porphyrin ligands (such as TXP; TXP = tetra(3,5-dimethylphenyl)porphyrin). In these experiments, the high steric strain between the two TXP ligands resulted in the exclusive formation of a dimetal diketone complex. Because only the dimetal diketone was synthesised in the TXP system, the IR stretching frequencies of (TXP)Rh\(^{\text{III}}\)-C(=O)-C(=O)-Rh\(^{\text{III}}\)(TXP) could be identified. These occurred at 1778 cm\(^{-1}\) and 1767 cm\(^{-1}\) for the \(^{12}\text{C}(=\text{O})-^{12}\text{C}(=\text{O})\) isomer, and at 1738 cm\(^{-1}\) and 1727 cm\(^{-1}\) for the \(^{13}\text{C}(=\text{O})-^{13}\text{C}(=\text{O})\) isomer. The presence of two carbonyl stretching vibrations in each complex suggested that the two carbonyl groups are not mutually \textit{trans} in these dimetal diketones. This is because only the asymmetric stretching vibration would be observed if the diketone unit had a \textit{trans} orientation, since the symmetric stretching vibration would not result in a net change to the dipole moment of the molecule. Because repulsion between the two carbonyl oxygen atoms would make a \textit{cis} orientation unlikely, it was concluded that the two carbonyl groups are neither fully \textit{cis} nor fully \textit{trans} in geometry, but are instead twisted somewhat away from a fully \textit{trans} orientation. The similarity of the carbonyl stretching frequencies of (TXP)Rh\(^{\text{III}}\)-C(=O)-C(=O)-Rh\(^{\text{III}}\)(TXP) to organic dialkyl \(\alpha\)-diketone complexes
(1710-1740 cm\(^{-1}\)) again suggested that this class of complexes can be described as dimetal diketones.\(^{233}\)

5.1.5.2 Formation of Rh\(^{III}\)(L)(CHO) complexes

Rhodium(III)-formyl complexes (Rh\(^{III}\)(L)(CHO); L = porphyrin or TMTAA) have been synthesised by reacting rhodium(II) dimers with carbon monoxide and a hydrogen source, or by reacting rhodium(III)-hydrides with carbon monoxide. Three different routes have been used to synthesise rhodium(III)-formyl complexes in high yield (usually greater than 95\%) under degassed conditions. In the first route (Figure 5.6), Rh\(^{III}\)(L)(CHO) complexes can be synthesised by adding carbon monoxide and dihydrogen to [Rh\(^{II}\)(L)]\(_2\) dimers in dry inert solvents, such as benzene-\(d_6\). The second reaction in Figure 5.6 illustrates that these rhodium(III)-formyl complexes can also be synthesised using water as the source of the formyl hydrogen atom, producing carbon dioxide as the by-product. Meanwhile, the third route in Figure 5.6 demonstrates that rhodium(III)-formyl complexes can also be produced from rhodium(III)-hydrides and carbon monoxide. Because these processes are reversible, Rh\(^{III}\)(L)(CHO) complexes are only stable under an atmosphere of carbon monoxide. Although the second reaction in Figure 5.6 is not reversible, if the carbon monoxide atmosphere is removed from this reaction, the formyl ligand is lost and [Rh\(^{II}\)(L)]\(_2\) forms via the reverse of the first reaction shown in Figure 5.6.\(^{24,238}\) If D\(_2\) or D\(_2\)O is used instead of H\(_2\) or H\(_2\)O, the corresponding Rh\(^{III}\)(L)(CDO) complex is synthesised,\(^{238}\) and if \(^{13}\)CO is used, the corresponding Rh\(^{III}\)(L)(\(^{13}\)CHO) complex is synthesised.\(^{239}\)

\[
[Rh^{II}(L)]_2 + H_2 + 2 CO \rightleftharpoons 2 Rh^{III}(L)(CHO)
\]

\[
[Rh^{II}(L)]_2 + H_2O + 3 CO \rightarrow 2 Rh^{III}(L)(CHO) + CO_2
\]

\[
Rh^{III}(L)H + CO \rightleftharpoons Rh^{III}(L)(CHO)
\]

Figure 5.6: Three different routes to the formation of Rh(III)-formyl complexes. L = macrocyclic ligand (such as OEP or TMTAA)

A mechanism has been proposed for the second reaction given Figure 5.6. This mechanism (Figure 5.7) begins with the formation of Rh\(^{III}\)(L)H and a highly reactive Rh\(^{III}\)(L)(C(=OH)OH)
intermediate from the reaction of $[\text{Rh}^{\text{III}}(\text{L})]_2$ with carbon monoxide and water. The $\text{Rh}^{\text{III}}(\text{L})(\text{C}(=\text{O})\text{OH})$ intermediate then loses carbon dioxide to form another equivalent of $\text{Rh}^{\text{III}}(\text{L})\text{H}$. Finally, $\text{Rh}^{\text{III}}(\text{L})\text{H}$ reacts with the excess carbon monoxide via the third reaction of Figure 5.6, giving $\text{Rh}^{\text{III}}(\text{L})(\text{CHO})$ as the ultimate product. This process is an example of a water-gas shift reaction, where the hydrogen atoms from the water molecule form a rhodium(III)-hydride complex instead of forming dihydrogen gas (see Figure 1.33 for a general water-gas shift reaction).\textsuperscript{238}

\[
[\text{Rh}^{\text{II}}(\text{L})]_2 + \text{H}_2\text{O} + \text{CO} \rightarrow \text{Rh}^{\text{III}}(\text{L})(\text{C}(=\text{O})\text{OH}) + \text{Rh}^{\text{III}}(\text{L})\text{H}
\]

\[
\text{Rh}^{\text{III}}(\text{L})(\text{C}(=\text{O})\text{OH}) \rightleftharpoons \text{Rh}^{\text{III}}(\text{L})\text{H} + \text{CO}_2
\]

\[
2 \text{Rh}^{\text{III}}(\text{L})\text{H} + 2 \text{CO} \rightleftharpoons 2 \text{Rh}^{\text{III}}(\text{L})(\text{CHO})
\]

\[
[\text{Rh}^{\text{II}}(\text{L})]_2 + \text{H}_2\text{O} + 3 \text{CO} \rightarrow 2 \text{Rh}^{\text{III}}(\text{L})(\text{CHO}) + \text{CO}_2
\]

\textbf{Figure 5.7: Postulated mechanism for the reaction of Rh(II) dimers with carbon monoxide and water, to form Rh(III)-metalloformyl complexes}

A mechanism has also been proposed for the reaction of $\text{Rh}^{\text{III}}(\text{OEP})\text{H}$ with carbon monoxide. In this mechanism (Figure 5.8), $\text{Rh}^{\text{III}}(\text{OEP})(\text{CHO})$ is believed to form via a radical chain reaction. This reaction begins with the formation of $[\text{Rh}^{\text{II}}(\text{OEP})]_2$ via the loss of dihydrogen from $\text{Rh}^{\text{III}}(\text{OEP})\text{H}$. The rhodium-rhodium bond of $[\text{Rh}^{\text{II}}(\text{OEP})]_2$ then breaks homolytically to form two $[\text{Rh}^{\text{II}}(\text{OEP})]^{\bullet}$ radicals. These radicals then react with carbon monoxide to form $[\text{Rh}^{\text{II}}(\text{OEP})(\text{CO})]^{\bullet}$ radicals, and the radical transfers from the rhodium centre to the carbonyl carbon atom. $[\text{Rh}^{\text{II}}(\text{OEP})(\text{CO})]^{\bullet}$ then abstracts a hydride radical from $\text{Rh}^{\text{III}}(\text{OEP})\text{H}$, forming $\text{Rh}^{\text{III}}(\text{OEP})(\text{CHO})$. Another $[\text{Rh}^{\text{II}}(\text{OEP})]^{\bullet}$ radical is generated in this process, which reacts with carbon monoxide to form more $[\text{Rh}^{\text{II}}(\text{OEP})(\text{CO})]^{\bullet}$, and $[\text{Rh}^{\text{II}}(\text{OEP})(\text{CO})]^{\bullet}$ in turn reacts with $\text{Rh}^{\text{III}}(\text{OEP})\text{H}$ to yield more $\text{Rh}^{\text{III}}(\text{OEP})(\text{CHO})$. Because the reaction is catalytic, only a small amount of $[\text{Rh}^{\text{II}}(\text{OEP})]_2$ has to form from $\text{Rh}^{\text{III}}(\text{OEP})\text{H}$ to initiate the reaction. The mechanism for the formation of $\text{Rh}^{\text{III}}(\text{OEP})(\text{CHO})$ from $[\text{Rh}^{\text{II}}(\text{OEP})]_2$, carbon monoxide, and dihydrogen (the first reaction in Figure 5.6) is believed to be similar to the mechanism in Figure 5.8.\textsuperscript{240}
Figure 5.8: Proposed radical chain mechanism for the synthesis of \( \text{Rh}^{\text{III}}(\text{L})(\text{CHO}) \) from \( \text{Rh}^{\text{III}}(\text{L})\text{H} \) and carbon monoxide. Although \( \text{L} = \text{OEP} \) in this reaction, this mechanism is also believed to occur for complexes of other \( \text{L} \) ligands, such as TMTAA.

Another method that can be used to synthesise \( \text{Rh}^{\text{III}}(\text{porphyrin})(\text{CHO}) \) complexes is shown in Figure 5.9. This involves the reaction of \( \text{Rh}^{\text{III}}(\text{porphyrin})(\text{Cl})(\text{CO}) \) with carbon monoxide and solid potassium hydroxide in benzene-\( d_6 \), yielding \( \text{Rh}^{\text{III}}(\text{porphyrin})(\text{CHO}) \), carbon dioxide, and potassium chloride. This route circumvents the use of \( [\text{Rh}^{\text{II}}(\text{L})]_2 \) or \( \text{Rh}^{\text{III}}(\text{L})\text{H} \). A mechanism has been postulated for this reaction (Figure 5.9). This begins with nucleophilic attack of the coordinated carbonyl ligand by potassium hydroxide, producing \( \text{Rh}^{\text{III}}(\text{porphyrin})(\text{C} (=\text{O})\text{OH}) \) and potassium chloride. \( \text{Rh}^{\text{III}}(\text{porphyrin})(\text{C} (=\text{O})\text{OH}) \) is unstable under these conditions and loses carbon dioxide to form \( \text{Rh}^{\text{III}}(\text{porphyrin})\text{H} \). Because this step is much faster than the first step, \( \text{Rh}^{\text{III}}(\text{porphyrin})(\text{C} (=\text{O})\text{OH}) \) was not observed when the reaction was monitored by \( ^1\text{H} \) NMR spectroscopy. In the final step, \( \text{Rh}^{\text{III}}(\text{porphyrin})\text{H} \) reacts reversibly with carbon monoxide to give the formyl complex. Like the \( \text{Rh}^{\text{III}}(\text{L})(\text{CHO}) \) complexes synthesised via the routes given in Figure 5.6, these \( \text{Rh}^{\text{III}}(\text{porphyrin})(\text{CHO}) \) complexes are only stable in the presence of excess carbon monoxide, and revert back to \( \text{Rh}^{\text{III}}(\text{porphyrin})\text{H} \) after removing the carbon monoxide atmosphere via freeze-pump-thaw degassing.
Rh\textsuperscript{III}(L)(Cl)(CO) + KOH $\rightarrow$ Rh\textsuperscript{III}(L)(C(=O)OH) + KCl

Rh\textsuperscript{III}(L)(C(=O)OH) $\rightarrow$ Rh\textsuperscript{III}(L)H + CO\textsubscript{2}

Rh\textsuperscript{III}(L)H + CO $\rightleftharpoons$ Rh\textsuperscript{III}(L)(CHO)

Rh\textsuperscript{III}(L)(Cl)(CO) + CO + KOH $\rightarrow$ Rh\textsuperscript{III}(L)(CHO) + KCl + CO\textsubscript{2}

Figure 5.9: Proposed mechanism for the synthesis of Rh\textsuperscript{III}(porphyrin)(CHO) complexes from the reaction of Rh\textsuperscript{III}(porphyrin)(CO)(Cl) complexes with carbon monoxide and potassium chloride in benzene-$d_6$

Rh\textsuperscript{III}(L)(CHO) complexes have been characterised by NMR and IR spectroscopies. For L = OEP, TPP, and TTP, formyl ligand protons have been observed at 2.90, 3.18, and 3.24 ppm, respectively, in benzene-$d_6$. These occur as doublets due to coupling between the $^1$H and $^{103}$Rh nuclei ($J_{1H-103Rh} = 1.75$-$1.8$ Hz). In comparison, the formyl proton of Rh\textsuperscript{III}(TMTAA)(CHO) was observed at 11.9 ppm in THF-$d_8$ and at 11.5 ppm in toluene-$d_8$ ($J_{1H-103Rh} = 0.6$ Hz). These differences were again due to the ring-current effect of the porphyrin ligands. In the proton-coupled $^{13}$C NMR spectra of these Rh\textsuperscript{III}(L)(CHO) complexes, the formyl carbon atom appeared as a doublet of doublets at 194.4 ppm for L = OEP ($J_{13C-1H} = 200$ Hz, $J_{13C-103Rh} = 29$ Hz) in benzene-$d_6$; at 194 ppm for L = TPP ($J_{13C-1H} = 200$ Hz, $J_{13C-103Rh} = 30$ Hz) in benzene-$d_6$; and at 220.1 ppm for L = TMTAA ($J_{13C-1H} = 178.2$ Hz, $J_{13C-103Rh} = 36.2$ Hz) in THF-$d_8$.

Carbonyl stretching frequencies for the formyl ligands of Rh\textsuperscript{III}(TMTAA)(CHO), Rh\textsuperscript{III}(OEP)(CHO), and Rh\textsuperscript{II}(OEP)(^{13}$CHO$) were observed at 1697 cm\textsuperscript{-1}, 1700 cm\textsuperscript{-1}, and 1667 cm\textsuperscript{-1}, respectively. The latter complex was synthesised using $^{13}$CO as the carbon monoxide source.\textsuperscript{15,24,238,239} These stretching frequencies are much higher than for most metalloformyl complexes (1550-1650 cm\textsuperscript{-1}), which usually have low oxidation state metal centres. This has been attributed to the weaker d-$\pi$ backbonding between the rhodium(III) metal centre and the formyl ligand in Rh\textsuperscript{III}(OEP)(CHO) and Rh\textsuperscript{III}(TMTAA)(CHO) than in the lower oxidation state metalloformyl complexes. The bonding between rhodium(III) and the formyl carbon in Rh\textsuperscript{III}(porphyrin)(CHO) and Rh\textsuperscript{III}(TMTAA)(CHO) has therefore been described as a normal covalent bond between an sp\textsuperscript{2} hybridised formyl carbon atom and a half-filled rhodium(III) $d_{z2}$ orbital, with minimal rhodium-formyl $\pi$-bonding.\textsuperscript{238,239} It is unlikely that the formyl ligand of Rh\textsuperscript{III}(OEP)(CHO) coordinates to the rhodium centre in a dihapto geometry, because the carbonyl

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stretching frequency of this complex is very different from typical dihapto formyl complexes (around 1470 cm\(^{-1}\)).\(^{227}\)

An X-ray-quality crystal of Rh\(^{III}\)(OEP)(CHO) was obtained by evaporation from a benzene solution under a stream of carbon monoxide. The relatively short C=O bond length of the formyl ligand in this complex (1.175(5) Å) compared to lower oxidation state metalloformyl complexes has also been attributed to the weaker d-\(\pi\) backbonding in Rh\(^{III}\)(OEP)(CHO). The Rh-C bond of Rh\(^{III}\)(OEP)(CHO) (1.896(6) Å) was significantly shorter than many other organometallic rhodium(III)-OEP complexes, such as Rh\(^{III}\)(OEP)(CH\(_3\)) (Rh-C = 2.031 Å). These bond length comparisons were used to infer that the formyl group is more like an organic aldehyde (Rh-C(=O)H) in the Rh\(^{III}\)(OEP)(CHO) complex than in the lower oxidation state monohapto metalloformyl complexes. This is because the Rh=C(-O)H resonance form contributes significantly to the structure of the latter complexes. Furthermore, the \(^{13}\)C-\(^{1}\)H coupling constants of the formyl carbon atoms of Rh\(^{III}\)(porphyrin)(CHO) and Rh\(^{III}\)(TMTAA)(CHO) (178.2 to 200 Hz) were much closer to the \(^{13}\)C-\(^{1}\)H coupling constants of organic aldehydes (170-180 Hz) than to the \(^{13}\)C-\(^{1}\)H coupling constants of the lower oxidation state monohapto formyl complexes (120-150 Hz).\(^{227}\) The stability of the formyl ligand of Rh\(^{III}\)(OEP)(CHO) has therefore been attributed to the ability of the rhodium complex to form covalent bonds, to the relatively high oxidation state of the rhodium(III) metal centre, and to the rigidity of the macrocycle.\(^{238}\)

An X-ray crystal structure of Rh\(^{III}\)(TMTAA)(CHO) was also obtained. Although the C=O bond length of Rh\(^{III}\)(TMTAA)(CHO) (1.179(3) Å) and Rh\(^{III}\)(OEP)(CHO) (1.175(5) Å) were similar, the Rh-C bond length was slightly longer for Rh\(^{III}\)(TMTAA)(CHO) (1.931(3) Å) than for Rh\(^{III}\)(OEP)(CHO) (1.896(6) Å), suggesting that formyl ligand coordination might be slightly stronger for Rh\(^{III}\)(OEP)(CHO).\(^{24}\)

When the reaction of [Rh\(^{III}\)(OEP)]\(_2\) with carbon monoxide and dihydrogen was irradiated at room temperature, formaldehyde formed catalytically. This reaction was conducted in a sealed NMR tube in dry, degassed benzene-\(\text{d}_6\). However, at 80 °C, methanol was produced catalytically instead of formaldehyde. Although both reactions were catalytic, after stopping the irradiation (with 300 nm light), the formaldehyde and methanol products slowly reacted with the rhodium(III)-OEP species to form Rh\(^{III}\)(OEP)(CHO) and Rh\(^{III}\)(OEP)H. In the postulated mechanism for the room temperature reaction, irradiation cleaves the rhodium-carbon bond of
the Rh\textsuperscript{III}(OEP)(CHO) intermediate formed in the reaction, forming a •CHO radical that then abstracts a hydrogen radical from a Rh\textsuperscript{III}(OEP)H intermediate, producing formaldehyde. A \([\text{Rh}\textsuperscript{II}(\text{OEP})]\)• radical is formed in this process, which can then react with a second \([\text{Rh}\textsuperscript{II}(\text{OEP})]\)• radical to reform the \([\text{Rh}\textsuperscript{II}(\text{OEP})]\)\textsubscript{2} complex and begin another turnover of the catalytic cycle. At 80 °C, methanol is believed to form because the formaldehyde product reacts with the hydride ligand of Rh\textsuperscript{III}(OEP)H. This forms a Rh\textsuperscript{III}(OEP)(CH\textsubscript{2}OH) intermediate which then reacts with a second Rh\textsuperscript{III}(OEP)H molecule, forming a \([\text{Rh}\textsuperscript{II}(\text{OEP})]\)• radical and generating methanol as a by-product.\textsuperscript{242}

The synthesis of Rh\textsuperscript{III}(OEP)(CHO) from \([\text{Rh}\textsuperscript{II}(\text{OEP})]\)\textsubscript{2}, carbon monoxide, and water in dry degassed CD\textsubscript{2}Cl\textsubscript{2} was found to be much slower than the analogous reaction in benzene-\textsubscript{d\textsubscript{6}}. This reaction took 19 days for \([\text{Rh}\textsuperscript{II}(\text{OEP})]\)\textsubscript{2} to completely react at room temperature, and three products were observed by \textsuperscript{1}H NMR spectroscopy: Rh\textsuperscript{III}(OEP)(CHO), Rh\textsuperscript{III}(OEP)H, and Rh\textsuperscript{III}(OEP)Cl, in a ratio of 11.4 : 1.0 : 1.4, respectively. In contrast, only Rh\textsuperscript{III}(OEP)(CHO) was observed in benzene-\textsubscript{d\textsubscript{6}}.\textsuperscript{228}

5.1.5.3 Formation of Rh\textsuperscript{III}(L)(C(=O)OEt) complexes

The aforementioned reaction of \([\text{Rh}\textsuperscript{II}(\text{OEP})]\)\textsubscript{2} with carbon monoxide and water in CD\textsubscript{2}Cl\textsubscript{2} was repeated with the addition of 0.7% (v/v) ethanol. After six hours at room temperature, a mixture of 1 : 3 : 0.5 of Rh\textsuperscript{III}(OEP)(CHO), Rh\textsuperscript{III}(OEP)Cl, and Rh\textsuperscript{III}(OEP)(C(=O)OEt), respectively, was observed. The C(=O)OEt carbethoxy ligand of Rh\textsuperscript{III}(OEP)(C(=O)OEt) was identified by the presence of a quartet (0.89 ppm, methylene) and a triplet (-1.10 ppm, methyl) in the \textsuperscript{1}H NMR spectrum, and by the presence of a carbonyl carbon doublet at 151.4 ppm (J\textsubscript{13C-103Rh} = 46 Hz) in the \textsuperscript{13}C NMR spectrum. The carbonyl stretching frequency of Rh\textsuperscript{III}(OEP)(C(=O)OEt) (at 1675 cm\textsuperscript{-1}) suggested that a carbethoxy ligand was indeed present. When \textsuperscript{13}CO was used as a reagent, Rh\textsuperscript{III}(OEP)(\textsuperscript{13}C(=O)OEt) was synthesised, which suggested that a carbonyl ligand first coordinates to the rhodium centre, followed by nucleophilic attack of this carbonyl carbon atom by ethanol. After removal of the carbon monoxide by freeze-pump-thaw degassing, Rh\textsuperscript{III}(OEP)(CHO) completely reacted to form Rh\textsuperscript{III}(OEP)H. However, when carbon monoxide was reintroduced, Rh\textsuperscript{III}(OEP)(CHO) reformed and no Rh\textsuperscript{III}(OEP)H was observed. \([\text{Rh}\textsuperscript{II}(\text{OEP})]\)\textsubscript{2} was not observed in these reactions, because any \([\text{Rh}\textsuperscript{II}(\text{OEP})]\)• radical formed in these reactions probably abstracts a chlorine radical from the CD\textsubscript{2}Cl\textsubscript{2} solvent to form Rh\textsuperscript{III}(OEP)Cl instead of reacting with another \([\text{Rh}\textsuperscript{II}(\text{OEP})]\)• radical to reform \([\text{Rh}\textsuperscript{II}(\text{OEP})]\)\textsubscript{2}. The relative amount of
\( \text{Rh}^{\text{III}}(\text{OEP})(\text{C}=\text{O})\text{OEt} \) did not change significantly during these manipulations, suggesting that this complex is stable in the absence of carbon monoxide.\textsuperscript{228}

Irradiation of the above reaction with 300 nm light gave \( \text{Rh}^{\text{III}}(\text{OEP})(\text{C}=\text{O})\text{OEt} \) in much higher yield.

In this method, carbon monoxide was added to \([\text{Rh}^{\text{II}}(\text{OEP})]_2\) in dry, degassed \( \text{CD}_2\text{Cl}_2 \) containing with 0.12% (v/v) ethanol. After three days at room temperature, the reaction was irradiated with 300 nm light for three hours at room temperature. Only \( \text{Rh}^{\text{III}}(\text{OEP})\text{Cl} \) and \( \text{Rh}^{\text{III}}(\text{OEP})(\text{C}=\text{O})\text{OEt} \) were detected under these conditions. Both complexes were relatively air stable, and were therefore separated by flash chromatography on silica gel. \( \text{Rh}^{\text{III}}(\text{OEP})(\text{C}=\text{O})\text{OEt} \) was obtained in 29% yield. Elemental analysis and X-ray crystallography confirmed the formulation as \( \text{Rh}^{\text{III}}(\text{OEP})(\text{C}=\text{O})\text{OEt} \). Although the carbonyl C=O bond length (1.163(9) Å) of the \( \text{C}(=\text{O})\text{OEt} \) ligand was significantly shorter than most organic esters (1.22-1.23 Å), it was similar to the C=O bond length of the formyl ligand in \( \text{Rh}^{\text{III}}(\text{OEP})(\text{CHO}) \) (1.175(5) Å). The Rh-C bond lengths of \( \text{Rh}^{\text{III}}(\text{OEP})(\text{C}=\text{O})\text{OEt} \) (1.918(9) Å) and \( \text{Rh}^{\text{III}}(\text{OEP})(\text{CHO}) \) (1.896(6) Å) were also similar.\textsuperscript{228}

### 5.1.6 Reactions of rhodium-rhodium dimers and derivatives with alkynes

A handful of papers have been published on the reaction of rhodium(II) dimers with alkynes. Only \([\text{Rh}^{\text{II}}(\text{OEP})]_2\) has been used in these reactions. When ethyne or phenylacetylene was added to \([\text{Rh}^{\text{II}}(\text{OEP})]_2\) in degassed benzene, the corresponding \( \text{trans}-(\text{OEP})\text{Rh}^{\text{III}}-\text{CH}=\text{CR}-\text{Rh}^{\text{III}}(\text{OEP}) \) complexes (\( R = \text{H, Ph} \)) were formed in approximately 70% yield after one day at room temperature. The complex in which \( R = \text{H} \) precipitated out of solution and was recrystallised from 19:1 dichloromethane/pyridine, affording the bis-pyridine adduct, \( \text{trans}-(\text{py})(\text{OEP})\text{Rh}^{\text{III}}-\text{CH}=\text{CH-Rh}^{\text{III}}(\text{OEP})(\text{py}) \). The two Rh-CH\(=\) protons were equivalent by \( ^1\text{H} \) NMR spectroscopy (\(-9.92 \text{ ppm doublet, } J_{1\text{H},103\text{Rh}} = 2 \text{ Hz} \)) and were shifted significantly upfield by the ring-current effect of the porphyrin ligands. Pyridine was not added to the \( R = \text{Ph} \) complex, which was therefore isolated as a \( \text{trans}-(\text{OEP})\text{Rh}^{\text{III}}-\text{CH}=\text{CPh-Rh}^{\text{III}}(\text{OEP}) \) species. Elemental analysis agreed with the expected formulations for both complexes. A homolytic reaction pathway has been postulated for the formation of these complexes, which begins with homolytic cleavage of \([\text{Rh}^{\text{II}}(\text{OEP})]_2\) to form two \([\text{Rh}^{\text{II}}(\text{OEP})]\) radicals. The alkyne then coordinates to one of these \([\text{Rh}^{\text{II}}(\text{OEP})]\) radicals, and the radical is transferred to the terminal carbon atom to form a
[Rh^{II}(OEP)(CH=C'R)] intermediate. In the final step, this intermediate reacts with the second [Rh^{II}(OEP)]• radical, yielding trans-(OEP)Rh^{III}-CH=CR-Rh^{II}(OEP).^{200,226

The reaction of monomeric rhodium-OEP complexes with alkynes have also been published. For example, the Na[Rh^{I}(OEP)] complex that is formed from the reduction of Rh^{III}(OEP)Cl with sodium borohydride (see Section 5.1.4) reacts with ethyne or phenylacetylene to form Rh^{III}(OEP)(CH=CH$_2$) or cis-Rh^{III}(OEP)(CH=CHPh), respectively. These complexes are air stable and were characterised by elemental analysis, $^1$H NMR spectroscopy, and UV-visible absorption spectroscopy. A cis orientation for the alkene protons of the cis-Rh^{III}(OEP)(CH=CHPh) complex was confirmed by the small vicinal coupling constant ($J_{1H-1H} = 7.5$ Hz) compared to the trans-Rh^{III}(OEP)(CH=CHPh) isomer ($J_{1H-1H} = 13.0$ Hz). This trans isomer was synthesised from Na[Rh^{I}(OEP)] and trans-β-bromostyrene. The stability of cis-Rh^{III}(OEP)(CH=CHPh) was surprising considering the steric bulk of the phenyl group and its subsequent close approach to the OEP ligand. Consequently, the =CHPh group protons of the cis isomer were shifted significantly upfield compared to the trans isomer, due to the strong influence of the porphyrin ring-current.\textsuperscript{231

The reaction of alkynes with Rh^{III}(OEP)(H$_2$O)Cl has also been reported. It was found that different alkynes gave different products. For example, ethyne reacts with Rh^{III}(OEP)(H$_2$O)Cl in benzene to give only the trans-Rh^{III}(OEP)(CH=CHCl) product, whereas hex-1-yne (HC≡C₆Bu) gave only Rh^{III}(OEP)(C(=O)CH$_2$Bu). Phenylacetylene (HC≡CPh) gave a mixture of Rh^{III}(OEP)(CH=C(Cl)Ph) and Rh^{III}(OEP)(C(=O)CH$_2$Ph) in a ratio of approximately 1:1. A possible mechanism for the formation of these products is illustrated in Figure 5.10. In the first route (top half of Figure 5.10), the alkyne displaces the water and chloride ligands on Rh^{III}(OEP)(H$_2$O)Cl to give a π-bound alkyne intermediate. This intermediate then reacts with the chloride anion lost from Rh^{III}(OEP)(H$_2$O)Cl, forming Rh^{III}(OEP)(CH=CRCl). The R group occurs on the terminal carbon atom due to its steric bulk. The chloride anion probably reacts with the terminal carbon atom because the CH carbon atom of the π-bound alkyne intermediate is closer to the rhodium centre than the CR carbon atom (due to the steric bulk of the R group), and so more positive charge density will reside on the CR carbon atom than on the CH carbon atom, making it more susceptible to nucleophilic attack. For trans-Rh^{III}(OEP)(CH=CHCl), the chlorine atom is cis to the proton on the α-carbon atom, whereas in Rh^{III}(OEP)(CH=C(Cl)Ph), the chlorine atom is trans to the proton on the α-carbon atom. These differences are believed to be due to differences in steric bulk between the R groups, because the chlorine atom is the

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bulkiest group on the terminal carbon atom in the former complex, whereas the phenyl group is the bulkiest group on the terminal carbon atom in the latter complex.\textsuperscript{243}

In the second route (lower half of Figure 5.10), the \( \pi \)-bound alkyne intermediate rearranges to a vinylidene intermediate. This intermediate then reacts with the water ligand lost from \( \text{Rh}^{\text{III}}(\text{OEP})(\text{H}_2\text{O})\text{Cl} \) to form \( \text{Rh}^{\text{III}}(\text{OEP})(\text{C}(=\text{O})\text{CH}_2\text{R}) \), which then loses a proton to form \( \text{Rh}^{\text{III}}(\text{OEP})(\text{C}(=\text{O})\text{CH}_2\text{R}) \). Thus, different \( \text{R} \) groups on the alkyne (\( \text{CH}=\text{CR} \)) favour either the first route (for \( \text{R} = \text{H} \)) or the second route (for \( \text{R} = \text{"Bu} \)), or both routes are favoured to similar extents (for \( \text{R} = \text{Ph} \)). This is perhaps because the \( \pi \)-bound alkyne and vinylidene intermediates are favoured to different extents with different \( \text{R} \) groups. For example, a vinylidene intermediate would be unlikely to form if \( \text{R} = \text{H} \).\textsuperscript{243}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure510.png}
\caption{Proposed mechanism for the synthesis of \( \text{Rh}^{\text{III}}(\text{OEP})(\text{CH}=\text{CRCI}) \) and \( \text{Rh}^{\text{III}}(\text{OEP})(\text{C}(=\text{O})\text{CH}_2\text{R}) \) from \( \text{Rh}^{\text{III}}(\text{OEP})(\text{H}_2\text{O})\text{Cl} \) and alkynes}
\end{figure}

In the \(^1\text{H}\) NMR spectrum of \textit{trans}-\( \text{Rh}^{\text{III}}(\text{OEP})(\text{CH}=\text{CHCl}) \), the \( \text{Rh}-\text{CH} \) proton was observed as a doublet of doublets at -1.48 ppm (\( J_{\text{HH}} = 12 \text{ Hz} \), \( J_{\text{HH}-103\text{Rh}} = 2 \text{ Hz} \)) and the \( =\text{CHCl} \) proton was observed as a doublet at -1.79 ppm (\( J_{\text{HH}} = 12 \text{ Hz} \)) in CDCl\(_3\). The \textit{trans} orientation of the alkene
protons was confirmed by comparing the vicinal coupling constant to trans-Rh\textsuperscript{III}(OEP)(CH=CHPh) (13.0 Hz). The trans orientation was also confirmed by comparing the chemical shift of the =CHCl proton of Rh\textsuperscript{III}(OEP)(CH=CHCl) to the =CH\textsubscript{2} protons of Rh\textsuperscript{III}(OEP)(CH=CH\textsubscript{2}). In Rh\textsuperscript{III}(OEP)(CH=CH\textsubscript{2}), the =CH\textsubscript{2} proton that is trans to the Rh-CH= proton occurred at -2.07 ppm, whereas the =CH\textsubscript{2} proton that is cis to the Rh-CH= proton occurred at 0.60 ppm. Because the =CHCl proton of Rh\textsuperscript{III}(OEP)(CH=CHCl) (-1.79 ppm) was much closer to the former chemical shift than to the latter, this was taken as further evidence for a trans geometry in trans-Rh\textsuperscript{III}(OEP)(CH=CHCl).\textsuperscript{231,243}

5.1.7 Modification to the reactivities of rhodium-rhodium dimers in the presence of pyridine

Several studies have demonstrated that the reactivity of rhodium(II)-porphyrin and rhodium(II)-TMTAA dimers is modified in the presence of pyridine. In this section, similarities and differences to analogous reactions conducted in the absence of pyridine are discussed.\textsuperscript{24,225}

As discussed briefly in Sections 3.1.5 and 5.1.1, rhodium(II)-porphyrin dimers usually react with pyridines to form monomeric products. For example, it has been shown that the rhodium-rhodium bond of [Rh\textsuperscript{II}(OEP)]\textsubscript{2} breaks heterolytically in dry degassed pyridine-\textit{d}\textsubscript{5} to form a 1:1 mixture of [Rh\textsuperscript{III}(OEP)(py)]\textsuperscript{2+} and [Rh\textsuperscript{I}(OEP)]\textsuperscript{-}. The lack of pyridine coordination to the rhodium(I) centre of [Rh\textsuperscript{I}(OEP)]\textsuperscript{-} is believed to be due to the filled \textit{d}\textsubscript{z}\textsuperscript{2} orbital, which limits further ligand coordination. This [Rh\textsuperscript{III}(OEP)(py)]\textsuperscript{2+} complex was identical by \textit{1}H NMR spectroscopy to an authentic [Rh\textsuperscript{III}(OEP)(py)]\textsuperscript{2+} complex synthesised from the reaction of Rh\textsuperscript{III}(OEP)I with AgClO\textsubscript{4} in pyridine-\textit{d}\textsubscript{5}, and the [Rh\textsuperscript{I}(OEP)]\textsuperscript{-} complex was identical to an authentic [Rh\textsuperscript{I}(OEP)]\textsuperscript{-} complex synthesised by reduction of Rh\textsuperscript{III}(OEP)H with [K(18-crown-6-ether)]OH in pyridine-\textit{d}\textsubscript{5}. Analysis of the FAB mass spectra of [Rh\textsuperscript{III}(OEP)(py)]\textsuperscript{2+} and [Rh\textsuperscript{I}(OEP)]\textsuperscript{-} were also consistent with their expected formulations.\textsuperscript{225}

5.1.7.1 Reactions with dihydrogen

Earlier sections of this chapter described reactions of Rh\textsuperscript{II}(OEP)]\textsubscript{2} with substrates that cleave the rhodium-rhodium bond homolytically in low polarity solvents, to form monomeric
rhodium(III)-OEP products. Although similar monomeric rhodium(III)-OEP products are usually formed when these reactions are repeated in pyridine-$d_5$, the second axial site of these complexes are normally occupied by a pyridine-$d_5$ ligand. For example, when dihydrogen (>0.17 atmospheres) was added to a solution of [Rh$^{III}$(OEP)]$_2$ in dry, degassed pyridine-$d_5$, Rh$^{III}$(OEP)(H)(py) was synthesised, whereas in the analogous reaction in benzene-$d_6$ in the absence of pyridine, Rh$^{III}$(OEP)H was synthesised. Both reactions were reversible, and upon removing the dihydrogen atmosphere via freeze-pump-thaw degassing, Rh$^{III}$(OEP)H reverted back to [Rh$^{III}$(OEP)]$_2$, whereas Rh$^{III}$(OEP)(H)(py) formed a 1:1 mixture of [Rh$^{III}$(OEP)(py)$_2$]$^+$ and [Rh$^{I}$(OEP)]. As expected, the $^1$H NMR spectrum of Rh$^{III}$(OEP)(H)(py) synthesised in situ from [Rh$^{II}$(OEP)]$_2$ and dihydrogen in pyridine-$d_5$ was identical to the $^1$H NMR spectrum of an independently-synthesised Rh$^{III}$(OEP)H complex that was isolated and then dissolved in pyridine-$d_5$.²²⁵

FAB mass spectrometry of the Rh$^{III}$(OEP)(H)(py) complex agreed with the expected formulation. The hydride ligand signal in the $^1$H NMR spectrum of Rh$^{III}$(OEP)(H)(py) in pyridine-$d_5$ (-32.95 ppm) was shifted significantly downfield compared to Rh$^{III}$(OEP)H in benzene-$d_6$ (-41.61 ppm), and the $^1$H-$^{103}$Rh coupling was much smaller for Rh$^{III}$(OEP)(H)(py) (22 Hz) than for Rh$^{III}$(OEP)H (44 Hz). These differences were attributed to the *trans* effect of the axial pyridine-$d_5$ ligand.²²⁵ In contrast, the OEP ligand protons shift only slightly (<0.05 ppm) between Rh$^{III}$(OEP)(H)(py) and Rh$^{III}$(OEP)H. Similar effects have been observed in the analogous reaction of [Rh$^{II}$(TMTAA)]$_2$ with dihydrogen (0.6 atmospheres) in pyridine-$d_5$, where the hydride ligand of Rh$^{III}$(TMTAA)(H)(py) was observed at -13.6 ppm ($J_{H-103Rh} = 35.7$ Hz), compared to -20.2 ppm ($J_{H-103Rh} = 47.6$ Hz) for Rh$^{III}$(TMTAA)H in THF-$d_8$, and -24.1 ppm ($J_{H-103Rh} = 58.5$ Hz) for Rh$^{III}$(TMTAA)H in toluene-$d_8$. These results also suggested that THF may coordinate weakly to the Rh$^{III}$(TMTAA)H complex.¹⁵,²⁴

Neither [Rh$^{III}$(OEP)(py)$_2$]$^+$ nor [Rh$^{I}$(OEP)]$^-$ on their own reacted with dihydrogen in pyridine-$d_5$. The reason that [Rh$^{III}$(OEP)(py)$_2$]$^+$ on its own does not react with pyridine-$d_5$ to form Rh$^{III}$(OEP)(H)(py) is probably because a pyridinium cation would be formed as a by-product, and this reaction would probably be unfavourable under these conditions. It was therefore concluded that a base is required to form Rh$^{III}$(OEP)(H)(py) from [Rh$^{III}$(OEP)(py)$_2$]$^+$. Because [Rh$^{I}$(OEP)]$^-$ itself can act as a base for this reaction, Rh$^{III}$(OEP)(H)(py) is only formed if both [Rh$^{III}$(OEP)(py)$_2$]$^+$ and [Rh$^{I}$(OEP)]$^-$ are present in solution. The synthesis of Rh$^{III}$(OEP)(H)(py) from [Rh$^{I}$(OEP)]$^-$ and pyridinium chloride in pyridine-$d_5$ suggested that [Rh$^{I}$(OEP)]$^-$ is indeed
basic. Furthermore, when excess pyridinium chloride was used in this reaction, \([\text{Rh}^{I}(\text{OEP})]^-\) was oxidised to \([\text{Rh}^{III}(\text{OEP})(\text{py})]_2^+\) and dihydrogen gas was evolved as a by-product. Based on these results, a mechanism for the reaction of \([\text{Rh}^{II}(\text{OEP})]_2\) with dihydrogen in pyridine-\(d_5\) was postulated (Figure 5.11).

\[
[\text{Rh}^{II}(\text{OEP})]_2 + 2 \text{py} \rightleftharpoons [\text{Rh}^{II}(\text{OEP})(\text{py})]_2^+ + [\text{Rh}^{III}(\text{OEP})]^- \\
[\text{Rh}^{II}(\text{OEP})(\text{py})]_2^+ + \text{H}_2 \rightleftharpoons \text{Rh}^{III}(\text{OEP})(\text{H})(\text{py}) + \text{pyH}^+ \\
[\text{Rh}^{III}(\text{OEP})(\text{H})(\text{py})]^- + \text{pyH}^+ \rightleftharpoons \text{Rh}^{III}(\text{OEP})(\text{H})(\text{py}) \\
[\text{Rh}^{III}(\text{OEP})]_2 + \text{H}_2 \rightleftharpoons 2 \text{Rh}^{III}(\text{OEP})(\text{H})(\text{py})
\]

Figure 5.11: Proposed mechanism for the synthesis of \(\text{Rh}^{III}(\text{OEP})(\text{H})(\text{py})\) from \([\text{Rh}^{II}(\text{OEP})]_2\) and dihydrogen in pyridine-\(d_5\) (py)

5.1.7.2 Reactions with carbon monoxide

The reaction of \([\text{Rh}^{II}(\text{OEP})]_2\) with carbon monoxide has also been studied by \(^1\text{H}\) NMR spectroscopy in dry degassed pyridine-\(d_5\). For example, the reaction of \([\text{Rh}^{II}(\text{OEP})]_2\) with carbon monoxide (0.36 atmospheres) and dihydrogen (0.17 atmospheres) gave a 1:0.35 equilibrium mixture of \(\text{Rh}^{III}(\text{OEP})(\text{H})(\text{py})\) and \(\text{Rh}^{III}(\text{OEP})(\text{CHO})(\text{py})\) at room temperature. In contrast, the \(\text{Rh}^{III}(\text{OEP})(\text{CHO})\) complex synthesised from \([\text{Rh}^{II}(\text{OEP})]_2\), carbon monoxide, and dihydrogen in degassed benzene-\(d_6\) in the absence of pyridine was not ligated at the second axial site. Consequently, differences were observed in the \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra of these complexes. For example, the formyl proton was observed at 4.51 ppm \((J_{\text{H-H}}=103\text{Rh} = 3.95 \text{ Hz})\) for \(\text{Rh}^{III}(\text{OEP})(\text{CHO})(\text{py})\) and at 2.90 ppm \((J_{\text{H-H}}=103\text{Rh} = 1.75 \text{ Hz})\) for \(\text{Rh}^{III}(\text{OEP})(\text{CHO})\) in the \(^1\text{H}\) NMR spectra. Meanwhile, the formyl carbon was observed as a doublet of doublets at 213 ppm \((J_{\text{C-C}}=165 \text{ Hz}, J_{\text{C-C}}=103\text{Rh} = 27.5 \text{ Hz})\) for \(\text{Rh}^{III}(\text{OEP})(\text{CHO})(\text{py})\) and at 194.4 ppm \((J_{\text{C-C}}=165 \text{ Hz}, J_{\text{C-C}}=103\text{Rh} = 29 \text{ Hz})\) for \(\text{Rh}^{III}(\text{OEP})(\text{CHO})\) in the proton-coupled \(^{13}\text{C}\) NMR spectra. It has been proposed that these spectroscopic differences could be due to the formyl ligand becoming more carbene-like (\(\text{Rh}^+\text{C}(=\text{O})\text{H}\)) and less formyl-like (\(\text{RhC}(-\text{O})\text{H}\)) in character after pyridine coordination. Like \(\text{Rh}^{III}(\text{OEP})(\text{H})(\text{py})\) and \(\text{Rh}^{III}(\text{OEP})(\text{H})\), the difference in \(^1\text{H}\) NMR chemical shifts of the OEP ligand between \(\text{Rh}^{III}(\text{OEP})(\text{CHO})(\text{py})\) and \(\text{Rh}^{III}(\text{OEP})(\text{CHO})\)
was minor. Similar results were obtained with rhodium(III)-formyl complexes of the TMTAA ligand, where the formyl proton of Rh\textsuperscript{III}(TMTAA)(CHO)(py) was observed at 13.84 ppm in pyridine-\textit{d}_5 (~J\textsubscript{1H-103Rh} = 0.8 Hz), compared to 11.5 ppm (~J\textsubscript{1H-103Rh} = 0.6 Hz) for Rh\textsuperscript{III}(TMTAA)(CHO) in toluene-\textit{d}_8.\textsuperscript{15,24}

Although formyl complexes are formed when [Rh\textsuperscript{II}(OEP)]\textsubscript{2} reacts with carbon monoxide and dihydrogen in either benzene-\textit{d}_6 or pyridine-\textit{d}_5, the postulated mechanisms for these two reaction are rather different. For the reaction in benzene-\textit{d}_6, a radical chain reaction has been proposed (shown in Figure 5.8), which is initiated by homolytic cleavage of the rhodium-rhodium bond (see Section 5.1.5 for more detail). In contrast, a metalloanion chain reaction mechanism has been proposed for the reaction in pyridine-\textit{d}_5. In the first step of this mechanism (Figure 5.12), the rhodium-rhodium bond of [Rh\textsuperscript{II}(OEP)]\textsubscript{2} breaks heterolytically to form [Rh\textsuperscript{III}(OEP)(py)]\textsuperscript{+} and [Rh\textsuperscript{I}(OEP)]\textsuperscript{−}. In the next step, both [Rh\textsuperscript{III}(OEP)(py)]\textsuperscript{+} and [Rh\textsuperscript{I}(OEP)]\textsuperscript{−} react to form Rh\textsuperscript{III}(OEP)(H)(py), via the reactions given in Figure 5.11. It has been proposed that the nucleophilic rhodium centre of [Rh\textsuperscript{I}(OEP)]\textsuperscript{−} reacts with carbon monoxide to form a rhodium(I) carbonyl complex, [Rh\textsuperscript{I}(OEP)(CO)]\textsuperscript{−}. This reaction is believed to be much more facile than the reaction of [Rh\textsuperscript{III}(OEP)(py)]\textsuperscript{+} with carbon monoxide. [Rh\textsuperscript{I}(OEP)(CO)]\textsuperscript{−} then reacts with Rh\textsuperscript{III}(OEP)(H)(py) to form Rh\textsuperscript{III}(OEP)(CHO)(py), and [Rh\textsuperscript{I}(OEP)]\textsuperscript{−} is generated as a by-product. Because this [Rh\textsuperscript{I}(OEP)]\textsuperscript{−} by-product reacts further via the third and fourth steps in Figure 5.12 to generate more Rh\textsuperscript{III}(OEP)(CHO)(py) and more [Rh\textsuperscript{I}(OEP)]\textsuperscript{−}, this reaction has been called a metalloanion chain reaction. This reaction is related to the radical chain reaction that forms Rh\textsuperscript{III}(OEP)(CHO) from [Rh\textsuperscript{II}(OEP)]\textsubscript{2}, carbon monoxide, and dihydrogen in benzene-\textit{d}_6 (Figure 5.8), where the [Rh\textsuperscript{II}(OEP)(CO)]\textsuperscript{−} radical (formed from the reaction of [Rh\textsuperscript{II}(OEP)]\textsuperscript{•} with carbon monoxide) reacts with Rh\textsuperscript{III}(OEP)H, generating Rh\textsuperscript{III}(OEP)(CHO) and another [Rh\textsuperscript{II}(OEP)]\textsuperscript{•} radical, the latter of which undergoes further reaction to form more Rh\textsuperscript{III}(OEP)(CHO).\textsuperscript{24,225} The mechanism for the formation of Rh\textsuperscript{III}(TMTAA)(CHO)(py) from [Rh\textsuperscript{II}(TMTAA)]\textsubscript{2}, carbon monoxide, and dihydrogen in pyridine-\textit{d}_5 is believed to be the same as that shown in Figure 5.12.\textsuperscript{24}
Figure 5.12: Proposed mechanism for the synthesis of Rh_{III}^{III}(OEP)(CHO)(py) from the reaction of [Rh_{II}^{II}(OEP)]_{2} with carbon monoxide and dihydrogen in pyridine-\textit{d}_{5} (py)

\[
[Rh^{II}(OEP)]_{2} \quad 2 \text{py} \quad \rightleftharpoons \quad [Rh^{III}(OEP)(py)]_{2}^{\dagger} \quad + \quad [Rh^{I}(OEP)]^{-} \quad + \\
[Rh^{III}(OEP)(py)]_{2}^{\dagger} \quad + \quad [Rh^{I}(OEP)]^{-} \quad + \quad H_{2} \quad \rightleftharpoons \quad 2 Rh^{III}(OEP)(H)(py) \quad + \\
[Rh^{I}(OEP)]^{-} \quad + \quad CO \quad \rightleftharpoons \quad [Rh^{I}(OEP)(CO)]^{-} \quad + \\
[Rh^{I}(OEP)(CO)]^{-} \quad + \quad Rh^{III}(OEP)(H)(py) \quad \rightleftharpoons \quad Rh^{III}(OEP)(CHO)(py) \quad + \quad [Rh^{I}(OEP)]^{-} \quad + \\
[Rh^{II}(OEP)]_{2} \quad 2 \text{py} \quad + \quad 2 \text{CO} \quad + \quad H_{2} \quad \rightleftharpoons \quad 2 Rh^{III}(OEP)(CHO)(py)
\]

The heterolytic reaction of [Rh_{II}^{II}(OEP)]_{2} with carbon monoxide and dihydrogen in pyridine-\textit{d}_{5} to form Rh_{III}^{III}(OEP)(CHO)(py) is much faster than the analogous homolytic reaction in benzene-\textit{d}_{6} to form Rh_{III}^{III}(OEP)(CHO). It has been postulated that this is due to the much higher energy of the homolytic reaction pathway than the heterolytic reaction pathway, and the ability of pyridine-\textit{d}_{5} to support lower-energy ionic reaction pathways.\textsuperscript{225}

Rh_{III}^{III}(OEP)(CHO)(py) has also been synthesised from [Rh_{II}^{II}(OEP)]_{2} and carbon monoxide in degassed pyridine-\textit{d}_{5}, using a small amount of water as the formyl proton source instead of dihydrogen. It was found that the dimer cleaved heterolytically in this reaction and that the [Rh^{I}(OEP)]^{-} intermediate reacted much faster (over minutes) than the [Rh^{III}(OEP)(py)]_{2}^{\dagger} intermediate (over days) to form the Rh_{III}^{III}(OEP)(CHO)(py) complex. Carbon dioxide was generated as a by-product in this reaction. Thus, when a \textsuperscript{1}H NMR spectrum of the reaction mixture was obtained a few minutes after the addition of carbon monoxide, only Rh_{III}^{III}(OEP)(CHO)(py) and [Rh_{III}^{III}(OEP)(py)]_{2}^{\dagger} were observed, while several days later, only Rh_{III}^{III}(OEP)(CHO)(py) was observed. In contrast, it has been proposed that [Rh_{II}^{II}(OEP)]_{2} cleaves homolytically in the analogous reaction of [Rh_{II}^{II}(OEP)]_{2} with carbon monoxide and water in benzene-\textit{d}_{6}, forming a Rh_{III}^{III}(C(=O)OH) intermediate which reacts rapidly and is not observed by \textsuperscript{1}H NMR spectroscopy (see Figure 5.7 for this postulated mechanism). Therefore, only Rh_{III}^{III}(OEP)(CHO) and [Rh_{III}^{III}(OEP)]_{2} are observed by \textsuperscript{1}H NMR spectrum of this reaction in benzene-\textit{d}_{6}, with [Rh_{II}^{II}(OEP)]_{2} disappearing once the reaction reaches completion.
A heterolytic reaction mechanism has been postulated for the reaction of $[\text{Rh}^{\text{II}}(\text{OEP})]_2$ with carbon monoxide and water in pyridine-$d_5$ (Figure 5.13). In the first step of this mechanism, the rhodium-rhodium bond breaks heterolytically to form $[\text{Rh}^{\text{III}}(\text{OEP})(\text{py})_2]^+$ and $[\text{Rh}^{\text{I}}(\text{OEP})]^\cdot$. $[\text{Rh}^{\text{I}}(\text{OEP})]^\cdot$ then reacts rapidly with carbon monoxide and water to form $\text{Rh}^{\text{III}}(\text{OEP})(\text{CHO})(\text{py})$, generating a hydroxide anion as a by-product. $[\text{Rh}^{\text{III}}(\text{OEP})(\text{py})_2]^+$ then slowly reacts with the hydroxide anion and two equivalents of carbon monoxide to form more $\text{Rh}^{\text{III}}(\text{OEP})(\text{CHO})(\text{py})$. Carbon dioxide is generated as a by-product in this final step.\textsuperscript{225}

$$[\text{Rh}^{\text{II}}(\text{OEP})]_2 + 2 \text{py} \leftrightarrow [\text{Rh}^{\text{III}}(\text{OEP})(\text{py})_2]^+ + [\text{Rh}^{\text{I}}(\text{OEP})]^\cdot$$

$$[\text{Rh}^{\text{I}}(\text{OEP})]^\cdot + \text{CO} + \text{H}_2\text{O} \xrightarrow{\text{fast}} \text{Rh}^{\text{III}}(\text{OEP})(\text{CHO})(\text{py}) + \text{OH}^-$$

$$[\text{Rh}^{\text{III}}(\text{OEP})(\text{py})_2]^+ + 2 \text{CO} + \text{OH}^- \xrightarrow{\text{slow}} \text{Rh}^{\text{III}}(\text{OEP})(\text{CHO})(\text{py}) + \text{CO}_2 + \text{py}$$

$$[\text{Rh}^{\text{II}}(\text{OEP})]_2 + 2 \text{py} + 3 \text{CO} + \text{H}_2\text{O} \overset{\text{equiv}}{\leftrightarrow} 2 \text{Rh}^{\text{III}}(\text{OEP})(\text{CHO})(\text{py}) + \text{CO}_2$$

Figure 5.13: Proposed mechanism for the synthesis of $\text{Rh}^{\text{III}}(\text{OEP})(\text{CHO})(\text{py})$ from the reaction of $[\text{Rh}^{\text{II}}(\text{OEP})]_2$ with carbon monoxide and water in pyridine-$d_5$ (py)

5.1.7.3 Reactions with methyl iodide

When methyl iodide was added to a solution of $[\text{Rh}^{\text{II}}(\text{OEP})]_2$ in degassed pyridine-$d_5$, the $[\text{Rh}^{\text{I}}(\text{OEP})]^\cdot$ complex reacted, but the $[\text{Rh}^{\text{III}}(\text{OEP})(\text{py})_2]^+$ complex did not react. A 1:1 mixture of $\text{Rh}^{\text{III}}(\text{OEP})\text{Me}$ and $[\text{Rh}^{\text{III}}(\text{OEP})(\text{py})_2]^+$ was therefore observed by $^1\text{H}$ NMR spectroscopy. This contrasts with the analogous reaction in benzene-$d_6$, where a 1:1 mixture of $\text{Rh}^{\text{III}}(\text{OEP})\text{Me}$ and $\text{Rh}^{\text{III}}(\text{OEP})\text{I}$ formed. This has been attributed to the presence of a homolytic reaction pathway in benzene-$d_6$, where $[\text{Rh}^{\text{II}}(\text{OEP})]_2$ forms two $[\text{Rh}^{\text{I}}(\text{OEP})]^\cdot$ radicals, one of which abstracts a methyl radical from methyl iodide to form $\text{Rh}^{\text{III}}(\text{OEP})\text{Me}$, while the second $[\text{Rh}^{\text{II}}(\text{OEP})]^\cdot$ radical reacts with the iodide radical generated in this reaction to form $\text{Rh}^{\text{III}}(\text{OEP})\text{I}$.

The methyl ligand of $\text{Rh}^{\text{II}}(\text{OEP})\text{Me}$ was observed as a doublet at -6.61 ppm ($J_{\text{H}-103\text{Rh}} = 3.0$ Hz) in pyridine-$d_5$ and at -6.01 ppm ($J_{\text{H}-103\text{Rh}} = 3.0$ Hz) in benzene-$d_6$. Although this change in chemical shift may suggest that pyridine-$d_5$ coordinates weakly to the second axial site of $\text{Rh}^{\text{III}}(\text{OEP})\text{Me}$, this could instead be due to solvent effects alone. The absence of a pyridine-$d_5$
ligand in the mass spectrum of Rh^{III}(OEP)Me in pyridine-$d_{5}$ using the relatively soft FAB ionisation technique also suggests that pyridine either coordinates weakly or not at all to the metal centre. In contrast, air-stable bridging Me(TPP)Rh^{III}-L-Rh^{III}(TPP)Me complexes have been synthesised from the reaction of bidentate 4-cyanopyridine and 4,4'-bipyridine ligands (L) with Rh^{III}(TPP)Me in dichloromethane.

5.1.7.4 Other reactions

In other studies, $^1$H NMR spectroscopy and elemental analysis has strongly suggested that the addition of pyridine-$d_{5}$ to Rh^{III}(OEP)I results in the formation of a six-coordinate complex, Rh^{III}(OEP)(I)(py).

In the following section (Section 5.2), the reactivity of Na[[Rh^{II}(L_m)]_2Cl] and its dimeric and monomeric derivatives is discussed, with a focus on reactions with coordinating solvents, pyridine, dihydrogen, triphenylphosphine, sodium borohydride, alkyl halides, carbon monoxide, and acetylene. The ability of these rhodium-$L_m$ complexes to catalyse small molecule activation is discussed in Section 5.3.

5.2 Reaction chemistry of Na[[Rh^{II}(L_m)]_2Cl] and its dimeric and monomeric derivatives

In this section, reactions of Na[[Rh^{II}(L_m)]_2Cl] and selected dimeric and monomeric derivatives of this complex are described and discussed. The reactivities of these complexes are compared to those of related compounds that have been reported (see Section 5.1), and activation of selected small molecules by these rhodium-$L_m$ complexes is discussed.
5.2.1 General conditions

For most of the reported complexes with direct unsupported rhodium-rhodium bonds and macrocyclic supporting ligands discussed in Section 5.1 (for example, [RhII(OEP)]2 and [RhII(TMTAA)]2), reactions were carried out in aprotic low polarity solvents (such as benzene or toluene), which do not coordinate to the metal centre and have minimal interference with the products formed. Aprotic coordinating solvents, such as THF or pyridine, were sometimes used in these reactions when products with these axial solvent ligands were desired.

Unlike [RhII(OEP)]2 and [RhII(TMTAA)]2, Na[[RhII(Lm)]2Cl] is insoluble in aprotic low polarity solvents. In fact, Na[[RhII(Lm)]2Cl] is highly insoluble in most organic solvents and is also highly insoluble in water. This complex does, however, have a low solubility (around 0.1-0.3 mg mL−1) in alcohols. Therefore, the reactions of Na[[RhII(Lm)]2Cl] with various substrates have been conducted in alcohols in this section. Because alcohols are polar protic solvents that may coordinate weakly to the metal centre and may promote ionic reaction pathways, some differences might be expected compared to the analogous reactions using [RhII(porphyrin)]2 and [RhII(TMTAA)]2 dimers in non-coordinating aprotic solvents. Although Na[[RhII(Lm)]2Cl] appeared to be reasonably soluble (>50 mg mL−1) in DMSO, DMF, pyridine, and 4-picoline, this was because DMSO and DMF break the rhodium-rhodium bond of Na[[RhII(Lm)]2Cl] to form soluble monomeric products, while pyridine and 4-picoline coordinate to Na[[RhII(Lm)]2Cl] to form more soluble adducts where the rhodium-rhodium bond remains intact. Spectroscopic evidence for these reactions is described and discussed in Section 5.2.2 below. In contrast, spectroscopic evidence discussed in Section 3.2.6 suggested that Na[[RhII(Lm)]2Cl] remains intact in alcohols and also suggested that alcohols do not appreciably coordinate to Na[[RhII(Lm)]2Cl]. This is another reason why alcohols have been used as solvents in the reactions of Na[[RhII(Lm)]2Cl] with various reagents described in this chapter.

5.2.2 Reactions of Na[[RhII(Lm)]2Cl] with coordinating solvents

NMR experiments were conducted to see whether the rhodium-rhodium bond of Na[[RhII(Lm)]2Cl] remains intact in the presence of potentially coordinating solvents. These experiments were also performed in order to investigate possible solvents that may be suitable for the reaction of the Na[[RhII(Lm)]2Cl] with substrates. From these results, it was concluded...
that THF, acetone, and acetonitrile do not coordinate appreciably to Na[[Rh$^{II}$(L$_m$)$_2$Cl], whereas pyridine and 4-picoline form stable Na[[Rh$^{II}$(L$_m$)$_2$Cl](py)] and Na[[Rh$^{II}$(L$_m$)$_2$Cl](4-picoline)] adducts. Furthermore, DMSO and DMF cleave the rhodium-rhodium bond of Na[[Rh$^{II}$(L$_m$)$_2$Cl] to form monomeric [Rh$^{III}$(L$_m$)(DMSO)$_2$]$^+$ and [Rh$^{III}$(L$_m$)(DMF)$_2$]$^+$ complexes. These experiments are described and discussed below.

5.2.2.1 Reactions of Na[[Rh$^{II}$(L$_m$)$_2$Cl] with THF, acetone, and acetonitrile

To see whether various coordinating solvents would react with Na[[Rh$^{II}$(L$_m$)$_2$Cl], small and large excesses (5 to 50 equivalents) of a potentially coordinating solvent were added to solutions of Na[[Rh$^{II}$(L$_m$)$_2$Cl], dissolved in methanol-$d_4$. When THF, acetone, or acetonitrile were added to Na[[Rh$^{II}$(L$_m$)$_2$Cl] in methanol-$d_4$, no change to the $^1$H NMR spectrum was observed in each case, suggesting that Na[[Rh$^{II}$(L$_m$)$_2$Cl] remains intact and is not appreciably ligated by these solvents. As described in Section 3.2.6, one of the key features of the $^1$H NMR spectrum of Na[[Rh$^{II}$(L$_m$)$_2$Cl] in methanol-$d_4$ is the inequivalence of the four “halves” of the L$_m$ ligands (as shown in Figure 3.19). Thus, the chemical shifts and integrations of these signals remain unchanged after the addition of THF, acetone, or acetonitrile. High resolution positive ion mass spectrometry of these reaction mixtures also suggests that the dimer remains intact in the presence of THF, acetone, or acetonitrile. This is because these mass spectra were very similar to the mass spectrum of Na[[Rh$^{II}$(L$_m$)$_2$Cl] in methanol in the absence of THF, acetone, or acetonitrile described in Section 3.2.6. Thus, in all these mass spectra, the highest intensity signal was consistent with a formulation of [Rh$^{III}$(L$_m$)$_2$] + H$^+$. The $^1$H NMR spectra in neat acetonitrile-$d_3$, THF-$d_8$, or acetone-$d_6$ were not obtained, because Na[[Rh$^{II}$(L$_m$)$_2$Cl] is highly insoluble in these solvents.

5.2.2.2 Reactions of Na[[Rh$^{II}$(L$_m$)$_2$Cl] with DMSO and DMF

When an excess of DMSO or DMF (about 10 equivalents) was added to Na[[Rh$^{II}$(L$_m$)$_2$Cl] in methanol-$d_4$, substantial changes to the $^1$H NMR spectra were observed after stirring these solutions for a few minutes at room temperature in air. In these $^1$H NMR spectra, only one major product was observed, which corresponded to a formulation of [Rh$^{III}$(L$_m$)(L)$_2$]$^+$ (L = DMSO or DMF).
As described in Section 3.2.6, the four “halves” of the \( L_m \) ligands in Na[\( \text{[Rh} \text{II}(L_m)]_2\text{Cl} \)] are inequivalent on the \(^1\text{H} \) NMR timescale at room temperature in methanol-\( d_4 \) (see Figure 3.19 for more details). However, for the \([\text{Rh} \text{III}(L_m)(L)]_2^+\) complexes (\( L = \text{DMSO} \) or DMF), only one set of signals was observed in the \(^1\text{H} \) NMR spectrum – that is, the two “halves” of the \( L_m \) ligands were now equivalent. Because only one geminal-C-methyl signal was observed for the \([\text{Rh} \text{III}(L_m)(L)]_2^+\) complexes, the rhodium-rhodium bond of the dimer must have broken to form a single monomeric product, with two identical axial ligands. This is because the geminal-C-methyl groups would be inequivalent if the rhodium-rhodium bond remained intact, since the methyl groups pointing towards the rhodium-rhodium bond are shielded to a different extent relative to the methyl groups that point away from the rhodium-rhodium bond. The most likely axial ligands on \([\text{Rh} \text{III}(L_m)(L)]_2^+\) in methanol-\( d_4 \) are DMSO/DMF, because there is not enough chloride in the Na[\( \text{[Rh} \text{II}(L_m)]_2\text{Cl} \)] dimer to form Na[\( \text{[Rh} \text{III}(L_m)(\text{Cl})]_2 \)] as a major product. Additionally, a formulation of \([\text{Rh} \text{III}(L_m)(\text{methanol-}d_4)]_2^+\) is unlikely because the \(^1\text{H} \) NMR spectrum for \([\text{Rh} \text{III}(L_m)(\text{DMSO})]_2^+\) differs slightly from the \(^1\text{H} \) NMR spectrum of \([\text{Rh} \text{III}(L_m)(\text{DMF})]_2^+\), indicating that a different product is formed when DMF is used instead of DMSO. A formulation of \([\text{Rh} \text{III}(L_m)(\text{methanol-}d_4)]_2^+\) is also unlikely because DMSO and DMF are expected to coordinate more strongly to the rhodium centre than methanol-\( d_4 \). The counteranion on \([\text{Rh} \text{III}(L_m)(L)]_2^+\) is probably a mixture of hydroxide (arising from oxidation of the rhodium(II) dimer by oxygen from the atmosphere) and chloride from the displaced chloride ligand.

High resolution positive ion mass spectra of \([\text{Rh} \text{III}(L_m)(L)]_2^+\) (\( L = \text{DMSO} \) or DMF) are consistent with a rhodium(III) formulation. This is because the only major species observed in these mass spectra corresponded to \([\text{Rh} \text{III}(L_m)]^+\). Any axial ligands originally present are expected to be weakly coordinated and easily lost in the electrospray ionisation process. Loss of the axial ligands during the electrospray ionisation process has also been observed for many of the monomeric metal(III)-\( L_m \) complexes described in Chapter 3. No signals were observed in these mass spectra that would correspond to the presence of a dimeric species (for example, \([\text{Rh} \text{II}(L_m)]_2^+ \text{H}^+\) or \([\text{Rh} \text{II}(L_m)]_2^+ \text{Na}^+\)), again indicating that the rhodium-rhodium bond has been broken.

The above results are therefore consistent with the coordination of DMSO or DMF to the axial site(s) of Na[\( \text{[Rh} \text{II}(L_m)]_2\text{Cl} \)], which weakens the rhodium-rhodium bond and causes it to break to form monomeric products. There are three possible ways that DMSO/DMF can coordinate to
Na[[Rh$^{II}$(L$_m$)]$_2$Cl] and weaken the rhodium-rhodium bond (Figure 5.14): 1) by coordinating to the vacant coordination site to form a Na[[Rh$^{II}$(L$_m$)]$_2$(Cl)(L)] intermediate (L = DMSO or DMF); 2) by displacing the coordinated chloride ligand to form a [Rh$^{II}$(L$_m$)]$_2$(L) intermediate; or 3) by coordinating to the vacant coordination site, followed by displacement of the chloride ligand by a second DMSO/DMF molecule, to form a [Rh$^{II}$(L$_m$)]$_2$(L)$_2$ intermediate. For routes 1 and 3, it is possible that the rhodium-rhodium bond is weakened because the increased coordination number of the rhodium centre that was previously five-coordinate. This increases the planarity of the L$_m$ ligand, thus elongating (and weakening) the rhodium-rhodium bond. Weakening of the rhodium-rhodium bond in route 2 could be because the coordinated DMSO/DMF ligand of Na[[Rh$^{II}$(L$_m$)]$_2$(Cl)(L)] may weaken the rhodium-rhodium bond more than the coordinated chloride ligand of Na[[Rh$^{II}$(L$_m$)]$_2$Cl], although it is difficult to explain clearly why this would occur. This may suggest that routes 1 and 3 are more likely than route 2.

Figure 5.14: Three possible routes for the initial coordination of DMSO or DMF to Na[[Rh$^{II}$(L$_m$)]$_2$Cl], prior to cleavage of the rhodium-rhodium bond

In Section 5.1.1 above, two main pathways for cleavage of the rhodium-rhodium bond in dimeric rhodium(II) complexes are described: heterolytic bond cleavage pathways and homolytic bond cleavage pathways. As discussed below, the formation of [Rh$^{III}$(L$_m$)(L)$_2$]$^{+}$ from the addition of DMSO/DMF to Na[[Rh$^{II}$(L$_m$)]$_2$Cl] is more consistent with a heterolytic cleavage pathway than homolytic cleavage pathway.
A proposed heterolytic reaction pathway for the synthesis of [Rh$^{III}$$(\text{L}_m)$(L)$_2$]$^+$ ($\text{L} = \text{DMSO}$ or DMF) from Na[[Rh$^{II}$$(\text{L}_m)$(Cl)] and DMSO/DMF is given in Figure 5.15. Although this particular reaction pathway begins from the Na[[Rh$^{II}$$(\text{L}_m)$(Cl)] intermediate formed in route 1 (Figure 5.14), similar reactions pathways would be expected from the [Rh$^{II}$$(\text{L}_m)$(L)] and [Rh$^{II}$$(\text{L}_m)$(Cl)]$_2$(L)$_2$ intermediates formed in routes 2 and 3. After formation of Na[[Rh$^{II}$$(\text{L}_m)$(Cl)](L)], the rhodium-rhodium bond breaks heterolytically to form a rhodium(I) intermediate and a rhodium(III) intermediate (Figure 5.15). The rhodium-chlorine bond also breaks heterolytically, forming a chloride anion. This occurs because it is unlikely that heterolytic cleavage of the rhodium-rhodium bond results in the formation of a dianionic [Rh$^{I}$$(\text{L}_m)$(Cl)]$^2-$ species, which would be expected to be relatively high in energy. Furthermore, because a four-coordinate square planar geometry is highly favoured for the rhodium(I) intermediate, any axial ligands on the rhodium(I) centre would readily dissociate.$^{24,225}$ This rhodium(I) intermediate is then expected to oxidise rapidly to a rhodium(III) intermediate under the aerobic conditions used in the reaction. Indeed, rhodium(I)-porphyrin and rhodium(I)-TMTAA complexes have been shown to be highly air-sensitive,$^{15,226}$ and studies described below in Section 5.2.5 indicate that an isolated rhodium(I)-L$_m$ complex is also highly air-sensitive. After oxidation of the rhodium(I) intermediate, DMSO/DMF ligates the rhodium(III) species to give [Rh$^{III}$$(\text{L}_m)$(L)$_2$]$^+$. Meanwhile, the rhodium(III) intermediate ([Rh$^{III}$$(\text{L}_m)$(L)]$^+$) formed from the rhodium-rhodium bond cleavage step becomes ligated by a second DMSO/DMF ligand, also forming [Rh$^{III}$$(\text{L}_m)$(L)$_2$]$^+$. Therefore, [Rh$^{III}$$(\text{L}_m)$(L)$_2$]$^+$ is formed as the only major product in this reaction.

A homolytic cleavage pathway for the reaction of Na[[Rh$^{II}$$(\text{L}_m)$(Cl)] with DMSO/DMF in methanol-$d_4$ is much less likely than the heterolytic cleavage pathway described above. This is because homolytic bond cleavage would result in the formation of reactive rhodium(II) intermediates (such as [Rh$^{II}$$(\text{L}_m)$(DMSO)]$^+$), which would then be expected to react to form a variety of products.$^{24,225}$ No other products aside from [Rh$^{III}$$(\text{L}_m)$(L)$_2$]$^+$ were observed in the reaction of Na[[Rh$^{II}$$(\text{L}_m)$(Cl)] with DMSO or DMF, suggesting that a homolytic reaction pathway does not occur. Note, however, that a homolytic cleavage pathway followed by rapid air oxidation of the rhodium(II) intermediates to rhodium(III) product(s), and subsequent ligation of these product(s) by DMSO/DMF to form [Rh$^{III}$$(\text{L}_m)$(L)$_2$]$^+$ cannot presently be completely ruled out. As described in Section 5.1.7, it has been postulated that [Rh$^{II}$$(\text{porphyrin})$_2$] and [Rh$^{II}$$(\text{TMTAA})$_2$] dimers react with various substrates in pyridine-$d_5$ via heterolytic reaction pathways. This is believed to be due to the polar pyridine-$d_5$ solvent favouring ionic reaction pathways, thus lowering the energy of heterolytic reactions compared to homolytic reactions.$^{24,225}$ Therefore, it is likely that the polar methanol-$d_4$ solvent used in the

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above reactions with Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}]Cl] also favours heterolytic reaction pathways over homolytic reaction pathways. Because reactions of DMSO and DMF with related rhodium(II) dimers have not been reported in the literature, it is unknown if rhodium(II) dimers other than Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}]Cl] also react in this way with DMSO or DMF.

**Figure 5.15:** Possible heterolytic reaction pathway for the formation of [Rh\textsuperscript{III}(L\textsubscript{m})(L\textsubscript{r})\textsuperscript{2}]\textsuperscript{+} from Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}]Cl] and L under aerobic conditions, via a Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}](Cl)(L)] intermediate (L = DMSO or DMF)

5.2.2.3 Reactions of Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}]Cl] with pyridine and 4-picoline

When excess pyridine or 4-picoline (about 5 equivalents) was added to Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}]Cl] in methanol-\textit{d}_4, stable pyridine and 4-picoline adducts were formed, and the rhodium-rhodium bond remained intact (Figure 5.16). Spectroscopic studies described below agree with the formulations Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}](Cl)(py)] and Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}](Cl)(4-picoline)], respectively, for these adducts. These adducts are more stable to air and are much higher in solubility than Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}]Cl].
The preliminary reaction of Na[[Rh$^{II}$(L$_m$)]$_2$Cl] with pyridine in methanol-$d_4$ was scaled up, using methanol (CH$_3$OH) as the solvent. In a typical reaction, pyridine (5 equivalents) was added to Na[[Rh$^{II}$(L$_m$)]$_2$Cl] in methanol in air. After 40 minutes at room temperature, the solvent was removed under vacuum and the residue was purified by column chromatography on alumina (using 19 : 1 : 0.02 dichloromethane/methanol/pyridine as eluent), collecting the yellow-orange band (see Section 5.4.2 for experimental details). A small amount of pyridine was added to the eluent because Na[[Rh$^{II}$(L$_m$)]$_2$(Cl)(py)] partially reverts back to Na[[Rh$^{II}$(L$_m$)]$_2$Cl] on the column in the absence of pyridine. Therefore, in the absence of pyridine in the eluent, a mixture of Na[[Rh$^{II}$(L$_m$)]$_2$(Cl)(py)] and Na[[Rh$^{II}$(L$_m$)]$_2$Cl] was observed by $^1$H NMR spectroscopy (in methanol-$d_4$) after the eluate had been evaporated to dryness and dried briefly under vacuum. Furthermore, upon drying the eluate for extended times under vacuum, a mixture of Na[[Rh$^{II}$(L$_m$)]$_2$(Cl)(py)] and Na[[Rh$^{II}$(L$_m$)]$_2$Cl] was observed by $^1$H NMR spectroscopy, even when pyridine was used in the eluent. Thus, mixtures of Na[[Rh$^{II}$(L$_m$)]$_2$(Cl)(py)] and Na[[Rh$^{II}$(L$_m$)]$_2$Cl] were only observed when no free pyridine was present in the $^1$H NMR spectra of the Na[[Rh$^{II}$(L$_m$)]$_2$(Cl)(py)] samples. Additionally, Na[[Rh$^{II}$(L$_m$)]$_2$(Cl)(py)] reformed and all the Na[[Rh$^{II}$(L$_m$)]$_2$Cl] disappeared upon addition of free pyridine to these product mixtures. No products other than Na[[Rh$^{II}$(L$_m$)]$_2$(Cl)(py)] and Na[[Rh$^{II}$(L$_m$)]$_2$Cl] were observed in any of these manipulations. This suggests that there is an equilibrium between Na[[Rh$^{II}$(L$_m$)]$_2$Cl] and Na[[Rh$^{II}$(L$_m$)]$_2$(Cl)(py)], and that in the absence of excess pyridine, the equilibrium shifts to partially form Na[[Rh$^{II}$(L$_m$)]$_2$Cl]. Because the alumina column should have removed any free sodium chloride from Na[[Rh$^{II}$(L$_m$)]$_2$(Cl)(py)], reformation of Na[[Rh$^{II}$(L$_m$)]$_2$Cl] after columnning suggests that a chloride ligand is still coordinated to Na[[Rh$^{II}$(L$_m$)]$_2$(Cl)(py)]. Therefore, this complex is best represented by a formulation of Na[[Rh$^{II}$(L$_m$)]$_2$(Cl)(py)].

Attempts were also made to crystallise Na[[Rh$^{II}$(L$_m$)]$_2$(Cl)(py)] from various solvent mixtures, after first partially purifying Na[[Rh$^{II}$(L$_m$)]$_2$(Cl)(py)] via alumina column chromatography with
pyridine was added to the eluent (as described above). In the absence of free pyridine, the crystallised samples always showed a mixture of $\text{Na}[\text{Rh}^{II}(\text{Lm})_2(\text{Cl})(\text{py})]$ and $\text{Na}[\text{Rh}^{II}(\text{Lm})_2\text{Cl}]$ by $^1\text{H}$ NMR spectroscopy, perhaps because the much lower solubility of $\text{Na}[\text{Rh}^{II}(\text{Lm})_2\text{Cl}]$ than $\text{Na}[\text{Rh}^{II}(\text{Lm})_2(\text{Cl})(\text{py})]$ means that the former complex precipitates before the latter complex. Although $\text{Na}[\text{Rh}^{II}(\text{Lm})_2(\text{Cl})(\text{py})]$ was isolated without any $\text{Na}[\text{Rh}^{II}(\text{Lm})_2\text{Cl}]$ by adding a small amount of pyridine to the solvent used to crystallise the sample, a small amount of free pyridine was still present in the $^1\text{H}$ NMR spectrum of this $\text{Na}[\text{Rh}^{II}(\text{Lm})_2(\text{Cl})(\text{py})]$ sample. When this same sample of $\text{Na}[\text{Rh}^{II}(\text{Lm})_2(\text{Cl})(\text{py})]$ was washed thoroughly with diethyl ether to remove the excess free pyridine, the $^1\text{H}$ NMR spectrum of this complex again showed a mixture of $\text{Na}[\text{Rh}^{II}(\text{Lm})_2(\text{Cl})(\text{py})]$ and $\text{Na}[\text{Rh}^{II}(\text{Lm})_2\text{Cl}]$, and no free pyridine was present. This again demonstrates that an equilibrium that exists between $\text{Na}[\text{Rh}^{II}(\text{Lm})_2\text{Cl}]$ and $\text{Na}[\text{Rh}^{II}(\text{Lm})_2(\text{Cl})(\text{py})]$. Consequently, $\text{Na}[\text{Rh}^{II}(\text{Lm})_2(\text{Cl})(\text{py})]$ was characterised with a small amount of free pyridine present in the sample, and elemental analysis of this complex therefore was not obtained.

In contrast to $\text{Na}[\text{Rh}^{II}(\text{Lm})_2(\text{Cl})(\text{py})]$, it was reported that when the pyridine adduct, $[\text{Rh}^{II}(\text{pc})(\text{py})]_2$, was purified by washing the sample with diethyl ether, followed by drying the sample thoroughly under vacuum, no loss of the pyridine ligand was observed, and the $[\text{Rh}^{II}(\text{pc})]_2$ dimer did not reform (note: pc = phthalocyanine, see Figure 3.12 for the structure of this ligand).$^{210}$

The $\text{Na}[\text{Rh}^{II}(\text{Lm})_2(\text{Cl})(\text{py})]$ sample that was used for characterisation studies (described below) was purified by alumina column chromatography (using an eluent ratio of 19 : 1 : 0.02 dichloromethane/methanol/pyridine), and was then dried briefly under vacuum. A small amount of free pyridine was therefore present in the $\text{Na}[\text{Rh}^{II}(\text{Lm})_2(\text{Cl})(\text{py})]$ sample used for characterisation, in order to prevent loss of the axial pyridine ligand and formation of $\text{Na}[\text{Rh}^{II}(\text{Lm})_2\text{Cl}]$.

Only one major species was observed in the high resolution mass spectrum of $\text{Na}[\text{Rh}^{II}(\text{Lm})_2(\text{Cl})(\text{py})]$, which corresponded to a $[\text{Rh}^{II}(\text{Lm})]_2 + \text{H}^+$ species. This indicates that the rhodium-rhodium bond remains intact in this complex, and that the pyridine and chloride axial ligands are lost during the electrospray ionisation process. This is not unexpected, because these axial ligands are probably weakly coordinated and so will easily dissociate. Furthermore,
a [Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}] + H\textsuperscript{+} species was also observed in the positive ion mass spectrum Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}]Cl], due to loss of the chloride axial ligand during the electrospray ionisation process.

The high resolution negative ion mass spectrum of Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}(Cl)(py)] was obtained, and all of major signals identified in this spectrum are given in Table 5.1. All of these species were also found in the negative ion mass spectrum of Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}Cl] (also given in Table 5.1). Although no species were identified in the negative ion mass spectrum of Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}(Cl)(py)] that would correspond to the presence of an axial pyridine ligand, this is probably because the axial pyridine ligand is rather weakly coordinated, and is easily lost in the electrospray ionisation process. The relative intensity of the chloride-containing species are much lower in the negative ion mass spectrum of Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}(Cl)(py)] than they are in the negative ion mass spectrum of Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}Cl]. This could be because the pyridine axial ligand of Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}(Cl)(py)] increases labilisation of the chloride axial ligand, making it more prone to exchange by other anionic ligands, such as formate, during the electrospray ionisation process. The formate axial ligands arise from the sodium formate that was added to the Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}(Cl)(py)] sample. The similarity in the absolute intensity (in counts) of the highest intensity signals in the positive and negative ion mass spectra of Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}(Cl)(py)] suggests that the species observed in negative ion mass spectrum (Table 5.1) are not just due to the presence of trace anionic species in the Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}(Cl)(py)] sample.

Like Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}Cl] (Section 3.2.6), the \textsuperscript{1}H NMR spectrum of Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}(Cl)(py)] in methanol-\textit{d}_\textsubscript{4} at room temperature shows that the four “halves” of the L\textsubscript{m} ligands are inequivalent on the NMR timescale (see Figure 3.19 for more details). These \textsuperscript{1}H NMR signals are shifted somewhat from the corresponding signals for Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}Cl]. As was speculated for Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}Cl] (Section 3.2.6), this inequivalence observed in the \textsuperscript{1}H NMR spectrum of Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}(Cl)(py)] may arise from the different axial ligands present on the two rhodium centres, combined with restricted rotation of the complex. This restricted rotation is perhaps due to buckling of the L\textsubscript{m} ligands, which hinders internal rotation of these ligands about the rhodium-rhodium bond, thus destroying any vertical mirror plane (as per Figure 3.19) that relates the two halves of each L\textsubscript{m} ligand.
Table 5.1: Species identified in the high resolution negative ion mass spectrum of Na[[Rh\(^{II}\)(L\(_m\))]\(_2\)(Cl)(py)], compared to the negative ion mass spectrum of Na[[Rh\(^{II}\)(L\(_m\))]\(_2\)Cl]

<table>
<thead>
<tr>
<th>Calculated m/z (charge) (^a)</th>
<th>Assignment</th>
<th>Na[[Rh(^{II})(L(_m))](_2)Cl] (^c)</th>
<th>Na[[Rh(^{II})(L(_m))](_2)(Cl)(py)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1069.1413 (-1)</td>
<td>[[Rh(^{II})(L(_m))](_2)(Cl)](^+)</td>
<td>50%</td>
<td>10%</td>
</tr>
<tr>
<td>1079.1701 (-1)</td>
<td>[[Rh(^{II})(L(_m))](_2)(HCOO)](^+)</td>
<td>15%</td>
<td>30%</td>
</tr>
<tr>
<td>1101.1669 (-1)</td>
<td>[[Rh(^{II})(L(_m))](_2)(Cl)(CH(_3)OH)](^+)</td>
<td>20%</td>
<td>0%</td>
</tr>
<tr>
<td>1105.1179 (-1)</td>
<td>[[Rh(^{II})(L(_m))](_2)(Cl)](^2^+) + H(^+)</td>
<td>100%</td>
<td>5%</td>
</tr>
<tr>
<td>1115.1462 (-1)</td>
<td>[[Rh(^{II})(L(_m))](_2)(HCOO)](^2^+) + H(^+)</td>
<td>85%</td>
<td>30%</td>
</tr>
<tr>
<td>1125.1755 (-1)</td>
<td>[[Rh(^{II})(L(_m))](_2)(HCOO)](^2^+) + H(^+)</td>
<td>30%</td>
<td>100%</td>
</tr>
</tbody>
</table>

\(^a\) Calculated m/z values for each species. The charge of these species is given inside brackets here. Observed m/z values for Na[[Rh\(^{II}\)(L\(_m\))]\(_2\)(Cl)(py)] are given in Section 5.4.2. No major species other than those tabulated here were identified for this complex.

\(^b\) Relative intensity of the species observed in the negative ion mass spectra of Na[[Rh\(^{II}\)(L\(_m\))]\(_2\)Cl] and Na[[Rh\(^{II}\)(L\(_m\))]\(_2\)(Cl)(py)], calibrated relative to the highest intensity signal (set to 100%).

\(^c\) See Table 3.4 for the observed m/z values of Na[[Rh\(^{II}\)(L\(_m\))]\(_2\)Cl].

The higher stability and solubility of Na[[Rh\(^{II}\)(L\(_m\))]\(_2\)(Cl)(py)] than Na[[Rh\(^{II}\)(L\(_m\))]\(_2\)Cl] meant that \(^{13}\)C NMR spectra could be obtained, and with the help of 2D NMR techniques, all of the \(^1\)H and \(^{13}\)C NMR assignments for Na[[Rh\(^{II}\)(L\(_m\))]\(_2\)(Cl)(py)] were determined (Figure 5.17). As described in Section 3.2.6, specific assignments were not determined for Na[[Rh\(^{II}\)(L\(_m\))]\(_2\)Cl], because of its limited solubility and stability in methanol-\(d_4\), and the considerable overlap between adjacent signals in the aromatic region, which precluded good \(^{13}\)C and 2D NMR spectra from being obtained. Therefore, specific assignments for Na[[Rh\(^{II}\)(L\(_m\))]\(_2\)(Cl)(py)] were not compared to specific assignments for Na[[Rh\(^{II}\)(L\(_m\))]\(_2\)Cl].
Figure 5.17: $^1$H and $^{13}$C NMR signals identified for Na[$\text{Rh}^{II}(\text{L}_{\text{m}})^2(\text{Cl})(\text{py})$] in methanol-$d_4$. The thick dashed lines indicate that the signals for the dimethylmalonamide “tail” end of the macrocycles could not be correlated with the rest of the molecule. About 0.75 equivalents of free pyridine (relative to one equivalent of Na[$\text{Rh}^{II}(\text{L}_{\text{m}})^2(\text{Cl})(\text{py})$]) are present in this sample, in order to stabilise this complex.
The presence of four separate geminal-C-methyl signals in both the $^1$H and $^{13}$C NMR spectra of Na[$\text{Rh}^{\text{II}}(L_m)\text{]_2(Cl)(py)}$] strongly suggest a dimeric formulation, because a monomeric product would have a maximum of two separate geminal-C-methyl signals. It is interesting that in the $^1$H NMR spectrum of Na[$\text{Rh}^{\text{II}}(L_m)\text{]_2(Cl)(py)}$], the chemical shifts of the two geminal-C-methyl signals belonging to one macrocycle are the farthest upfield (0.48 ppm) and farthest downfield (1.32 ppm) of the four geminal-C-methyl signals, whereas the other macrocycle has two geminal-C-methyl signals that are of intermediate chemical shift (0.87 and 1.05 ppm) (Figure 5.17). This may be due to the influence of the two different axial ligands (pyridine and chlorine) on the chemical shifts of the geminal-C-methyl groups. Although the $^1$H and $^{13}$C NMR chemical shifts of the two dimethylmalonamide “tails” were clearly identified, these could not be correlated to the rest of the macrocycles using 2D NMR techniques. A thick dashed line is therefore drawn between the dimethylmalonamide groups and the rest of the macrocycle in Figure 5.17, because it is unknown which of the two dimethylmalonamide “tails” belongs to which of the two macrocycles. Furthermore, from these NMR studies, it was not possible to determine which axial ligand (pyridine or chloride) was coordinated to which rhodium centre.

The coordinated pyridine ligand of Na[$\text{Rh}^{\text{II}}(L_m)\text{]_2(Cl)(py)}$] was also identified by $^1$H and $^{13}$C NMR spectroscopies (Figure 5.17), and integration of the former spectrum indicates that only one pyridine ligand is present in this complex. This coordinated pyridine ligand is shifted considerably from free pyridine. Proton NMR integrations indicate that about 0.75 equivalents of free pyridine was present in the particular sample of Na[$\text{Rh}^{\text{II}}(L_m)\text{]_2(Cl)(py)}$] that was used for these NMR studies.

In the literature, the reactions of various rhodium-rhodium dimers with pyridine have been reported. Although most of these dimers cleave in the presence of excess pyridine to form monomeric products, the [Rh$^{\text{II}}$(pc)]$_2$ complex was reported to form a stable bis-pyridine adduct, [Rh$^{\text{II}}$(pc)(py)]$_2$, in the presence of excess pyridine. However, stable mono-pyridine adducts of rhodium(II) dimers have not been reported.

The procedure used to synthesise Na[$\text{Rh}^{\text{II}}(L_m)\text{]_2(Cl)(py)}$] was repeated, using 4-picoline instead of pyridine. Proton NMR spectroscopy of the product formed from this reaction indicates that a mono-4-picoline adduct, Na[$\text{Rh}^{\text{II}}(L_m)\text{]_2(Cl)(4-picoline)}$], was indeed synthesised. Like Na[$\text{Rh}^{\text{II}}(L_m)\text{]_2(Cl)(py)}$], each of the four “halves” of the $L_m$ ligands of Na[$\text{Rh}^{\text{II}}(L_m)\text{]_2(Cl)(4-$}
picoline) were inequivalent on the NMR timescale in the \( ^1\)H NMR spectrum. These signals are shifted somewhat from the \( ^1\)H NMR signals for Na[[Rh\( \text{II}(L_m)\)]_2(Cl)(py)]. The presence of [Rh\( \text{II}(L_m)\)]_2 + H\(^+\) in the mass spectrum of Na[[Rh\( \text{II}(L_m)\)]_2(Cl)(4-picoline)] also suggests that the rhodium-rhodium bond remains intact after the addition of 4-picoline to Na[[Rh\( \text{II}(L_m)\)]_2Cl]. Due to time constraints, Na[[Rh\( \text{II}(L_m)\)]_2(Cl)(4-picoline)] was not purified or characterised further, although preliminary purification attempts suggested that, like Na[[Rh\( \text{II}(L_m)\)]_2(Cl)(py)], Na[[Rh\( \text{II}(L_m)\)]_2(Cl)(4-picoline)] is in equilibrium with Na[[Rh\( \text{II}(L_m)\)]_2Cl], and partially reforms Na[[Rh\( \text{II}(L_m)\)]_2Cl] in the absence of free 4-picoline.

When 2-picoline was added to a solution of Na[[Rh\( \text{II}(L_m)\)]_2Cl] in methanol-\( d_4\), no change was observed in the \( ^1\)H NMR spectrum. This is probably because the 2-picoline methyl group sterically hinders the N-donor atom, preventing coordination to the rhodium centre.

Considering that pyridine and 4-picoline are expected to be stronger donors than DMSO and DMF, it is difficult to explain why DMSO and DMF result in cleavage of the rhodium-rhodium bond of Na[[Rh\( \text{II}(L_m)\)]_2Cl], whereas pyridine and 4-picoline form stable adducts by coordinating to one of the rhodium centres, without cleaving the rhodium-rhodium bond. Because the donor numbers of pyridine (33.1) and 4-picoline (34.0) are higher than the donor numbers of DMSO (29.8) and DMF (26.6), cleavage of the rhodium-rhodium bond clearly does not depend on solvent donor numbers.\(^{137}\) As discussed in the sections below, the rhodium-rhodium bond of Na[[Rh\( \text{II}(L_m)\)]_2Cl] also cleaves in the presence of reagents such as triphenylphosphine, carbon monoxide, and acetylene to form monomeric products. It is not immediately obvious why the rhodium-rhodium bond of Na[[Rh\( \text{II}(L_m)\)]_2Cl]] should break readily in the presence of all these reagents, but not in the presence pyridine or 4-picoline. Further experiments will need to be conducted in the future to determine why this occurs.

The following sections report investigations into the reactions of Na[[Rh\( \text{II}(L_m)\)]_2Cl] with substrates that are known to break the rhodium-rhodium bonds of [Rh\( \text{II}(\text{porphyrin})\)]_2 and [Rh\( \text{II}(\text{TMTAA})\)]_2. These substrates include dihydrogen, triphenylphosphine, sodium borohydride, alkyl halides, carbon monoxide, and acetylene. Reactions between Na[[Rh\( \text{II}(L_m)\)]_2(Cl)(py)] and most of these substrates are also discussed (Section 5.2.8).
5.2.3 Reactions of Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}Cl] with dihydrogen

Many of the rhodium(II) dimers reported in the literature that are structurally-related to Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}Cl] are known to react reversibly with dihydrogen to form rhodium(III) hydride complexes. Two main routes have been used to synthesise these rhodium(III) hydride complexes: 1) reducing the rhodium(II) dimer to rhodium(I) monomers with sodium borohydride, followed by the addition of glacial acetic acid, and 2) reacting the rhodium(II) dimer with dihydrogen in solution\textsuperscript{15,204,226,227} Although both routes were attempted with Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}Cl], no Rh\textsuperscript{III}(L\textsubscript{m})H was observed under a range of conditions.

In the first route, Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}Cl] was reduced with sodium borohydride, and then various amounts of acetic acid were added, ranging from stoichiometric amounts to large excesses. In each reaction, the \textsuperscript{1}H NMR spectrum of the isolated product (in methanol-\textit{d}\textsubscript{4}) showed a very large number of product signals and a very low overall signal-to-noise ratio. This suggests that the rhodium complex decomposes under these conditions. A clear upfield hydride ligand signal was not observed in the \textsuperscript{1}H NMR spectrum for any of these products. Similar results were obtained when hydrochloric acid was used instead of acetic acid. The reduction of Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}Cl] with sodium borohydride is explored in more detail in Section 5.2.5.

In the second route, dihydrogen was bubbled through a solution of Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}Cl] in methanol-\textit{d}\textsubscript{4} for a few minutes inside an NMR tube. The NMR tube was then sealed tightly under about 1 atmosphere of dihydrogen, and \textsuperscript{1}H NMR spectra were obtained at regular intervals. Even after several days at room temperature, no reaction of Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}Cl] was observed. The reaction was repeated by placing the NMR tube under about 7 atmospheres of dihydrogen inside a Parr hydrogenator overnight. The NMR tube was then quickly sealed under about 1 atmosphere of dihydrogen, and the \textsuperscript{1}H NMR spectrum was run immediately. Again, no reaction of Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}Cl] was observed. Published Rh\textsuperscript{III}(L)H (L = porphyrin or TMTAA) complexes are known to revert back to the corresponding [Rh\textsuperscript{II}(L)\textsubscript{2} dimers in the absence of a dihydrogen atmosphere in low polarity solvents (see Section 5.1.2 for more detail)\textsuperscript{15,204} Although these Rh\textsuperscript{II}(L)H complexes are clearly observed at dihydrogen pressures below 1 atmosphere,\textsuperscript{15,204} dihydrogen pressures greater than 1 atmosphere may be required to form appreciable amounts of Rh\textsuperscript{III}(L\textsubscript{m})H. However, high-pressure NMR tubes were not available to conduct NMR experiments at higher dihydrogen pressures.
A possible reason why no Rh^{III}(L_m)H was detected in the second route is perhaps because the rhodium-rhodium bond of Na[[Rh^{II}(L_m)]_2Cl] is less prone to cleavage than the rhodium-rhodium bond of [Rh^{II}(porphyrin)]_2 and [Rh^{II}(TMTAA)]_2. To further investigate reactions that might result in cleavage of the rhodium-rhodium bond in Na[[Rh^{II}(L_m)]_2Cl] when dissolved in alcohol solvents, the reaction of Na[[Rh^{II}(L_m)]_2Cl] with excess triphenylphosphine was investigated, and the results are reported in the next section. Triphenylphosphine was selected as a reactant, because even relatively strong rhodium-rhodium bonds (for example, in [Rh^{II}(Rpe)]_2) are known to cleave in the presence of excess phosphines.\textsuperscript{211}

### 5.2.4 Reactions of Na[[Rh^{II}(L_m)]_2Cl] and derivatives with triphenylphosphine

Because Na[[Rh^{II}(L_m)]_2Cl] did not react with dihydrogen (Section 5.2.3), reactions were attempted with other reagents to see whether the rhodium-rhodium bond would cleave to give monomeric products. This section therefore describes investigations into the reaction of Na[[Rh^{II}(L_m)]_2Cl] with triphenylphosphine, a reagent which is known to break even reasonably strong rhodium-rhodium bonds to give monomeric products.\textsuperscript{211} From these experiments (which are described in detail below), the diamagnetic monomeric complex, [Rh^{III}(L_m)(PPh_3)][PF_6], was successfully synthesised, purified, and characterised. It was also surmised from these results that the rhodium-rhodium bond of Na[[Rh^{II}(L_m)]_2Cl] cleaves heterolytically to form [Rh^{III}(L_m)(PPh_3)][PF_6].

[Rh^{III}(L_m)(PPh_3)][PF_6] was synthesised by stirring 3 equivalents of triphenylphosphine with Na[[Rh^{II}(L_m)]_2Cl] in methanol. After 20 minutes at room temperature in air, the solvent was removed under vacuum and the residue was suspended in toluene, followed by extraction of the product into deionised water. To exchange the counteranion on the product, a large excess of ammonium hexafluorophosphate was added to the aqueous solution, and the green precipitate that formed was collected by filtration. The dried precipitate was then purified by column chromatography on alumina, giving [Rh^{III}(L_m)(PPh_3)][PF_6] in 71% yield (see Section 5.4.3 for detailed experimental procedure).
Only one major species was observed in the high resolution positive ion mass spectrum of \([\text{Rh}^{\text{III}}(\text{L}_m)(\text{PPh}_3)[\text{PF}_6]],\) which corresponded to a formulation of \([\text{Rh}^{\text{III}}(\text{L}_m)(\text{PPh}_3)]^+\). A small amount of \([\text{Rh}^{\text{II}}(\text{L}_m)]^+\) was also observed in this mass spectrum (12% intensity relative to the \([\text{Rh}^{\text{III}}(\text{L}_m)(\text{PPh}_3)]^+\) peak), which presumably arises from loss of the triphenylphosphine ligand in the electrospray ionisation process. The \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra of \([\text{Rh}^{\text{III}}(\text{L}_m)(\text{PPh}_3)])[\text{PF}_6]\) in methanol-\(d_4\) also agreed with the presence of one triphenylphosphine ligand per rhodium centre. The two geminal-C-methyl signals were inequivalent by \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectroscopy (observed at 1.51 and 1.17 ppm in the \(^1\text{H}\) NMR spectrum, and at 29.0 and 28.3 ppm in the \(^{13}\text{C}\) NMR spectrum), indicating that \([\text{Rh}^{\text{III}}(\text{L}_m)(\text{PPh}_3)])[\text{PF}_6]\) is five-coordinate. Furthermore, elemental analysis was consistent with a formulation of \([\text{Rh}^{\text{III}}(\text{L}_m)(\text{PPh}_3)])[\text{PF}_6],\) indicating that only one axial ligand is present in the solid state and that there are no water(s) of crystallisation.

The reason that \([\text{Rh}^{\text{III}}(\text{L}_m)(\text{PPh}_3)])[\text{PF}_6]\) is five-coordinate, with only one axial triphenylphosphine ligand, may be that the triphenylphosphine ligand pulls the rhodium centre of this complex out of the plane defined by the four nitrogen donors of the \(\text{L}_m\) ligand, on the side towards the triphenylphosphine ligand. This would then make coordination of a second axial ligand to the vacant coordination site unfavourable. Additionally, if two triphenylphosphine ligands were present on each rhodium centre, there may be too much steric strain between the \(\text{L}_m\) ligand and the two triphenylphosphine ligands for this complex to be stable. This is because, when one axial triphenylphosphine ligand is present, the somewhat flexible \(\text{L}_m\) ligand can bend away from the triphenylphosphine ligand, but a second triphenylphosphine ligand would restrict this bending and would increase steric strain.

The formation of \([\text{Rh}^{\text{III}}(\text{L}_m)(\text{PPh}_3)])[\text{PF}_6]\) from \(\text{Na}[[\text{Rh}^{\text{II}}(\text{L}_m)]_2\text{Cl}]\) and triphenylphosphine is expected to begin with coordination of triphenylphosphine to \(\text{Na}[[\text{Rh}^{\text{II}}(\text{L}_m)]_2\text{Cl}],\) which weakens the rhodium-rhodium bond and makes it susceptible to heterolytic cleavage. Like the reaction pathway proposed for the reaction of DMSO or DMF with \(\text{Na}[[\text{Rh}^{\text{II}}(\text{L}_m)]_2\text{Cl}]\) (Figure 5.15), there are a number of possible reaction pathways for the synthesis of \([\text{Rh}^{\text{III}}(\text{L}_m)(\text{PPh}_3)])[\text{PF}_6]\) from \(\text{Na}[[\text{Rh}^{\text{II}}(\text{L}_m)]_2\text{Cl}]\) and triphenylphosphine in air. One of these possible reaction pathways is shown in Figure 5.18, and begins with heterolytic cleavage of the rhodium-rhodium bond of \(\text{Na}[[\text{Rh}^{\text{II}}(\text{L}_m)]_2(\text{Cl})(\text{PPh}_3)]\), forming \([\text{Rh}^{\text{III}}(\text{L}_m)(\text{PPh}_3)]^+\) and a rhodium(I) intermediate. Aerial oxidation of this air-sensitive rhodium(I) intermediate produces a rhodium(III) intermediate, which is then ligated by the excess triphenylphosphine to form more \([\text{Rh}^{\text{III}}(\text{L}_m)(\text{PPh}_3)]^+\).

Therefore, only one product is formed via this reaction pathway, as was indeed observed in this
reaction. From this reaction, the counteranion on $[\text{Rh}^{\text{III}}(\text{L}_m)(\text{PPh}_3)]^+$ is probably a mixture of chloride (from Na[[$\text{Rh}^{\text{II}}(\text{L}_m)]_2\text{Cl}$]) and hydroxide (from aerial oxidation of the rhodium(I) intermediate). These counteranions were therefore exchanged for hexafluorophosphate, and were removed during product isolation to give pure $[\text{Rh}^{\text{III}}(\text{L}_m)(\text{PPh}_3) ][\text{PF}_6]$.

![Figure 5.18: Possible heterolytic reaction pathway for the formation of $[\text{Rh}^{\text{III}}(\text{L}_m)(\text{PPh}_3)]^+$ from triphenylphosphine and Na[[$\text{Rh}^{\text{II}}(\text{L}_m)]_2\text{Cl}$] under aerobic conditions, via a Na[[$\text{Rh}^{\text{II}}(\text{L}_m)]_2(\text{Cl})(\text{PPh}_3)$] intermediate](image)

A homolytic reaction pathway is unlikely for the formation of $[\text{Rh}^{\text{III}}(\text{L}_m)(\text{PPh}_3)][\text{PF}_6]$ from Na[[$\text{Rh}^{\text{II}}(\text{L}_m)]_2\text{Cl}$] and triphenylphosphine in methanol. This is because homolytic cleavage of the rhodium-rhodium bond would result in the formation of reactive rhodium(II) intermediates (such as $[\text{Rh}^{\text{II}}(\text{L}_m)(\text{PPh}_3)]^+$), which might then be expected to react to form a range of products. No other products aside from $[\text{Rh}^{\text{III}}(\text{L}_m)(\text{PPh}_3)]^+$ were observed in the reaction of Na[[$\text{Rh}^{\text{II}}(\text{L}_m)]_2\text{Cl}$] and triphenylphosphine, suggesting that a homolytic reaction pathway does not occur. Note, however, that a homolytic cleavage pathway followed by rapid air oxidation of the rhodium(II) intermediates to rhodium(III) product(s), and subsequent ligation of the rhodium(III) product(s) by triphenylphosphine to form $[\text{Rh}^{\text{III}}(\text{L}_m)(\text{PPh}_3)]^+$ cannot presently be ruled out.

As described in Section 5.2.5, a monomeric rhodium(III) complex, $\text{Rh}^{\text{III}}(\text{L}_m)(\text{OCD}_3)(\text{CD}_3\text{OD})$, has been synthesised by passing an isolated $\text{Rh}^{\text{III}}(\text{L}_m)\text{Me}$ complex through an alumina column, and then allowing this complex to decompose in air in methanol-$d_4$ overnight. When triphenylphosphine was added to $\text{Rh}^{\text{III}}(\text{L}_m)(\text{OCD}_3)(\text{CD}_3\text{OD})$ in methanol-$d_4$, $[\text{Rh}^{\text{III}}(\text{L}_m)(\text{PPh}_3)]^+$
formed in high yield. This \([\text{Rh}^{III}(\text{L}_m)(\text{PPh}_3)]^+\) complex was identical by \(^1\)H NMR spectroscopy to the \([\text{Rh}^{III}(\text{L}_m)(\text{PPh}_3)]^+\) complex synthesised from \(\text{Na}[\text{Rh}^{II}(\text{L}_m)]_2\text{Cl}\) and triphenylphosphine in methanol. This suggests that the synthesis of \([\text{Rh}^{III}(\text{L}_m)(\text{PPh}_3)]^+\) from \(\text{Na}[\text{Rh}^{II}(\text{L}_m)]_2\text{Cl}\) may indeed occur via the formation of rhodium(III) intermediates. The synthesis of \([\text{Rh}^{III}(\text{L}_m)(\text{PPh}_3)]^+\) from \(\text{Rh}^{III}(\text{L}_m)(\text{OCD}_3)(\text{CD}_3\text{OD})\) was faster (about 3 minutes to reach completion) than the synthesis of \([\text{Rh}^{III}(\text{L}_m)(\text{PPh}_3)]^+\) from \(\text{Na}[\text{Rh}^{II}(\text{L}_m)]_2\text{Cl}\) (about 20 minutes to reach completion). This suggests that the slowest step in the synthesis of \([\text{Rh}^{III}(\text{L}_m)(\text{PPh}_3)]^+\) from \(\text{Na}[\text{Rh}^{II}(\text{L}_m)]_2\text{Cl}\) is the formation of the initial triphenylphosphine-coordinated dimer and/or cleavage of the rhodium-rhodium bond.

A number of studies reported in the literature have investigated the reaction of excess trialkylphosphines and triarylphosphines with \([\text{Rh}^{II}(\text{corrole})]^2\) and \([\text{Rh}^{II}(\text{porphyrin})]^2\) complexes.\(^{222-224,229}\) \([\text{Rh}^{II}(\text{corrole})]^2\) complexes usually react with trialkylphosphines and triarylphosphines to form \([\text{Rh}^{III}(\text{corrole})(\text{PR}_3)]^+\) complexes under aerobic conditions, which, like \([\text{Rh}^{III}(\text{L}_m)(\text{PPh}_3)]^+\), are air-stable and have only one phosphine ligand.\(^{222-224}\) However, \([\text{Rh}^{II}(\text{porphyrin})]^2\) complexes can react with excess phosphine to form monomeric complexes with either one or two axial phosphine ligands. These phosphine complexes of rhodium-porphyrins are usually highly air-sensitive and oxidise further upon exposure to air. For example, \([\text{Rh}^{II}(\text{TPP})]^2\) reacts with triethylphosphine under air-free conditions to give the complex, \([\text{Rh}^{III}(\text{TPP}*)(\text{PEt}_3)_2]\), which oxidises to \([\text{Rh}^{III}(\text{TPP})(\text{PEt}_3)_2]^+\) upon exposure to air. For \([\text{Rh}^{III}(\text{TPP}*)(\text{PEt}_3)_2]\), the TPP ligand is non-innocent and the rhodium centre has a formal oxidation state of +II. In contrast, \([\text{Rh}^{II}(\text{OEP})]^2\) reacts with triethylphosphine under air-free conditions to give \([\text{Rh}^{III}(\text{OEP}*)(\text{PEt}_3)_2]\), which oxidises to a peroxo-bridged \((\text{PEt}_3)(\text{OEP})\text{Rh}^{III}\text{-O-O-Rh}^{III}(\text{OEP})(\text{PEt}_3)\) complex upon exposure to air.\(^{229}\) Therefore, on exposure to phosphines and air, \(\text{Na}[\text{Rh}^{II}(\text{L}_m)]_2\text{Cl}\) behaves more like \([\text{Rh}^{II}(\text{corrole})]^2\) complexes than \([\text{Rh}^{II}(\text{porphyrin})]^2\) complexes.

### 5.2.5 Reduction of \(\text{Na}[\text{Rh}^{II}(\text{L}_m)]_2\text{Cl}\) with \(\text{NaBH}_4\) and subsequent reactions with alkyl halides

Because it has been proposed (in Section 5.2.4) that the synthesis of \([\text{Rh}^{III}(\text{L}_m)(\text{PPh}_3)]^+\) from \(\text{Na}[\text{Rh}^{II}(\text{L}_m)]_2\text{Cl}\) and triphenylphosphine proceeds via heterolytic cleavage of the rhodium-rhodium bond, followed by oxidation of the rhodium(I) intermediate, a rhodium(I)-\(\text{L}_m\) complex

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was deliberately synthesised in order to gain a better understanding this reaction. Studies have shown that \([\text{Rh}^{II}(L)]_2\) complexes (\(L = \text{porphyrin or TMTAA}\)) can be reduced to \(\text{Na}[\text{Rh}^I(L)]\) using sodium borohydride. These monomeric rhodium(I) complexes are stable under air- and water-free conditions in the absence of electrophiles, and some have even been characterised by \(^1\text{H}\) NMR spectroscopy in dry degassed benzene-\(d_6\).\(^{15,231}\) However, upon exposure to air, these \(\text{Na}[\text{Rh}^I(L)]\) complexes rapidly oxidise to rhodium(III) species. Additionally, if an electrophile is added to these \(\text{Na}[\text{Rh}^I(L)]\) complexes, air-stable monomeric rhodium(III) products can often be synthesised.\(^{15}\) For example, \(\text{Rh}^{III}(\text{OEP})(\text{alkyl})\) complexes can be synthesised by the addition of alkyl halides to \(\text{Na}[\text{Rh}^I(\text{OEP})]\).\(^{226}\)

This section describes and discusses the synthesis and reactivity of a highly air-sensitive complex, \(\text{Na}[\text{Rh}^I(\text{L}_m)]\). Reactions of \(\text{Na}[\text{Rh}^I(\text{L}_m)]\) with air in alcohols were shown to produce \(\text{Rh}^{III}(\text{L}_m)(\text{OR})(\text{ROH})\) complexes, while reactions of \(\text{Na}[\text{Rh}^I(\text{L}_m)]\) with various alkyl halides to were shown to produce \(\text{Rh}^{III}(\text{L}_m)(\text{alkyl})\) complexes. These reactions are described and discussed in this section, along with the spectroscopic properties, structural properties, and stabilities of these complexes.

5.2.5.1 Synthesis of \(\text{Na}[\text{Rh}^I(\text{L}_m)]\) and aerial oxidation to \(\text{Rh}^{III}(\text{L}_m)(\text{OCD}_3)(\text{CD}_3\text{OD})\) in methanol-\(d_4\)

\(\text{Na}[\text{Rh}^I(\text{L}_m)]\) was synthesised by stirring a suspension of \(\text{Na}[\text{Rh}^{II}(\text{L}_m)_2\text{Cl}]\) with a large excess of sodium borohydride in ethanol, under a nitrogen atmosphere. After 35 minutes at room temperature, the solution became clear red-orange and the solvent was removed under vacuum. Upon exposing the residue to air, the red-orange solid rapidly became brown, suggesting that, like the analogous \(\text{Na}[\text{Rh}^I(\text{porphyrin})]\) and \(\text{Na}[\text{Rh}^I(\text{TMTAA})]\) complexes,\(^{15,231}\) \(\text{Na}[\text{Rh}^I(\text{L}_m)]\) oxidises rapidly in air. Because of this high air-sensitivity, \(\text{Na}[\text{Rh}^I(\text{L}_m)]\) was not successfully characterised. However, reactivity studies (described in Section 5.2.5.2 below) do indicate that \(\text{Na}[\text{Rh}^I(\text{L}_m)]\) was indeed synthesised in this reaction.

Although \(\text{Na}[\text{Rh}^I(\text{L}_m)]\) was not fully characterised, the rhodium(III) complex produced from aerial oxidation of \(\text{Na}[\text{Rh}^I(\text{L}_m)]\) in methanol-\(d_4\) was characterised by mass spectrometry and NMR spectroscopy. Based on the spectroscopic data discussed below, the product formed in
this reaction was tentatively formulated as \( \text{Rh}^{\text{III}}(\text{L}_m)(\text{OCD}_3)(\text{CD}_3\text{OD}) \). A general scheme for this reaction is shown in Figure 5.19.

\[
\begin{align*}
\text{Na}[[\text{Rh}^{\text{II}}(\text{L}_m)]_2\text{Cl}] & \xrightarrow{\text{NaBH}_4, \text{Ethanol}} \text{Na}[[\text{Rh}^{\text{I}}(\text{L}_m)] \xrightarrow{\text{air, CD}_3\text{OD}} \text{Rh}^{\text{III}}(\text{L}_m)(\text{OCD}_3)(\text{CD}_3\text{OD})
\end{align*}
\]

**Figure 5.19:** General reaction for the synthesis of \( \text{Rh}^{\text{III}}(\text{L}_m)(\text{OCD}_3)(\text{CD}_3\text{OD}) \) from \( \text{Na}[[\text{Rh}^{\text{I}}(\text{L}_m)] \)

In the high resolution positive ion mass spectrum of \( \text{Rh}^{\text{III}}(\text{L}_m)(\text{OCD}_3)(\text{CD}_3\text{OD}) \) in methanol-\( d_4 \), only one major signal was observed, which corresponded to a \( [\text{Rh}^{\text{III}}(\text{L}_m)]^+ \) species, where any axial ligands were presumably lost during the electrospray ionisation process. This suggests that the rhodium centre of \( \text{Rh}^{\text{III}}(\text{L}_m)(\text{OCD}_3)(\text{CD}_3\text{OD}) \) is indeed in the +III oxidation state. Furthermore, no signals were observed in the high resolution negative ion mass spectrum that would correspond to an anionic rhodium(I) complex, suggesting that all the \( \text{Na}[[\text{Rh}^{\text{I}}(\text{L}_m)] \) has oxidised to rhodium(III) product(s).

In the \(^1\text{H}\) NMR spectrum of \( \text{Rh}^{\text{III}}(\text{L}_m)(\text{OCD}_3)(\text{CD}_3\text{OD}) \) in methanol-\( d_4 \), only one major product was observed. No indication of \( \text{Na}[[\text{Rh}^{\text{II}}(\text{L}_m)]_2\text{Cl}] \) was observed in this \(^1\text{H}\) NMR spectrum. A single set of sharp non-contact shifted signals were observed for \( \text{Rh}^{\text{III}}(\text{L}_m)(\text{OCD}_3)(\text{CD}_3\text{OD}) \), which was stable for weeks in air at room temperature in methanol-\( d_4 \) without any noticeable changes to its \(^1\text{H}\) NMR spectrum. The similarity of the \(^1\text{H}\) NMR chemical shifts for the \( \text{L}_m \) ligand of \( \text{Rh}^{\text{III}}(\text{L}_m)(\text{OCD}_3)(\text{CD}_3\text{OD}) \) (given in Section 5.4.5) to other rhodium(III)-\( \text{L}_m \) complexes described in this chapter suggests that the rhodium centre is indeed in the +III oxidation state. A monomeric rhodium(II) metal centre can be ruled out because it would have broad paramagnetic contact-shifted \(^1\text{H}\) NMR signals and would be highly air-sensitive.

Only one \( \text{L}_m \) ligand geminal-C-methyl signal was observed in the \(^1\text{H}\) NMR spectrum of \( \text{Rh}^{\text{III}}(\text{L}_m)(\text{OCD}_3)(\text{CD}_3\text{OD}) \), which suggests that both axial ligands are identical on the NMR timescale. Although it was not possible to identify these axial ligands based on mass spectrometry and NMR spectroscopy, it would seem reasonable to expect that these could be \( \text{CD}_3\text{OD} \) and/or \( \text{CD}_3\text{O}^- \) from the methanol-\( d_4 \) solvent. Thus, even though it was not possible to distinguish between possible formulations of \( \text{Rh}^{\text{III}}(\text{L}_m)(\text{OCD}_3)(\text{CD}_3\text{OD}) \) and
[Rh\text{III}(L_m)(CD_3OD)_2]^+ for this complex, for consistency, the former formulation is used throughout this thesis. Despite their being two different axial ligands in Rh\text{III}(L_m)(OCD)(CD_3OD), the presence of a single geminal-C-methyl signal in the $^1$H NMR spectrum could be due to rapid exchange between these two ligands and the methanol-$d_4$ solvent on the NMR timescale, as has been observed for a similar reported complex that is discussed below.\textsuperscript{245} In reality, there is probably rapid exchange between CD_3OD and CD_3O\textsuperscript{-} ligands (and counteranions) in solution, and there is possibly also rapid exchange with H_2O and OH\textsuperscript{-} ligands/counteranions that arise from the traces of water present in the methanol-$d_4$ solvent. Further experiments do, however, rule out a formulation of [Rh\text{III}(L_m)(OH)]^+, because the addition of excess sodium hydroxide to Rh\text{III}(L_m)(OCD)(CD_3OD) in methanol-$d_4$ gives a single new monomeric product in high yield with only one geminal-C-methyl signal. Further experiments will be carried out in future to determine the nature of the axial ligands on Rh\text{III}(L_m)(OCD)(CD_3OD).

Rapid exchange between two different axial ligands has also been postulated for a published complex, Rh\text{III}(TMP)(OCH_3)(CH_3OH) (TMP = tetramesitylporphyrin).\textsuperscript{245} This complex was synthesised by adding a large excess of methanol to a solution of Rh\text{III}(TMP)(OCH_3) in benzene-$d_6$. Analogously to the geminal-C-methyl groups of the postulated Rh\text{III}(L_m)(OCD)(CD_3OD) complex, the mesityl ortho-methyl groups of the TMP ligand in Rh\text{III}(TMP)(OCH_3)(CH_3OH) were equivalent by $^1$H NMR spectroscopy. Because these mesityl ortho-methyl groups are oriented perpendicular to the porphyrin core of the TMP ligand, it was concluded that the OCH_3 ligand and the CH_3OH ligand are in rapid equilibrium on the NMR timescale. It is believed that this is due to rapid exchange of the OCH_3/CH_3OH ligands with the excess free methanol solvent in solution, via exchange of the CH_3OH protons. A similar process could be occurring if the rhodium(III)-L_m complex has a formulation of Rh\text{III}(L_m)(OCD)(CD_3OD) in methanol-$d_4$. The equivalence of the mesityl ortho-methyl groups of Rh\text{III}(TMP)(OCH_3)(CH_3OH) is not due to the rotation of the mesityl groups, because the barrier to this rotation is too large to occur in these experiments. Furthermore, using smaller excesses of free methanol in benzene-$d_6$, separate resonances were observed for the OCH_3 (-2.38 ppm) and CH_3OH (-1.97 ppm) ligands, but at higher free methanol concentrations, these signals merged into a single broad signal at an averaged position (-2.17 ppm), due to rapid exchange with the free methanol solvent.\textsuperscript{245}

Rh\text{III}(L_m)(OR)(ROH) complexes, where R = CH_3 or Et, were also synthesised by dissolving the isolated complex, Na[Rh\text{I}(L_m)], in methanol or ethanol, respectively, in the presence of air. After
removing the solvent under vacuum, the residue was dissolved in methanol-\textit{d}_4 and the \textit{^1}\text{H} NMR spectrum was obtained. These \textit{^1}\text{H} NMR spectra were identical to the Rh\textsuperscript{III}(L\textsubscript{m})(OCD\textsubscript{3})(CD\textsubscript{3}OD) complex prepared by dissolving Na[Rh\textsuperscript{I}(L\textsubscript{m})] directly in methanol-\textit{d}_4 in air, except that the corresponding free alcohol (ROH) solvent was also observed in the former spectra. This is probably because the OR/ROH axial ligands of the Rh\textsuperscript{III}(L\textsubscript{m})(OR)(ROH) complexes rapidly exchange on the NMR timescale for OCD/CD\textsubscript{3}OD ligands upon dissolution in methanol-\textit{d}_4. Although attempts were made to purify the Rh\textsuperscript{III}(L\textsubscript{m})(OR)(ROH) complexes (R = CH\textsubscript{3} or Et) by column chromatography and via recrystallisations, these resulted in large increases in the relative amount of impurities. This suggests that these rhodium(III) compounds are rather reactive. Indeed, as discussed in more detail in Sections 5.2.6 and 5.2.7 below, these Rh\textsuperscript{III}(L\textsubscript{m})(OR)(ROH) complexes react readily with carbon monoxide or acetylene to give new rhodium(III) products in high yield.

5.2.5.2 Reactivity studies of the Na[Rh\textsuperscript{I}(L\textsubscript{m})] complex and synthesis of Rh\textsuperscript{III}(L\textsubscript{m})Me from Na[Rh\textsuperscript{I}(L\textsubscript{m})]

Because the product tentatively formulated as Na[Rh\textsuperscript{I}(L\textsubscript{m})] could not be fully characterised, this section describes reactivity studies of Na[Rh\textsuperscript{I}(L\textsubscript{m})] with various alkyl halides that were carried out in order to indirectly confirm that Na[Rh\textsuperscript{I}(L\textsubscript{m})] was synthesised. These studies were also conducted in to order to isolate and characterise various Rh\textsuperscript{III}(L\textsubscript{m})(alkyl) complexes (Sections 5.2.5.3 and 5.2.5.4).

Reactivity studies indeed confirm that Na[Rh\textsuperscript{I}(L\textsubscript{m})] was synthesised when Na[[Rh\textsuperscript{II}(L\textsubscript{m})]_2Cl] was reduced with sodium borohydride in ethanol. Thus, in an initial reactivity study, Na[[Rh\textsuperscript{II}(L\textsubscript{m})]_2Cl] was reduced to Na[Rh\textsuperscript{I}(L\textsubscript{m})] using excess sodium borohydride in ethanol under a nitrogen atmosphere (as per the reaction discussed in Section 5.2.5.1). Once this reaction had reached completion, a large excess of methyl iodide was added, taking care not to introduce any air into the reaction. The solution was then stirred for 45 minutes at room temperature, followed by removal of the solvent under reduced pressure (see Section 5.4.4 for full experimental procedure). Spectroscopic studies described in Section 5.2.5.3 below confirmed that Rh\textsuperscript{III}(L\textsubscript{m})Me was synthesised in high yield in this reaction. This experiment indirectly confirmed that sodium borohydride reduces Na[[Rh\textsuperscript{II}(L\textsubscript{m})]_2Cl] to Na[Rh\textsuperscript{I}(L\textsubscript{m})], because the electrophilic methyl group from methyl iodide reacts with the nucleophilic rhodium(I) centre, forming Rh\textsuperscript{III}(L\textsubscript{m})Me (Figure 5.20). Furthermore, it has been reported that rhodium(I)-porphyrin
complexes have nucleophilic metal centres, whereas rhodium(III)-porphyrin complexes usually have electrophilic metal centres. It has been reported that similar reactions have been used to synthesise Rh\textsuperscript{III}(porphyrin)Me and Rh\textsuperscript{III}(TMTAA)Me complexes from the corresponding dimers.\textsuperscript{15,204,232}

\[ \text{Na}[\text{Rh}^{II}(L_m)_2\text{Cl}] \xrightarrow{\text{NaBH}_4, \text{Ethanol}} \text{Na}[\text{Rh}^{I}(L_m)] \xrightarrow{\text{MeI}} \text{Rh}^{III}(L_m)\text{Me} \]

**Figure 5.20: General reaction for the synthesis of Rh\textsuperscript{III}(L_m)Me from Na[[Rh\textsuperscript{II}(L_m)]\text{Cl}], sodium borohydride, and methyl iodide in ethanol**

Further reactivity studies were conducted to confirm that Na[[Rh\textsuperscript{II}(L_m)]\text{Cl}] itself does not react with methyl iodide to form Rh\textsuperscript{III}(L_m)Me. It has been shown in the literature\textsuperscript{15,232} that [Rh\textsuperscript{II}(L)]\text{2} dimers (L = porphyrin or TMTAA) react directly with methyl iodide to form a 1:1 mixture of Rh\textsuperscript{III}(L)Me and Rh\textsuperscript{III}(L)I. However, when this reaction was attempted with Na[[Rh\textsuperscript{II}(L_m)]\text{2}Cl] in methanol-\text{d}_4, the reaction was very slow and after several days at room temperature, most of the Na[[Rh\textsuperscript{II}(L_m)]\text{2}Cl] remained unreacted. Only a few minor products were observed in the $^1$H NMR spectrum, none of which were Rh\textsuperscript{III}(L_m)Me. This indicates that formation of Rh\textsuperscript{III}(L_m)Me from sodium borohydride-reduced Na[[Rh\textsuperscript{II}(L_m)]\text{2}Cl] and methyl iodide is not due to the direct reaction of Na[[Rh\textsuperscript{II}(L_m)]\text{2}Cl] with methyl iodide over the time of the experiments.

In a further experiment, Na[Rh\textsuperscript{I}(L_m)] was isolated, exposed to air, and then redissolved in ethanol. Methyl iodide was then added to this Rh\textsuperscript{III}(L_m)(OEt)(EtOH) complex, and portions of the solution were removed and evaporated to dryness at regular intervals. The residue was then dissolved in methanol-\text{d}_4 and the $^1$H NMR spectrum was obtained. As expected, even after 4 hours at room temperature, no Rh\textsuperscript{III}(L_m)Me was observed, and the only major product detected was identical to the Rh\textsuperscript{III}(L_m)(OCD\textsubscript{3})(CD\textsubscript{3}OD) complex described in Section 5.2.5.1. None of the minor by-products observed had doublet signals in the region expected for a methyl ligand. Thus, the rhodium(III) product does not react with methyl iodide under these conditions, strongly indicating that Na[Rh\textsuperscript{I}(L_m)] is indeed formed upon reacting Na[[Rh\textsuperscript{II}(L_m)]\text{2}Cl] with sodium borohydride, and also indicating that Na[Rh\textsuperscript{I}(L_m)] does not oxidise to a rhodium(III) complex prior to the addition of methyl iodide.
5.2.5.3 Characterisation of Rh\textsuperscript{III}(L\textsubscript{m})Me

The methyl ligand of Rh\textsuperscript{III}(L\textsubscript{m})Me was observed as an upfield doublet at 0.12 ppm ($J_{\text{1H-103Rh}} = 3.0$ Hz) by \textsuperscript{1}H NMR spectroscopy and at -6.0 ppm ($J_{\text{13C-103Rh}} = 35.6$ Hz) by \textsuperscript{13}C NMR spectroscopy in methanol-$d_4$. This $J_{\text{1H-103Rh}}$ coupling constant is similar to reported Rh\textsuperscript{III}(TMTAA)Me and Rh\textsuperscript{III}(porphyrin)Me complexes (2.9 to 3.6 Hz). The \textsuperscript{1}H NMR chemical shift of the Rh\textsuperscript{III}(L\textsubscript{m})Me methyl ligand is much closer to Rh\textsuperscript{III}(TMTAA)Me (2.20 ppm) than to Rh\textsuperscript{III}(porphyrin)Me complexes (-5.25 to -6.16 ppm), due to the porphyrin ring-current effect in the latter complexes.\textsuperscript{15,204,205,232}

In both the \textsuperscript{1}H and \textsuperscript{13}C NMR spectra of Rh\textsuperscript{III}(L\textsubscript{m})Me in methanol-$d_4$, the two geminal-C-methyl groups of the L\textsubscript{m} ligand were inequivalent. This suggests that Rh\textsuperscript{III}(L\textsubscript{m})Me is either five-coordinate with one axial ligand or six-coordinate with two different axial ligands (such as water and the methyl ligand). Elemental analysis and X-ray crystallography of this complex was not obtained to clarify the coordination geometry of Rh\textsuperscript{III}(L\textsubscript{m})Me, because this complex decomposes in air after purification. Studies into this decomposition are described in Section 5.2.5.5. Despite this, a formulation of Rh\textsuperscript{III}(L\textsubscript{m})Me is used throughout this thesis.

The only major signal observed in the high resolution positive ion mass spectrum of Rh\textsuperscript{III}(L\textsubscript{m})Me corresponded to formulation of [Rh\textsuperscript{III}(L\textsubscript{m})]\textsuperscript{+}. No Rh\textsuperscript{III}(L\textsubscript{m})Me + H\textsuperscript{+} or Rh\textsuperscript{III}(L\textsubscript{m})Me + Na\textsuperscript{+} species were observed, suggesting that the methyl group is easily lost in the mass spectrum during the electrospray ionisation process. Axial ligand loss has also been observed in the mass spectra of Fe\textsuperscript{III}(L\textsubscript{m})Cl and Co\textsuperscript{III}(L\textsubscript{m})Br. In contrast, the methyl ligand of the Rh\textsuperscript{III}(porphyrin)Me complexes is not lost in the positive ion FAB mass spectrum.\textsuperscript{205,232} These differences may be due to the FAB mode used to run these mass spectra, which is a softer ionisation method than the ESI technique. Loss of the methyl ligand from Rh\textsuperscript{III}(L\textsubscript{m})Me could also be due to the strong donating properties of the L\textsubscript{m} ligand, which would labilise axial ligands and would therefore cause the methyl ligand to be easily lost during the ionisation process used for mass spectrometry.

5.2.5.4 Synthesis of Rh\textsuperscript{III}(L\textsubscript{m})Et and Rh\textsuperscript{III}(L\textsubscript{m})Bn from Na[Rh\textsuperscript{I}(L\textsubscript{m})]

Attempts were made to synthesise Rh\textsuperscript{III}(L\textsubscript{m})Et. Thus, the reaction conditions used to synthesise Rh\textsuperscript{III}(L\textsubscript{m})Me were repeated, using ethyl iodide instead of methyl iodide. The \textsuperscript{1}H NMR spectrum
of the crude Rh\textsuperscript{III}(L\textsubscript{m})Et complex in methanol-\textit{d}_4 showed only one major product (Rh\textsuperscript{III}(L\textsubscript{m})Et) and many minor by-products. The \textsuperscript{1}H NMR chemical shifts for the L\textsubscript{m} ligand of Rh\textsuperscript{III}(L\textsubscript{m})Et were similar to those of Rh\textsuperscript{III}(L\textsubscript{m})Me. For the ethyl ligand of Rh\textsuperscript{III}(L\textsubscript{m})Et, the methyl group was observed as an upfield triplet of doublets at 0.23 ppm ($J_{1H-1H} = 7$ Hz; $J_{1H-103Rh} = 2.1$ Hz), and the methylene group was observed at approximately 1.42 ppm. Coupling constants were not determined for this methylene group because they overlapped the methyl signal of the remaining ethanol solvent. Although attempts were made to remove the ethanol solvent, by the time that Rh\textsuperscript{III}(L\textsubscript{m})Et had been dried long enough under vacuum to remove most of this solvent, Rh\textsuperscript{III}(L\textsubscript{m})Et had completely decomposed.

The \textsuperscript{1}H NMR spectra of Rh\textsuperscript{III}(TMTAA)Et and Rh\textsuperscript{III}(TPP)Et have also been published in the literature. For Rh\textsuperscript{III}(TMTAA)Et, the ethyl ligand protons occur at 0.75 ppm (CH\textsubscript{2}CH\textsubscript{3}, $J_{1H-103Rh} = 2.5$ Hz) and 3.08 ppm (CH\textsubscript{2}CH\textsubscript{3}, $J_{1H-103Rh} = 3.4$ Hz), whereas for Rh\textsuperscript{III}(TPP)Et, the ethyl ligand protons occur at -4.18 ppm (CH\textsubscript{2}CH\textsubscript{3}) and -4.40 ppm (CH\textsubscript{2}CH\textsubscript{3}).\textsuperscript{15,204} Therefore, the chemical shift of the ethyl ligands in Rh\textsuperscript{III}(L\textsubscript{m})Et is similar to Rh\textsuperscript{III}(TMTAA)Et, but very different from Rh\textsuperscript{III}(TPP)Et. This is due to the ring-current effect of the porphyrin ligand in the latter complex. Furthermore, the \textsuperscript{1}H-\textsuperscript{103}Rh coupling constant of the methyl group belonging to the ethyl ligands of Rh\textsuperscript{III}(L\textsubscript{m})Et (2.1 Hz) and Rh\textsuperscript{III}(TMTAA)Et (2.5 Hz) are similar.\textsuperscript{15} However, coupling constants could not be compared to Rh\textsuperscript{III}(TPP)Et because they have not been reported.

Decomposition of the crude Rh\textsuperscript{III}(L\textsubscript{m})Et complex was investigated further. After removing the bulk of the ethanol solvent from a crude sample of Rh\textsuperscript{III}(L\textsubscript{m})Et, the solid residue was dried briefly under vacuum (about 30 minutes), and this residue was then dissolved in methanol-\textit{d}_4. Although the \textsuperscript{1}H NMR spectrum of this solution showed that Rh\textsuperscript{III}(L\textsubscript{m})Et was the major product, after leaving this solution in air at room temperature for one hour, most of the Rh\textsuperscript{III}(L\textsubscript{m})Et had decomposed. Only one major decomposition product was observed in this \textsuperscript{1}H NMR spectrum, which was identical to the complex, Rh\textsuperscript{III}(L\textsubscript{m})(OCD\textsubscript{3})(CD\textsubscript{3}OD), described in Section 5.2.5.1. Furthermore, the relative amount of free ethanol increased noticeably over this time. This suggests that the ethyl ligand is mostly lost as ethanol, and the rhodium complex is then presumably ligated by CD\textsubscript{3}O/CD\textsubscript{3}OD ligands originating from the methanol-\textit{d}_4, thus forming Rh\textsuperscript{III}(L\textsubscript{m})(OCD\textsubscript{3})(CD\textsubscript{3}OD). A possible pathway for this reaction is discussed in Section 5.2.5.5 (see Figure 5.22) for the methyl ligand analogue of this complex, Rh\textsuperscript{III}(L\textsubscript{m})Me.
In contrast to the crude Rh\textsuperscript{III}(L\textsubscript{m})Et complex, which decomposes in methanol-$d_4$ in the presence of air over a few hours at room temperature, the crude Rh\textsuperscript{III}(L\textsubscript{m})Me complex was stable for weeks in methanol-$d_4$ and air, and no observable decomposition occurred over this time. This suggests that the ethyl ligand is lost more easily than the methyl ligand. This is not surprising, because the rhodium-methyl bond is expected to be stronger than the rhodium-ethyl bond. This is because methyl ligands are expected to be more electron releasing than ethyl ligands. Unlike Rh\textsuperscript{III}(L\textsubscript{m})Et, the reported Rh\textsuperscript{III}(TMTAA)Et and Rh\textsuperscript{III}(TPP)Et complexes did not readily decompose in benzene-$d_6$ and were isolated as air-stable solids. However, the addition of methanol-$d_4$ and other protic solvents to these complexes was not reported, and it is unknown whether they too decompose in the presence of these solvents.\textsuperscript{15,204} Nevertheless, Rh\textsuperscript{III}(L\textsubscript{m})Et appears to be much less stable than Rh\textsuperscript{III}(TMAA)Et and Rh\textsuperscript{III}(TPP)Et. This might be because the L\textsubscript{m} ligand is a stronger donor than the TMTAA and TPP ligands, causing the ethyl axial ligand to be labilised much more readily in Rh\textsuperscript{III}(L\textsubscript{m})Et than in Rh\textsuperscript{III}(TMAA)Et and Rh\textsuperscript{III}(TPP)Et.

To see whether other Rh\textsuperscript{III}(L\textsubscript{m})(alkyl) complexes also decompose readily in air, Rh\textsuperscript{III}(L\textsubscript{m})Bn was synthesised using the same method as for Rh\textsuperscript{III}(L\textsubscript{m})Me, except that excess benzyl chloride was used instead of excess methyl iodide. The benzyl chloride was first passed through a plug of alumina to remove any hydrochloric acid that may be present. Because the rhodium-benzyl bond is expected to be weaker than rhodium-ethyl bonds, this complex was expected to decompose more rapidly than Rh\textsuperscript{III}(L\textsubscript{m})Et. This was indeed found to be the case. Thus, when the reaction had reached completion, the solvent was removed under vacuum, and the residue was dried for the same length of time as in the experiment used to synthesise Rh\textsuperscript{III}(L\textsubscript{m})Et (about 30 minutes). Although comparing the $^1$H NMR spectrum of this crude Rh\textsuperscript{III}(L\textsubscript{m})Bn complex in methanol-$d_4$ to the $^1$H NMR spectra of literature Rh\textsuperscript{III}(porphyrin)Bn complexes\textsuperscript{205} suggested that Rh\textsuperscript{III}(L\textsubscript{m})Bn was indeed synthesised, Rh\textsuperscript{III}(L\textsubscript{m})Bn was a minor product compared to the Rh\textsuperscript{III}(L\textsubscript{m})(OCD$_3$)(CD$_3$OD) decomposition product and other unidentified by-products. This suggests that Rh\textsuperscript{III}(L\textsubscript{m})Bn has already decomposed appreciably over this time. Furthermore, all the Rh\textsuperscript{III}(L\textsubscript{m})Bn disappeared once the $^1$H NMR spectrum of the same solution was obtained about thirty minutes later.
5.2.5.5 Purification of Rh\textsuperscript{III}(L\textsubscript{m})Me and stability of the purified Rh\textsuperscript{III}(L\textsubscript{m})Me complex

Of the crude Rh\textsuperscript{III}(L\textsubscript{m})Me, Rh\textsuperscript{III}(L\textsubscript{m})Et, and Rh\textsuperscript{III}(L\textsubscript{m})Bn complexes, only the crude Rh\textsuperscript{III}(L\textsubscript{m})Me complex appears to be stable in air. Attempts were therefore made to purify this complex by column chromatography, to separate Rh\textsuperscript{III}(L\textsubscript{m})Me from the sodium borate salts and other by-products from the reaction. Because the crude Rh\textsuperscript{III}(L\textsubscript{m})Me complex is soluble and stable in methanol, and because Rh\textsuperscript{III}(L\textsubscript{m})Me also does not decompose after suspending this complex for a few hours in dichloromethane, a 19:1 dichloromethane/methanol eluent mixture was used to purify Rh\textsuperscript{III}(L\textsubscript{m})Me by column chromatography on neutral alumina. Column chromatography on silica gel was not carried out because much higher percentages of methanol in dichloromethane were required to get Rh\textsuperscript{III}(L\textsubscript{m})Me to move appreciably on the column, and the band containing Rh\textsuperscript{III}(L\textsubscript{m})Me broadened considerably on elution. Rh\textsuperscript{III}(L\textsubscript{m})Me moved as a narrow orange band on the alumina column and the eluate was collected and dried immediately under vacuum. After drying the solid residue for one hour under high vacuum to remove most of the methanol solvent, the residue was dissolved in dry degassed methanol-\textit{d}\textsubscript{4} and the \textit{\textsuperscript{1}H NMR} spectrum was obtained. This \textit{\textsuperscript{1}H NMR} spectrum suggested that this purified Rh\textsuperscript{III}(L\textsubscript{m})Me complex was actually less pure than the crude pre-columned Rh\textsuperscript{III}(L\textsubscript{m})Me complex. Although Rh\textsuperscript{III}(L\textsubscript{m})Me was still observed as the major species in this \textit{\textsuperscript{1}H NMR} spectrum, one other by-product was observed in this spectrum, which was identical to the complex, Rh\textsuperscript{III}(L\textsubscript{m})(OCD\textsubscript{3})(CD\textsubscript{3}OD), described in Section 5.2.5.1. By integration, about 15\% of the Rh\textsuperscript{III}(L\textsubscript{m})Me had decomposed to form Rh\textsuperscript{III}(L\textsubscript{m})(OCD\textsubscript{3})(CD\textsubscript{3}OD). After leaving this solution overnight at room temperature in methanol-\textit{d}\textsubscript{4} in air, almost all of the Rh\textsuperscript{III}(L\textsubscript{m})Me had converted to Rh\textsuperscript{III}(L\textsubscript{m})(OCD\textsubscript{3})(CD\textsubscript{3}OD).

In contrast to the Rh\textsuperscript{III}(L\textsubscript{m})Me complex that was partially purified by column chromatography, the unpurified (crude) Rh\textsuperscript{III}(L\textsubscript{m})Me complex was stable for weeks in methanol-\textit{d}\textsubscript{4} in air, and no Rh\textsuperscript{III}(L\textsubscript{m})(OCD\textsubscript{3})(CD\textsubscript{3}OD) was observed by \textit{\textsuperscript{1}H NMR} spectroscopy. This suggests that the by-products present in the crude Rh\textsuperscript{III}(L\textsubscript{m})Me sample stabilise Rh\textsuperscript{III}(L\textsubscript{m})Me and prevent loss of the methyl ligand. It is possible that solutions of the crude Rh\textsuperscript{III}(L\textsubscript{m})Me complex are stabilised by the presence of the basic sodium borate salts and other by-products, and this may protect Rh\textsuperscript{III}(L\textsubscript{m})Me from decomposition through protolytic reactions. Thus, after column chromatography, Rh\textsuperscript{III}(L\textsubscript{m})Me may become more prone to loss of the axial methyl ligand. One way that this may occur is that, prior to column chromatography, the second axial site of Rh\textsuperscript{III}(L\textsubscript{m})Me may be occupied by axial ligands from the crude reaction mixture (such as chloride, iodide, or borates). Upon column chromatography, these ligands are perhaps lost, and
Rh\textsuperscript{III}(L\textsubscript{m})Me may become five-coordinate. If this complex becomes five-coordinate, the rhodium centre is expected to be displaced further out of the plane defined by the four nitrogen donors of the L\textsubscript{m} ligand (on the side towards the rhodium-methyl bond) than in a six-coordinate complex, and this may make the methyl ligand more susceptible to reaction with oxygen or protic solvents.

Loss of the methyl ligand from the alumina columned Rh\textsuperscript{III}(L\textsubscript{m})Me complex is not unexpected, considering that the alkyl ligands of Rh\textsuperscript{III}(L\textsubscript{m})Et and Rh\textsuperscript{III}(L\textsubscript{m})Bn are lost readily prior to purification by column chromatography, and that the Rh-Me bond is expected to be only slightly stronger than the Rh-Et and Rh-Bn bonds. Furthermore, loss of the methyl ligand from the crude Rh\textsuperscript{III}(L\textsubscript{m})Me complex during the mass spectrometric ionisation process also suggests that the Rh-Me bond is susceptible to cleavage.

Analysis of the \textsuperscript{1}H NMR spectrum of the Rh\textsuperscript{III}(L\textsubscript{m})Me sample in methanol-\textit{d}_4 that was partially purified by column chromatography suggests that the methyl ligand is lost as methanol (technically, as CH\textsubscript{3}OD). This is because a signal corresponding to free methanol increases in relative amount over time, and relative integrations suggest that almost all of the methyl ligand is converted to methanol. No methane was observed in the \textsuperscript{1}H NMR spectrum, even when the NMR tube was capped tightly. Two possible reagents that are involved in the conversion of the methyl ligand to methanol are water and dioxygen. An experiment was therefore conducted to investigate whether these reagents play an important role in methanol formation. In this experiment, Rh\textsuperscript{III}(L\textsubscript{m})Me was purified by column chromatography on alumina (using 19:1 dichloromethane/methanol as eluent), and the collected eluate containing Rh\textsuperscript{III}(L\textsubscript{m})Me was evaporated to dryness immediately. After drying the solid residue for one hour under high vacuum to remove most of the methanol solvent, the residue was dissolved in dry degassed methanol-\textit{d}_4, and the solution was freeze-pump-thaw degassed four times. This solution was then divided into three equal portions, and each portion was transferred via a dry gas-tight syringe into separate NMR tubes. Each NMR tube had previously been placed inside a narrow Schlenk tube fitted with a rubber septum and, after heating the glassware under vacuum to remove residual water, the atmosphere inside these Schlenk tubes was purged with a dry nitrogen atmosphere. This heating and purging cycle was repeated three more times. After transferring the solution into the NMR tubes, these tubes were capped while purging nitrogen through the Schlenk tubes. The first NMR tube was left sealed under nitrogen; in the second NMR tube, dry dioxygen was bubbled through the solution for one minute, and the NMR tube
was then capped under about 1 atmosphere of dry dioxygen; while to the third NMR tube, about 30 µL of degassed water had been added to the NMR tube prior to the addition of the Rh(III)(L₃)Me solution in methanol-d₄, and the tube was then capped under nitrogen. The ¹H NMR spectra were recorded regularly and the relative ratio of Rh(III)(L₃)(OCD₃)(CD₃OD) to Rh(III)(L₃)Me was plotted as function of time (Figure 5.21). This ratio was calculated using the relative integrations of the most downfield doublet signals for both Rh(III)(L₃)(OCD₃)(CD₃OD) and Rh(III)(L₃)Me. These ¹H NMR signals were selected because they do not overlap with neighbouring signals, unlike many of the other signals observed in the ¹H NMR spectrum of the product mixture.

Figure 5.21: Ratio of Rh(III)(L₃)(OCD₃)(CD₃OD) to Rh(III)(L₃)Me over time in solutions of the alumina columned Rh(III)(L₃)Me complex in methanol-d₄ at room temperature (where 1 = 100% Rh(III)(L₃)(OCD₃)(CD₃OD) on the y-axis). Solid circles: under N₂; open circles: under dry O₂; crosses: under N₂, in the presence of excess H₂O. Dry O₂ was bubbled through the solution under N₂ (solid circles) after about 3.9 days.

Figure 5.21 illustrates that decomposition of Rh(III)(L₃)Me to Rh(III)(L₃)(OCD₃)(CD₃OD) is much slower for the degassed solutions than for the solution under dry dioxygen. Additionally, the rate of decomposition for the anhydrous degassed solution is similar to the rate of decomposition for the degassed solution that contains water. This suggests that loss of the methyl ligand from Rh(III)(L₃)Me to form methanol is due to the presence of dioxygen rather than water. When dry
Dioxygen was bubbled through the anhydrous degassed NMR sample after about 3.9 days at room temperature, the rate of Rh	extsuperscript{III}(L\textsubscript{m})Me decomposition increased markedly, again suggesting that dioxygen is involved in the rate determining step for loss of the methyl ligand. For both degassed solutions (with and without water added), Rh\textsuperscript{III}(L\textsubscript{m})Me decomposition was reasonably rapid at first, but the conversion then slowed down until it plateaued at approximately 50% conversion. This is probably because a small amount of air may have been accidentally introduced into these NMR tubes, and the dioxygen in this air is used up by the time that conversion reaches 50%. Data for the degassed sample that contains water suggest that decomposition may continue, albeit very slowly. This slow decomposition may be due to slow diffusion of air through the NMR cap. Repeating the experiment using an inert atmosphere glovebox to set up the experiment in air-tight screw-cap NMR tubes may give better results.

Note that some Rh\textsuperscript{III}(L\textsubscript{m})Me decomposition has occurred at t = 0 (the time at which the first \textsuperscript{1}H NMR spectrum was obtained). Most of this arises during the column chromatography and sample drying steps, prior to dissolution in methanol-\textit{d}_4. If the number of equivalents of methanol formed in the reaction (determined by integration of the \textsuperscript{1}H NMR spectrum) is plotted as a function of time, the plot appears very similar to the plot shown in Figure 5.21, and almost 100% of the methyl ligand is converted to methanol.

A possible reaction pathway for loss of the methyl ligand from Rh\textsuperscript{III}(L\textsubscript{m})Me in methanol-\textit{d}_4 and air is shown in Figure 5.22. This reaction pathway begins with insertion of dioxygen into the rhodium-methyl bond, forming a peroxo-metal complex. This rhodium(III)-peroxo complex then loses the peroxo ligand by reaction with methanol-\textit{d}_4 to form Rh\textsuperscript{III}(L\textsubscript{m})(OCD\textsubscript{3})(CD\textsubscript{3}OD) and methyl deuteroperoxide. This step would have to be rapid because no Rh\textsuperscript{III}(L\textsubscript{m})(O-O-CH\textsubscript{3}) complex was observed in the \textsuperscript{1}H NMR spectrum of this reaction. Furthermore, no methyl deuteroperoxide was observed in the \textsuperscript{1}H NMR spectrum of this reaction, perhaps because it rapidly oxidises methanol-\textit{d}_4 to formaldehyde-\textit{d}_2 and D\textsubscript{2}O, which would not be observed in the \textsuperscript{1}H NMR spectrum. The CH\textsubscript{3}OD product would also be formed in this step. Although Rh\textsuperscript{III}(L\textsubscript{m})Me and Rh\textsuperscript{III}(L\textsubscript{m})(O-O-CH\textsubscript{3}) are depicted as five-coordinate complexes in Figure 5.22, this is currently unknown, and it may be possible that the vacant axial site is occupied by another axial ligand, such as methanol-\textit{d}_4.
Because the results in Figure 5.21 suggest that Rh\textsuperscript{III}(L\textsubscript{m})Me is air-sensitive, attempts were made to purify this complex under air-free conditions. These included recrystallisations under air-free conditions using various solvent mixtures; extractions under air-free conditions; and columns using degassed eluents, where the head of column and the collection vessel were placed under a nitrogen atmosphere. Although the extent of decomposition was low using some of these techniques, some Rh\textsuperscript{III}(L\textsubscript{m})(OCD\textsubscript{3})(CD\textsubscript{3}OD) was still observed in each sample. When basic alumina was used instead of neutral alumina, all of the Rh\textsuperscript{III}(L\textsubscript{m})Me decomposed to Rh\textsuperscript{III}(L\textsubscript{m})(OCD\textsubscript{3})(CD\textsubscript{3}OD) by the time the eluate was collected. This suggests that decomposition is much faster under basic conditions after removal of the by-products from the crude Rh\textsuperscript{III}(L\textsubscript{m})Me sample. The addition of pyridine to Rh\textsuperscript{III}(L\textsubscript{m})Me also resulted in much faster loss of the methyl ligand, and formed a mixture of products, none of which had \textsuperscript{1}H NMR signals that would correspond to the presence of a methyl ligand. This may be because coordination of pyridine \textit{trans} to the methyl ligand increases labilisation of the methyl ligand. Purification of Rh\textsuperscript{III}(L\textsubscript{m})Me inside an inert atmosphere glovebox may enable isolation of the pure complex, without contamination by Rh\textsuperscript{III}(L\textsubscript{m})(OCD\textsubscript{3})(CD\textsubscript{3}OD).

In contrast to the Rh\textsuperscript{III}(L\textsubscript{m})(alkyl) complexes described in this section, reported Rh\textsuperscript{III}(porphyrin)(alkyl) and Rh\textsuperscript{III}(TMTAA)(alkyl) complexes are usually air-stable and do not readily decompose in solution after purification\textsuperscript{15,204,232}. This is possibly because the Rh-C bonds in the Rh\textsuperscript{III}(L\textsubscript{m})(alkyl) complexes are activated towards reaction with dioxygen by the set of strong nitrogen donors of the L\textsubscript{m} ligand.
Because the methyl ligand is lost readily from Rh\textsuperscript{III}(L\textsubscript{m})Me through reaction with oxygen from the air, the following sections describe reactions of Na[[Rh\textsuperscript{II}(L\textsubscript{m})]\textsubscript{2}Cl] with carbon monoxide and acetylene in alcohols, which are expected to give organometallic complexes with stronger and more stable Rh-C bonds than Rh\textsuperscript{III}(L\textsubscript{m})Me.

5.2.6 Reactions of Na[[Rh\textsuperscript{II}(L\textsubscript{m})]\textsubscript{2}Cl] and derivatives with carbon monoxide

This section describes the reactions of Na[[Rh\textsuperscript{II}(L\textsubscript{m})]\textsubscript{2}Cl] with carbon monoxide in various alcohols. These reactions are restricted to alcohol solvents here, because of the very low solubility of Na[[Rh\textsuperscript{II}(L\textsubscript{m})]\textsubscript{2}Cl] in other suitable solvents. The reactions were studied in order to gain further insights into the reaction chemistry of Na[[Rh\textsuperscript{II}(L\textsubscript{m})]\textsubscript{2}Cl]; to synthesise organometallic complexes that are more stable than the Rh\textsuperscript{III}(L\textsubscript{m})(alkyl) complexes described in Section 5.2.5; and to investigate the potential catalytic activation of carbon monoxide by Na[[Rh\textsuperscript{II}(L\textsubscript{m})]\textsubscript{2}Cl].

As discussed in Sections 5.2.6.1 and 5.2.6.2 below, the addition of carbon monoxide to Na[[Rh\textsuperscript{II}(L\textsubscript{m})]\textsubscript{2}Cl] in alcohols gave the corresponding Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OR) metalloester complexes in high yield, where the OR group depends on the solvent used. Metalloester complexes with OCH\textsubscript{3}, OCD\textsubscript{3}, OEt, O\textsuperscript{n}Pr, and O\textsuperscript{i}Pr groups were synthesised, and the OCH\textsubscript{3} derivative was fully characterised. Reactivity studies strongly suggest that these reactions involve heterolytic reaction pathways. These studies are discussed in detail in Section 5.2.6.2.

5.2.6.1 Synthesis and characterisation of Rh\textsuperscript{II}(L\textsubscript{m})(C(=O)OR) complexes from the reaction of Na[[Rh\textsuperscript{II}(L\textsubscript{m})]\textsubscript{2}Cl] with carbon monoxide in various alcohols

The Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OR) metalloester complexes were synthesised in high yield by bubbling carbon monoxide through a dilute solution of Na[[Rh\textsuperscript{II}(L\textsubscript{m})]\textsubscript{2}Cl] in an alcohol for two minutes, followed by stirring the solution under an atmosphere of carbon monoxide (about one atmosphere in pressure) for 40 minutes at room temperature. The alcohol solvent was not degassed, so traces of air will still be present in the reaction. After this time, the solvent was removed under reduced pressure, and the solid residue was dissolved in methanol-\textit{d}\textsubscript{4}. Proton NMR spectra of the products were then obtained. Each Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OR) complex was
obtained in high yield by $^1$H NMR spectroscopy, with only a few minor by-products. However, the relative amount of by-products was noticeably higher for the O$n$Pr and O$^i$Pr complexes than for the OCH$_3$, OCD$_3$, and OEt complexes.

The $^1$H chemical shifts of the OR groups of each Rh$^{III}$(L$_m$)(C(=O)OR) complex are shown in Table 5.2. These integrated for the expected number of protons, suggesting that the OR groups of these complexes are not appreciably exchanged for OCD$_3$ from the methanol-$d_4$ solvent over several hours at room temperature. However, after leaving these complexes in methanol-$d_4$ in air over one week, the relative integrations of the C(=O)OR ligands decreased by 15-25%, suggesting that partial exchange of the OR group for OCD$_3$ occurs over this time. Furthermore, the ROD by-product formed in this process was also observed in approximately the expected amount. Thus, the only new products observed in the $^1$H NMR spectra over this period were Rh$^{III}$(L$_m$)(C(=O)OCD$_3$) and ROD. Further analysis of the $^1$H NMR spectra of these Rh$^{III}$(L$_m$)(C(=O)OR) complexes showed that the L$_m$ ligands occur at almost identical chemical shifts (within ±0.02 ppm) for complexes with different OR groups. This indicates that, as expected, changing the OR group of the C(=O)OR ligand has little affect upon the donating strength of the C(=O)OR ligand, and therefore does not change the electronic environment of the macrocyclic ligand significantly. The inequivalence of the two geminal-C-methyl groups of the L$_m$ ligands in the $^1$H NMR spectrum of each Rh$^{III}$(L$_m$)(C(=O)OR) complex (observed at 1.52 and 1.57 ppm) indicates that only one C(=O)OR ligand is present in each Rh$^{III}$(L$_m$)(C(=O)OR) complex, which is further confirmed by analysing the integrations of the L$_m$ and C(=O)OR $^1$H NMR signals.

Carbon-13 NMR spectra were obtained for the Rh$^{III}$(L$_m$)(C(=O)OCH$_3$) and Rh$^{III}$(L$_m$)(C(=O)OEt) complexes in methanol-$d_4$. As for the $^1$H NMR spectra, the $^{13}$C NMR spectra of the L$_m$ ligand were almost identical for the two complexes. Also like the $^1$H NMR spectra, the geminal-C-methyl groups were inequivalent (30.2 and 26.7 ppm) by $^{13}$C NMR spectroscopy. The C(=O)OR carbon atoms were identified by $^{13}$C NMR spectroscopy (see Section 5.4.6 for chemical shifts), with the C(=O) carbon atoms appearing as doublets, due to $^{13}$C-$^{103}$Rh coupling (49.3 Hz for Rh$^{III}$(L$_m$)(C(=O)OCH$_3$) and 58.1 Hz for Rh$^{III}$(L$_m$)(C(=O)OEt).
Table 5.2: Proton NMR chemical shifts of the axial ligands for various Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OR) complexes in methanol-\textit{d}_4

<table>
<thead>
<tr>
<th>Axial ligand \textsuperscript{a}</th>
<th>\textsuperscript{1}H NMR chemical shift of axial ligand \textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(=O)OCD\textsubscript{3}</td>
<td>-</td>
</tr>
<tr>
<td>C(=O)OCH\textsubscript{3}</td>
<td>\textit{CH}_3: 3.29 (s, 3H)</td>
</tr>
<tr>
<td>C(=O)OEt</td>
<td>\textit{CH}_2\textit{CH}<em>3: 3.76 (q, 2H, \textit{J}</em>{1H-1H} = 7.1 Hz) \textit{CH}_2\textit{CH}<em>3: 0.80 (t, 3H, \textit{J}</em>{1H-1H} = 7.1 Hz)</td>
</tr>
<tr>
<td>C(=O)O\textit{Pr}</td>
<td>\textit{CH}_2\textit{CH}_2\textit{CH}<em>3: 3.68 (t, 2H, \textit{J}</em>{1H-1H} = 6.0 Hz) \textit{CH}_2\textit{CH}_2\textit{CH}_3: 1.16-1.21 (m, 2H) \textsuperscript{c} \textit{CH}_2\textit{CH}_2\textit{CH}<em>3: 0.58 (t, 3H, \textit{J}</em>{1H-1H} = 7.5 Hz)</td>
</tr>
<tr>
<td>C(=O)O\textit{Pr}</td>
<td>\textit{CH}(\textit{CH}_3)<em>2: 4.67 (septet, 1H, \textit{J}</em>{1H-1H} = 6.3 Hz) \textit{CH}(\textit{CH}_3)<em>2: 0.76 (d, 6H, \textit{J}</em>{1H-1H} = 6.3 Hz)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Axial ligand on the Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OR) complex.

\textsuperscript{b} Chemical shift in ppm in methanol-\textit{d}_4. \textit{s} = singlet, \textit{d} = doublet, \textit{t} = triplet, \textit{q} = quartet, \textit{m} = multiplet.

\textsuperscript{c} Although this signal is probably a triplet of triplets, it was partially obscured by the by-product signals, and so is assigned as a multiplet here.

High resolution positive ion mass spectra of the Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OR) complexes also confirmed product formation. For each of these complexes, a major signal was observed that corresponded to the ion [Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OR) + Na\textsuperscript{+}]. The sodium cation probably arises from the sodium formate added to the solution used to obtain the mass spectrum. Each Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OR) complex was run in the corresponding alcohol solvent. The only other major signals observed in these mass spectra corresponded to a [Rh\textsuperscript{III}(L\textsubscript{m})\textsuperscript{+} species, which probably arises from loss of the C(=O)OR ligand during the electrospray ionisation process.

As expected, no signals were observed in the ATR FTIR spectrum of Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OCH\textsubscript{3}) that would correspond to the presence of a terminal carbonyl ligand. Unfortunately, a specific C=O stretching vibration for the C(=O)OCH\textsubscript{3} group was not identified (which would be expected at about 1700 cm\textsuperscript{-1}, based on comparison to a literature Rh\textsuperscript{III}(OEP)(C(=O)OEt) complex),\textsuperscript{228} due to the presence of strong stretching vibrations from the carboxamide moieties of the L\textsubscript{m} ligand in this region.
Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OCH\textsubscript{3}) was purified by recrystallisation from methanol/water, to yield a fine yellow-orange powder. Elemental analysis of the thoroughly-dried solid was consistent with the formulation Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OCH\textsubscript{3})\textsubscript{·}H\textsubscript{2}O. Although many attempts were made to grow X-ray quality crystals of Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OCH\textsubscript{3}), these all resulted in the formation of fine powders. Therefore, it is unknown whether the water molecule observed in the elemental analysis is present as a water of crystallisation or as an axial ligand. Both geometries would be compatible with the inequivalent geminal-C-methyl groups in the NMR spectra of Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OCH\textsubscript{3}). However, it seems unlikely that the water ligand is present as an axial ligand, because the relatively strongly coordinated axial C(=O)OR ligand is expected to pull the rhodium centre out of the plane defined by the four nitrogen donors of the L\textsubscript{m} ligand, on the side towards the C(=O)OR ligand. Both steric effects and the \textit{trans} effect of the C(=O)OR ligand would be expected to make coordination of a second axial ligand to the vacant coordination site unfavourable. Therefore, it is more likely that the water molecule is present as a water of crystallisation. A formulation of Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OCH\textsubscript{3})\textsubscript{·}H\textsubscript{2}O may therefore best represent this complex in the solid state. A similar effect was postulated in order to explain the five-coordinate geometry of the triphenylphosphine complex ([Rh\textsuperscript{III}(L\textsubscript{m})(PPh\textsubscript{3})][PF\textsubscript{6}]) in Section 5.2.4.

As summarised in Section 5.1.5.3, only one paper has been published for the reaction of rhodium(II) dimers with carbon monoxide in the presence of alcohols. In this reaction, a small amount of ethanol was added to [Rh\textsuperscript{II}(OEP)]\textsubscript{2} and carbon monoxide in CD\textsubscript{2}Cl\textsubscript{2}. A mixture of products formed in this reaction, which included Rh\textsuperscript{III}(OEP)Cl, Rh\textsuperscript{III}(OEP)(CHO), and Rh\textsuperscript{III}(OEP)(C(=O)OEt).\textsuperscript{228} In contrast, in neat alcohols, only Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OR) was synthesised from the reaction of Na[[Rh\textsuperscript{III}(L\textsubscript{m})\textsubscript{2}Cl] with carbon monoxide. However, like the Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OR) complexes, Rh\textsuperscript{III}(OEP)(C(=O)OEt) was air-stable and was characterised by \textit{1}H NMR spectroscopy.\textsuperscript{228} For Rh\textsuperscript{III}(OEP)(C(=O)OEt), the methylene and methyl protons of the C(=O)OEt ligand were observed at 0.89 ppm (quartet) and -1.10 ppm (triplet), respectively, and the carbonyl carbon was observed as a doublet at 151.4 ppm ($J_{\text{13C-103Rh}}$ = 46 Hz) in the $^{13}$C NMR spectrum.\textsuperscript{228} In comparison, the methylene group of Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OEt) was observed at 3.76 ppm (quartet) and the methyl group was observed at 0.80 ppm (triplet) in the $^{1}$H NMR spectrum, while the carbonyl carbon doublet was observed at 183.6 ppm ($J_{\text{13C-103Rh}}$ = 58.1 Hz) in the $^{13}$C NMR spectrum. The upfield shift of the C(=O)OEt ligand in Rh\textsuperscript{III}(OEP)(C(=O)OEt) relative to Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OEt) is probably due to the ring-current effect of the porphyrin ligand.
In the literature, besides the metalloester complexes discussed above, a variety of organometallic complexes have been synthesised from the reaction of [Rh\textsuperscript{II}(porphyrin)]\textsubscript{2} and [Rh\textsuperscript{II}(TMTAA)]\textsubscript{2} dimers with carbon monoxide. Depending on the reaction conditions, dimetal ketones, dimetal diketones, dimeric carbonyl adducts, or metalloformyl complexes can be synthesised, and these were summarised in Section 5.1.5.\textsuperscript{24,236,238} None of these complexes were observed in the reaction of Na[[Rh\textsuperscript{II}(L\textsubscript{m})]\textsubscript{2}Cl] with carbon monoxide in neat alcohols. Based on similar reported reactions,\textsuperscript{238,240} in an initial attempt to synthesise a rhodium(III)-\textsubscript{L\textsubscript{m}} metalloformyl complex (such as Rh\textsuperscript{III}(L\textsubscript{m})(CHO)), the reaction used to synthesise Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OCD\textsubscript{3}) in methanol-\textsubscript{d4} was repeated, using a mixture of carbon monoxide and dihydrogen gases (at atmosphere pressure) instead of just carbon monoxide gas. However, in this reaction, only Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OCD\textsubscript{3}) was observed in high yield, suggesting that Rh\textsuperscript{III}(L\textsubscript{m})(CHO) did not form under these conditions.

5.2.6.2 Studies into the reaction pathway for the synthesis of Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OR) from Na[[Rh\textsuperscript{II}(L\textsubscript{m})]\textsubscript{2}Cl] and carbon monoxide in alcohols

As discussed in Section 5.1.1, the rhodium-rhodium bond of Na[[Rh\textsuperscript{II}(L\textsubscript{m})]\textsubscript{2}Cl] can break either heterolytically, to form a rhodium(I) and a rhodium(III) species, or can break homolytically, to form two highly reactive paramagnetic rhodium(II) complexes. Although, in principle, either reaction pathway may form the single major Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OR) product in the reaction of Na[[Rh\textsuperscript{II}(L\textsubscript{m})]\textsubscript{2}Cl] with carbon monoxide in non-degassed alcohols, a heterolytic reaction pathway seems much more likely. The two pathways and evidence for the heterolytic reaction pathway are discussed in this section.

A postulated heterolytic reaction pathway for the synthesis of Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OR) from the reaction of Na[[Rh\textsuperscript{II}(L\textsubscript{m})]\textsubscript{2}Cl] with carbon monoxide in non-degassed alcohols is given in Figure 5.23. Like the reaction pathways proposed for the synthesis of [Rh\textsuperscript{III}(L\textsubscript{m})(L)]\textsuperscript{+} (L = DMSO or DMF) (Figure 5.15) and [Rh\textsuperscript{III}(L\textsubscript{m})(PPh\textsubscript{3})]\textsuperscript{+} (Figure 5.18) starting from Na[[Rh\textsuperscript{II}(L\textsubscript{m})]\textsubscript{2}Cl], there are a number of possible reaction pathways for the synthesis of Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OR) from Na[[Rh\textsuperscript{II}(L\textsubscript{m})]\textsubscript{2}Cl], carbon monoxide, and alcohols in air. One of these possible reaction pathways is given in Figure 5.23. This reaction pathway is closely related to the reaction pathway given in Figure 5.18, except that in the final step, nucleophilic attack of the rhodium(III) intermediates by the alcohol solvent yields Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OR) and generates H\textsuperscript{+} as a by-product.
Figure 5.23: Postulated reaction pathway for the synthesis of Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OR) from Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}Cl] and carbon monoxide in alcohols under aerobic conditions, via a Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}(Cl)(CO)] intermediate

It is unlikely that Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OR) forms via a homolytic reaction pathway, because homolytic cleavage of the rhodium-rhodium bond would form reactive paramagnetic rhodium(II) intermediates (such as [Rh\textsuperscript{II}(L\textsubscript{m})(CO)]\textsuperscript{+}), which would then react further to form a variety of products (such as (L\textsubscript{m})Rh\textsuperscript{III}-C(=O)-C(=O)-Rh\textsuperscript{III}(L\textsubscript{m})).\textsuperscript{236,238,246} None of these products were observed in the reaction of Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}Cl] with carbon monoxide in alcohols in air, suggesting that homolytic pathways are not occurring in this reaction. Note, however, than a homolytic cleavage pathway followed by rapid air oxidation of the rhodium(II) intermediates to form rhodium(III) product(s), and subsequent reaction of these rhodium(III) product(s) with carbon monoxide and the alcohol cannot presently be completely ruled out.

Further reactions were carried out to confirm that a heterolytic reaction pathway is indeed operating in the formation of Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OR) from Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}Cl] and carbon monoxide in alcohols. In the reaction pathway postulated in Figure 5.23, the rhodium(III)-L\textsubscript{m} intermediate formed from heterolytic cleavage of the rhodium-rhodium bond reacts with the alcohol solvent to form Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OR), whereas the rhodium(I)-L\textsubscript{m} intermediate has to oxidise to a rhodium(III)-L\textsubscript{m} complex before it too can react with carbon monoxide and the alcohol solvent
to form Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OR). Therefore, if the reaction pathway postulated in Figure 5.23 is indeed occurring, an authentic isolated rhodium(III)-L\textsubscript{m} complex would react with carbon monoxide and an alcohol to form Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OR), whereas an authentic isolated rhodium(I)-L\textsubscript{m} complex would not react with these reagents (provided that the rhodium(I)-L\textsubscript{m} complex does not oxidise to a rhodium(III)-L\textsubscript{m} complex first). This was indeed found to be the case. These experiments are described below, using the Rh\textsuperscript{III}(L\textsubscript{m})(OCD\textsubscript{3})(CD\textsubscript{3}OD) and Na[Rh\textsuperscript{I}(L\textsubscript{m})] complexes that were synthesised according to the procedures described in Section 5.2.5.

To test whether Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OR) can be formed from an authentic rhodium(III)-L\textsubscript{m} complex, carbon monoxide was added to a solution of the Rh\textsuperscript{III}(L\textsubscript{m})(OCD\textsubscript{3})(CD\textsubscript{3}OD) complex that was formed from decomposition of Rh\textsuperscript{III}(L\textsubscript{m})Me in methanol-d\textsubscript{4}. As expected, after a few minutes at room temperature, \textsuperscript{1}H NMR spectroscopy showed that a single major product formed in this reaction, which was identical to the Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OCD\textsubscript{3}) complex synthesised from Na[[Rh\textsuperscript{II}(L\textsubscript{m})]\textsubscript{2}Cl]. Therefore, Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OCD\textsubscript{3}) can indeed be synthesised from an authentic rhodium(III)-L\textsubscript{m} complex. Furthermore, the formation of Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OCD\textsubscript{3}) from Rh\textsuperscript{III}(L\textsubscript{m})(OCD\textsubscript{3})(CD\textsubscript{3}OD) was significantly faster (less than 2 minutes to reach completion) than the formation of Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OCD\textsubscript{3}) from Na[[Rh\textsuperscript{II}(L\textsubscript{m})]\textsubscript{2}Cl] (about 30 minutes to reach completion). This suggests that the slowest step in the latter reaction is the formation of the initial carbon monoxide-coordinated dimer and/or cleavage of the rhodium-rhodium bond.

To determine whether an authentic rhodium(I)-L\textsubscript{m} complex would react with carbon monoxide and an alcohol, Na[[Rh\textsuperscript{II}(L\textsubscript{m})]\textsubscript{2}Cl] was reduced to Na[Rh\textsuperscript{I}(L\textsubscript{m})] using sodium borohydride in stringently degassed ethanol, and carbon monoxide was then added to the solution, taking care not to introduce air into the reaction. After one hour at room temperature under about one atmosphere of carbon monoxide, the excess carbon monoxide and the solvent were removed under vacuum, and the residue was dissolved in methanol-d\textsubscript{4}. The \textsuperscript{1}H NMR spectrum of this solution showed only Rh\textsuperscript{III}(L\textsubscript{m})(OCD\textsubscript{3})(CD\textsubscript{3}OD) and a small amount (less than 5%) of Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OEt). This suggests that Na[Rh\textsuperscript{I}(L\textsubscript{m})] does not react with carbon monoxide and ethanol over one hour, and instead oxidises to Rh\textsuperscript{III}(L\textsubscript{m})(OCD\textsubscript{3})(CD\textsubscript{3}OD) upon exposure to air and dissolution in methanol-d\textsubscript{4}. The small amount of Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OEt) observed in the \textsuperscript{1}H NMR spectrum probably arises from traces of air in the original solution that oxidises Na[Rh\textsuperscript{I}(L\textsubscript{m})] to a rhodium(III) complex, which then reacts with carbon monoxide and ethanol to form Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OEt).
Reactions of Na[[Rh$^{II}$($L_m$)$_2$Cl]] with carbon monoxide in deoxygenated alcohols provide further confirmation that a heterolytic reaction pathway is operating in these reactions. In this experiment, the reaction used to synthesise Rh$^{III}$($L_m$)(C(=O)OCH$_3$) from Na[[Rh$^{II}$($L_m$)$_2$Cl]] and carbon monoxide in methanol (described in Section 5.2.6.1) was repeated under oxygen-free conditions, taking care not to introduce air into the reaction. After 30 minutes at room temperature under an atmosphere of carbon monoxide, the solvent was removed under vacuum, and the residue was dissolved in methanol-$d_4$ in air. The $^1$H NMR spectrum of this solution showed that, instead of forming Rh$^{III}$($L_m$)(C(=O)OCH$_3$) in high yield, a 1:1 mixture of Rh$^{III}$($L_m$)(C(=O)OCH$_3$) and Rh$^{III}$($L_m$)(OCD$_3$)(CD$_3$OD) formed. This is consistent with a heterolytic reaction pathway because the rhodium(III)-$L_m$-carbonyl intermediate formed from heterolytic cleavage of the dimer (as per Figure 5.23) reacts with methanol to form Rh$^{III}$($L_m$)(C(=O)OCH$_3$), whereas the rhodium(I)-$L_m$ intermediate does not react with carbon monoxide and the alcohol, and is instead oxidised to Rh$^{III}$($L_m$)(OCD$_3$)(CD$_3$OD) after all the carbon monoxide has been removed under vacuum, and the residue has been dissolved in methanol-$d_4$ in air. It is difficult to explain these results based on a homolytic reaction pathway.

Further studies into the possible reaction pathway of rhodium-rhodium bond cleavage during carbonylation were conducted by attempting to trap the rhodium(I)-$L_m$ intermediate formed from the reaction of Na[[Rh$^{II}$($L_m$)$_2$Cl]] with carbon monoxide in degassed methanol. Methyl iodide was chosen to trap the rhodium(I)-$L_m$ intermediate for several reasons: 1) reactivity studies (Section 5.2.5.2) indicate that methyl iodide reacts rapidly with Na[Rh$^I$($L_m$)], and reacts very slowly or not at all with Na[[Rh$^{II}$($L_m$)$_2$Cl]] and Rh$^{III}$($L_m$)(OCD$_3$)(CD$_3$OD); 2) the $^1$H NMR spectrum of Rh$^{III}$($L_m$)Me is already known (Section 5.2.5.3); 3) reactivity studies showed that the Rh$^{III}$($L_m$)(C(=O)OR) complexes do not react with methyl iodide; and 4) excess methyl iodide can easily be removed under vacuum at the end of the reaction. Therefore, the previous degassed reaction was modified so that methyl iodide was added to the degassed solution just before the addition of carbon monoxide. After 30 minutes at room temperature, the solvent, excess carbon monoxide, and excess methyl iodide were removed under vacuum, and the residue was dissolved in methanol-$d_4$. If heterolytic rhodium-rhodium bond cleavage had indeed occurred, a 1:1 mixture of Rh$^{III}$($L_m$)(C(=O)OCH$_3$) and Rh$^{III}$($L_m$)Me would be expected by $^1$H NMR spectroscopy. However, no Rh$^{III}$($L_m$)Me was observed in the $^1$H NMR spectrum of the isolated product mixture. Instead, three products were observed: Rh$^{III}$($L_m$)(C(=O)OCH$_3$), Rh$^{III}$($L_m$)(OCD$_3$)(CD$_3$OD) and a new unidentified complex, in a ratio of 1 : 0.4 : 0.6, respectively. The unidentified product did not have a doublet signal in the region expected for a methyl ligand. Later experiments showed that Rh$^{III}$($L_m$)Me itself can react with carbon
monoxide to form $\text{Rh}^{\text{III}}(L_m)(C(=O)OCH_3)$, probably via formation of the $\text{Rh}^{\text{III}}(L_m)(\text{OCD}_3)(\text{CD}_2\text{OD})$ complex that is known to form after loss of the methyl ligand from $\text{Rh}^{\text{III}}(L_m)\text{Me}$. The new unidentified product may arise from further reactions of $\text{Rh}^{\text{III}}(L_m)\text{Me}$ with carbon monoxide and/or methyl iodide. For example, carbon monoxide may insert into the Rh-Me bond to form $\text{Rh}^{\text{III}}(L_m)(C(=O)\text{CH}_3)$, which could even react further to form other products. A singlet at 2.04 ppm integrating for three protons relative to the $L_m$ signals of the unidentified product could perhaps belong to the methyl group of a $\text{Rh}^{\text{III}}(L_m)(C(=O)\text{CH}_3)$ complex.

Therefore, in hindsight, a better reaction method would have been to remove the excess carbon monoxide at the end of the reaction via freeze-pump-thaw degassing, and then to introduce degassed methyl iodide into the reaction. Thus, carbon monoxide would not be present to react with $\text{Rh}^{\text{III}}(L_m)\text{Me}$. This will be carried out in the future.

In the literature, homolytic reaction pathways have been proposed for reactions of $[\text{Rh}^{\text{II}}(L)]_2$ dimers ($L =$ porphyrin or TMTAA) with carbon monoxide in low polarity solvents (such as benzene), whereas heterolytic reaction pathways have been proposed for the reaction of $[\text{Rh}^{\text{II}}(L)]_2$ dimers with carbon monoxide in higher polarity solvents, such as pyridine-$d_5$ (see Sections 5.1.5 and 5.1.7.2 for a summary of these results). It has been speculated that heterolytic reaction pathways in pyridine-$d_5$ are due to the polar pyridine-$d_5$ solvent supporting ionic reaction pathways, which lowers the energy of heterolytic reaction pathways relative to homolytic reaction pathways. However, no conclusion has been made into whether the formation of $\text{Rh}^{\text{III}}(\text{OEP})(C(=O)\text{OEt})$ from $[\text{Rh}^{\text{II}}(\text{OEP})]_2$, carbon monoxide, and ethanol (0.7% v/v) in $\text{CD}_2\text{Cl}_2$ proceeds via a homolytic or a heterolytic reaction pathway. Like the literature reactions in pyridine-$d_5$, it is possible that the heterolytic reaction pathway postulated for the formation of $\text{Rh}^{\text{III}}(L_m)(C(=O)\text{OR})$ from $[\text{Na}[\text{Rh}^{\text{II}}(L_m)]_2\text{Cl}]$, carbon monoxide, and an alcohol (Figure 5.23) is also mediated by the high polarity alcohol solvent, which favours a heterolytic reaction pathway over a homolytic reaction pathway.
5.2.7  Reactions of Na[[Rh^{II}(L_m)]_2Cl] and derivatives with acetylene

This section describes the reactions of Na[[Rh^{II}(L_m)]_2Cl] with acetylene in alcohol solvents. As for all the other reactions described in this chapter, these reactions are restricted to alcohols here, because of the very low solubility of Na[[Rh^{II}(L_m)]_2Cl] in other suitable solvents. These reactions were studied in order to further investigate the reaction chemistry of Na[[Rh^{II}(L_m)]_2Cl]; to gain further understanding of the rhodium-rhodium bond cleavage pathways for Na[[Rh^{II}(L_m)]_2Cl] in alcohol solvents; and to investigate the potential catalytic activation of acetylene by Na[[Rh^{II}(L_m)]_2Cl]. An added advantage of using acetylene as a reagent is that excess acetylene can easily be removed under vacuum at the end of the reaction.

Reactions of rhodium(II) dimers with alkynes have only been reported in low polarity aprotic solvents, and the effect of adding alcohols to these reactions have not been investigated.236,238,239 As described in Sections 5.1.5 and 5.2.6, the reaction of rhodium(II) dimers with carbon monoxide in alcohol solvents forms different products to the analogous reactions in low polarity aprotic solvents. Therefore, the reaction of Na[[Rh^{II}(L_m)]_2Cl] with acetylene in alcohols may give different products to the literature reactions of rhodium(II) dimers in acetylene that were conducted in low polarity solvents in the absence of alcohols (such as trans-(porphyrin)Rh^{III}-CH=CH-Rh^{III}(porphyrin) complexes226). This was indeed found to be the case, and different trans-Rh^{III}(L_m)(CH=CHOR) complexes were successfully synthesised in high yield using different alcohols (methanol, methanol-d_4, ethanol, n-propanol, and isopropanol). The syntheses, spectroscopic properties, and possible reaction pathways for these trans-Rh^{III}(L_m)(CH=CHOR) complexes are described and discussed in this section.

Trans-Rh^{III}(L_m)(CH=CHOCH_3) was synthesised by bubbling acetylene through a solution of Na[[Rh^{II}(L_m)]_2Cl] in methanol for two minutes, followed by stirring the reaction mixture for two days at room temperature under an atmosphere of acetylene gas. The methanol solvent was not degassed, so traces of air were still present in this reaction. Once the reaction had reached completion, the solvent and excess acetylene were removed under reduced pressure. The residue was then purified by column chromatography on alumina. Upon evaporating the eluate under reduced pressure, a pure sample of trans-Rh^{III}(L_m)(CH=CHOCH_3) precipitated from solution and was collected by filtration (yield: 77%). The reaction was not heated to increase the rate of reaction, because Na[[Rh^{II}(L_m)]_2Cl] is known to undergo significant decomposition upon heating, and this decomposition might promote undesired side reactions.
The CH=CHOCH₃ ligand of \textit{trans}-Rh^{III}(L_m)(CH=CHOCH₃) in methanol-$d_4$ was clearly identified using $^1$H NMR spectroscopy. The OCH₃ protons were observed as a singlet at 3.15 ppm, while the CH=CH protons were observed as doublet of doublets at 4.95 ppm ($J_{1H-1H} = 12.6$ Hz, $J_{1H-103Rh} = 1.1$ Hz) and 4.91 ppm ($J_{1H-1H} = 12.6$ Hz, $J_{1H-103Rh} = 1.9$ Hz). All these signals integrated for the expected number of protons. The greater $^1$H-$^{103}$Rh coupling constant for the 4.91 ppm signal that for the 4.95 ppm signal indicates that the former belongs to the CH=CH proton closest to the rhodium centre. The $^{13}$C-$^{103}$Rh coupling constants in the $^{13}$C NMR spectrum of \textit{trans}-Rh^{III}(L_m)(CH=CHOCH₃) are also higher for the –CH= group closest to the rhodium centre (46.0 Hz for CH=CHOCH₃ versus 11.9 Hz for CH=CHOCH₃).

The vicinal coupling constant ($J_{1H-1H} = 12.6$ Hz) of \textit{trans}-Rh^{III}(L_m)(CH=CHOCH₃) is consistent with a \textit{trans} orientation for the CH=CH protons, because it is similar to the vicinal coupling constant of \textit{trans}-Rh^{III}(OEP)(CH=CHCl) (12.0 Hz) and \textit{trans}-Rh^{III}(OEP)(CH=CHPh) (13.0 Hz), but is much higher than the vicinal coupling constant of \textit{cis}-Rh^{III}(OEP)(CH=CHPh) (7.5 Hz). A \textit{trans} orientation for Rh^{III}(L_m)(CH=CH-OCH₃) complex would cause the OCH₃ group to point away from the L_m ligand, which would be much less sterically strained than the \textit{cis} isomer, where the OCH₃ group would point towards the L_m ligand. The CH=CHOCH₃ protons of \textit{trans}-Rh^{III}(L_m)(CH=CHOCH₃) (4.91 and 4.95 ppm) are significantly downfield of the CH=CHCl protons of \textit{trans}-Rh^{III}(OEP)(CH=CHCl) (-1.48 and -1.79 ppm), and are also significantly downfield of the CH=CHPh protons of \textit{trans}-Rh^{III}(OEP)(CH=CHPh) (about -0.7 and -1.0 ppm). The pronounced upfield shifts of these latter two complexes are due to the porphyrin ring-current effect.

Proton NMR integrations of the OCH₃ group of \textit{trans}-Rh^{III}(L_m)(CH=CHOCH₃) indicates that there is one axial CH=CHOCH₃ ligand on the rhodium centre. This also indicates that the OCH₃ group is not appreciably exchanged for OCD₃ from the methanol-$d_4$ solvent over several hours at room temperature. However, like the Rh^{III}(L_m)(C(=O)OR) complexes (Section 5.2.6), the relative integration of the OCH₃ group of \textit{trans}-Rh^{III}(L_m)(CH=CHOCH₃) decreases by about 20% after leaving this complex for one week at room temperature in methanol-$d_4$ in air, suggesting that partial exchange of the OCH₃ group for OCD₃ occurs over this time. Furthermore, the ROD by-product formed in this process was observed in approximately the expected amount. Further analysis of the $^1$H NMR spectrum of \textit{trans}-Rh^{III}(L_m)(CH=CHOCH₃) showed that both “halves” of the symmetric L_m were equivalent (see Section 5.4.7 for chemical
shifts), except for the two geminal-C-methyl groups, which were inequivalent. This is also consistent with the presence of one axial CH=CHOCH$_3$ ligand.

High resolution positive ion mass spectrometry was also consistent with a formulation of trans-Rh$^{III}$(L$_m$)(CH=CHOCH$_3$). Two high intensity signals were observed in this spectrum, one of which corresponded to the ion [Rh$^{III}$(L$_m$)(CH=CHOCH$_3$) + Na$^+$]. The other signal corresponded to the ion [Rh$^{III}$(L$_m$)]$^+$. The latter species probably arises from loss of the CH=CHOCH$_3$ ligand during the electrospray ionisation process. This effect has also been observed for the complexes, Rh$^{III}$(L$_m$)(C(=O)OR), and also for most of the metal-L$_m$ complexes described in this chapter and in Chapter 3.

Elemental analysis of thoroughly-dried trans-Rh$^{III}$(L$_m$)(CH=CHOCH$_3$) indicates that there is one equivalent of water present in the solid sample. It is unlikely that this water molecule is present as an axial ligand, because the relatively strongly coordinated axial CH=CHOCH$_3$ ligand is expected to pull the rhodium centre out of the plane defined by the four nitrogen donors of the L$_m$ ligand, on the side towards the CH=CHOCH$_3$ ligand. Both steric effects and the trans effect of the CH=CHOCH$_3$ ligand would be expected to make coordination of a second axial ligand to the vacant coordination site unfavourable. Therefore, it is more likely that the water molecule is present as a water of crystallisation. The complex is therefore best represented by a formulation of trans-Rh$^{III}$(L$_m$)(CH=CHOCH$_3$)·H$_2$O in the solid state. Although an X-ray crystal structure of this complex would provide clarification as to whether this water molecule is present as an axial ligand or as a water of crystallisation, crystals of trans-Rh$^{III}$(L$_m$)(CH=CHOCH$_3$) suitable for X-ray structure determination could not be obtained.

The reaction used to synthesise Rh$^{III}$(L$_m$)(CH=CHOCH$_3$) was repeated using different alcohols. The use of methanol-$d_4$, ethanol, $n$-propanol, and isopropanol all resulted in the formation of the corresponding Rh$^{III}$(L$_m$)(CH=CHOR) complexes. These reactions also took about two days to reach completion at room temperature, and product formation was confirmed by mass spectrometry and $^1$H NMR spectroscopy. Using $^1$H NMR spectroscopy, the crude OCD$_3$ complex was similar in purity to the OCH$_3$ complex, but the crude OEt, O$^\alpha$Pr, and O$i$Pr complexes were much lower in purity, with significant amounts of by-products. Like the Rh$^{III}$(L$_m$)(C(=O)OR) complexes, the $^1$H NMR signals for the L$_m$ ligands of the Rh$^{III}$(L$_m$)(CH=CHOR) complexes were almost identical for complexes with different OR
groups. This again suggests that changing the remote OR group does not cause significant changes to the donating strength of the (CH=CHOR) ligand, and therefore does not change the electronic properties of the macrocyclic ligand significantly. Also like the Rh$^{III}$($L_m$)(C(=O)OR) complexes, the OR groups of the Rh$^{III}$($L_m$)(CH=CHOR) complexes exchange very slowly for OCD$_3$ over weeks at room temperature in methanol-$d_4$ in air. Furthermore, the ROD by-product formed in these processes was also observed in approximately the expected amount. Thus, the only new products observed in these $^1$H NMR spectra over this period were Rh$^{III}$($L_m$)(CH=CHOCD$_3$) and ROD. This indicates that the CH=CHOR ligands are stable in solution and do not dissociate or rearrange to other geometries. This also indicates that the CH=CHOR ligands do not react further, for example, via protonation to form Rh($L_m$)(=CH-CH$_2$OR) or π-bound Rh($L_m$)(CH$_2$=CHOR) complexes; or by losing a proton to form Rh($L_m$)(=C=CHOR) complexes; or by undergoing β-hydrogen elimination to release the corresponding alkynes.

Although studies into the possible reaction pathway for the formation of Rh$^{III}$($L_m$)(CH=CHOCH$_3$) from Na[[Rh$^{II}$($L_m$)]$_2$Cl], acetylene, and methanol were not carried out, the fact that this complex was synthesised in high yield with minimal rhodium-containing by-products suggests that a heterolytic reaction pathway is occurring. This is because a reaction pathway involving homolytic cleavage of the rhodium-rhodium bond would form reactive paramagnetic rhodium(II) intermediates (such as [Rh$^{II}$($L_m$)(CH=CH)]$^+$), which would then be expected to react further to give a variety of products (such as trans-($L_m$)Rh$^{III}$-CH=CH-Rh$^{III}$($L_m$)), none of which were observed in the reaction of Na[[Rh$^{II}$($L_m$)]$_2$Cl] with acetylene in methanol. It also seems reasonable to assume that a heterolytic reaction pathway is operating in this reaction, because reactivity studies in Sections 5.2.4 and 5.2.6.2 strongly suggested that heterolytic reaction pathways are operating in the formation of [Rh$^{III}$($L_m$)(PPh$_3$)]$^+$ and Rh$^{III}$($L_m$)(C(=O)OR) from Na[[Rh$^{II}$($L_m$)]$_2$Cl] in alcohol solvents.

There are a number of possible heterolytic reaction pathways for the synthesis of Rh$^{III}$($L_m$)(CH=CHOR) from Na[[Rh$^{II}$($L_m$)]$_2$Cl], acetylene, and alcohols in air. One of these possible reaction pathways is shown in Figure 5.24. This reaction pathway is very similar to the reaction pathway proposed for the synthesis of Rh$^{III}$($L_m$)(C(=O)OR) from Na[[Rh$^{II}$($L_m$)]$_2$Cl], carbon monoxide, and alcohols in air (Figure 5.23), except that here the final Rh$^{III}$($L_m$)(CH=CHOR) product is formed via nucleophilic attack of a π-bound acetylene ligand by the alcohol.
Figure 5.24: Postulated reaction pathway for the formation of Rh\text{III}(L_m)(CH=CHOR) from Na[[Rh\text{II}(L_m)]_2Cl] and acetylene in alcohols under aerobic conditions, via a Na[[Rh\text{II}(L_m)]_2(Cl)(HC≡CH)] intermediate.

Apart from the initial dimer cleavage step, this postulated reaction pathway is similar to the reaction pathway proposed for the synthesis of Rh\text{III}(OEP)(CH=CHCl) from Rh\text{III}(OEP)(H_2O)Cl and acetylene (see Figure 5.10 in Section 5.1.6), except that here, ROH attacks the terminal alkyne carbon atom in the final step to form Rh\text{III}(L_m)(CH=CHOR), whereas in the reported reaction, the displaced Cl\text{−} anion attacks the terminal carbon atom in the final step, forming Rh\text{III}(OEP)(CH=CHCl).

It was found in Section 5.2.6.2 that the rate of Rh\text{III}(L_m)(C(=O)OCD_3) formation from Rh\text{III}(L_m)(OCD_3)(CD_3OD), carbon monoxide, and methanol-\text{d}_4 was significantly faster than the rate of Rh\text{III}(L_m)(C(=O)OCD_3) formation from Na[[Rh\text{II}(L_m)]_2Cl], carbon monoxide, and methanol-\text{d}_4. This was attributed to coordination of carbon monoxide to the dimer and/or heterolytic cleavage of the rhodium-rhodium bond being the slowest step(s) in the latter reaction. A similar effect was found in the reaction of Rh\text{III}(L_m)(OCD_3)(CD_3OD) and Na[[Rh\text{II}(L_m)]_2Cl] with acetylene, where the synthesis of Rh\text{III}(L_m)(CH=CHOCD_3) from Na[[Rh\text{II}(L_m)]_2Cl], acetylene, and methanol-\text{d}_4 was much slower (2 days to reach completion) than the synthesis of...
Rh<sup>III</sup>(L<sub>m</sub>)(CH=CHOCD<sub>3</sub>) from Rh<sup>III</sup>(L<sub>m</sub>)(OCD<sub>3</sub})(CD<sub>3</sub>OD), acetylene, and methanol-<i>d</i><sub>4</sub> (1.5 hours to reach completion). Assuming that the rhodium-rhodium bond breaks heterolytically and that only the rhodium(III) intermediate reacts with acetylene to form Rh<sup>III</sup>(L<sub>m</sub>)(CH=CHOCD<sub>3</sub>) (as per Figure 5.24), these results again suggest that acetylene coordination to Na[[Rh<sup>II</sup>(L<sub>m</sub>)<sub>2</sub>Cl]] and/or heterolytic rhodium-rhodium bond cleavage are the slowest step(s) for the former reaction. Both reactions gave Rh<sup>III</sup>(L<sub>m</sub>)(CH=CHOCD<sub>3</sub>) in high yield, with minimal by-products. Note that the Rh<sup>III</sup>(L<sub>m</sub>)(OCD<sub>3</sub})(CD<sub>3</sub>OD) complex used in this reaction was synthesised from the decomposition of Rh<sup>III</sup>(L<sub>m</sub>)Me in methanol-<i>d</i><sub>4</sub> in air (as per Section 5.2.5.5), rather than from oxidation of [Rh<sup>I</sup>(L<sub>m</sub>)<sup>-</sup>] in air and methanol-<i>d</i><sub>4</sub>. This is because the by-products salts were removed from the former complex, but not from the latter complex.

Although it appears that rhodium-rhodium bond cleavage and/or the coordination of carbon monoxide or acetylene to the dimer is the slowest step in the reaction of Na[[Rh<sup>II</sup>(L<sub>m</sub>)<sub>2</sub>Cl]] with carbon monoxide and with acetylene, the latter reaction was much slower than the former reaction. This suggests that the coordination of carbon monoxide to Na[[Rh<sup>II</sup>(L<sub>m</sub>)<sub>2</sub>Cl]] weakens the rhodium-rhodium bond much more than the coordination of acetylene to Na[[Rh<sup>II</sup>(L<sub>m</sub>)<sub>2</sub>Cl]]. This could be due to the greater <i>trans</i> influence of coordinated carbon monoxide than coordinated acetylene.

### 5.2.8 Reactions of Na[[Rh<sup>II</sup>(L<sub>m</sub>)<sub>2</sub>(Cl)(py)] with various reagents

As was discussed in Section 5.2.2.3, the addition of pyridine to Na[[Rh<sup>II</sup>(L<sub>m</sub>)<sub>2</sub>Cl]] formed a Na[[Rh<sup>II</sup>(L<sub>m</sub>)<sub>2</sub>(Cl)(py)] adduct. Na[[Rh<sup>II</sup>(L<sub>m</sub>)<sub>2</sub>(Cl)(py)]] was found to be more air stable and much more soluble than Na[[Rh<sup>II</sup>(L<sub>m</sub>)<sub>2</sub>Cl]]. Reactions were therefore performed to see whether Na[[Rh<sup>II</sup>(L<sub>m</sub>)<sub>2</sub>(Cl)(py)] also reacts with triphenylphosphine, carbon monoxide, and acetylene in alcohol solvents to give the same products that were formed in the analogous reactions of Na[[Rh<sup>II</sup>(L<sub>m</sub>)<sub>2</sub>Cl]] with these reagents. This was indeed found to be the case, when identical conditions were used for these reactions. These conditions are described in Sections 5.2.4, 5.2.6, and 5.2.7. Therefore, [Rh<sup>III</sup>(L<sub>m</sub>)(PPh<sub>3</sub>)]<sup>+</sup>, Rh<sup>III</sup>(L<sub>m</sub>)(C(=O)OCH<sub>3</sub>), and Rh<sup>III</sup>(L<sub>m</sub>)(CH=CHOCH<sub>3</sub>) were all successfully synthesised from Na[[Rh<sup>II</sup>(L<sub>m</sub>)<sub>2</sub>(Cl)(py)]], and formation of these products was confirmed by <sup>1</sup>H NMR spectroscopy (in methanol-<i>d</i><sub>4</sub>). Both sets of reactions gave products in similar yield, with minimal by-products. Furthermore, when excess pyridine was added the [Rh<sup>III</sup>(L<sub>m</sub>)(PPh<sub>3</sub>)]<sup>+</sup>, Rh<sup>III</sup>(L<sub>m</sub>)(C(=O)OCH<sub>3</sub>), and Rh<sup>III</sup>(L<sub>m</sub>)(CH=CHOCH<sub>3</sub>) complexes
synthesised from Na[[Rh\(^{II}\)(L\(_m\))\(_2\)Cl], no change to the \(^1\)H NMR spectra of these complexes in methanol-\(d_4\) was observed. This therefore suggests that pyridine does not coordinate to any important extent to the second axial site of these products. This is probably because the axial PPh\(_3\), C(=O)OCH\(_3\), and CH=CHOCH\(_3\) ligands are coordinated relatively strongly to the rhodium centres, pulling the rhodium atom out of the plane defined by the four nitrogen donors of the L\(_m\) ligand, on the side towards this axial ligand. This would then make coordination of pyridine to the vacant coordination site sterically unfavourable. The relatively large \textit{trans} influences of these ligands would also make coordination of pyridine in a \textit{trans} position unfavourable.

In contrast, related hydrido and formyl five-coordinate rhodium(III)-porphyrin and rhodium(III)-TMTAA complexes have been reported to add pyridine to form the corresponding six-coordinate species (for example, Rh\(^{III}\)(TMTAA)(H)(py) and Rh\(^{III}\)(OEP)(CHO)(py)).\(^{24,225}\) The different behaviour of the Rh\(^{III}\)(L\(_m\))\((\text{R})\) complexes perhaps arises because the L\(_m\) ligand is expected to donate more strongly to the rhodium centre than the porphyrin and TMTAA ligands, which would cause greater labilisation of axial ligands, making pyridine coordination to the rhodium(III)-L\(_m\) complexes less favourable.

The synthesis of Rh\(^{III}\)(L\(_m\))(PPh\(_3\))\(^+\), Rh\(^{III}\)(L\(_m\))(C(=O)OCH\(_3\)), and Rh\(^{III}\)(L\(_m\))(CH=CHOCH\(_3\)) from Na[[Rh\(^{II}\)(L\(_m\))\(_2\)Cl]] was found to be significantly slower than the synthesis of the same complexes from Na[[Rh\(^{II}\)(L\(_m\))\(_2\)Cl]]. Thus, [Rh\(^{III}\)(L\(_m\))(PPh\(_3\))]\(^+\) took less than 20 minutes to form from Na[[Rh\(^{II}\)(L\(_m\))\(_2\)Cl]] and about 5 hours from Na[[Rh\(^{II}\)(L\(_m\))\(_2\)Cl](py)]; Rh\(^{III}\)(L\(_m\))(C(=O)OCH\(_3\)) took less than 40 minutes to form from Na[[Rh\(^{II}\)(L\(_m\))\(_2\)Cl]] and about 8 hours from Na[[Rh\(^{II}\)(L\(_m\))\(_2\)Cl](py)]; and Rh\(^{III}\)(L\(_m\))(CH=CHOCH\(_3\)) took 2 days to synthesise from Na[[Rh\(^{II}\)(L\(_m\))\(_2\)Cl]], whereas less than 40% conversion of Na[[Rh\(^{II}\)(L\(_m\))\(_2\)Cl](py)] to Rh\(^{III}\)(L\(_m\))(CH=CHOCH\(_3\)) occurred after 2 weeks in methanol under an acetylene atmosphere. This is probably because the reagent (pyridine, carbon monoxide, or acetylene) has to displace the pyridine ligand of Na[[Rh\(^{II}\)(L\(_m\))\(_2\)Cl]] before the rhodium-rhodium bond can break. In contrast, this coordination site is vacant in Na[[Rh\(^{II}\)(L\(_m\))\(_2\)Cl]] (or else coordinated very weakly with water or the alcohol solvent), and so the reagent can coordinate much more readily to this site. Thus, rhodium-rhodium bond cleavage becomes faster for Na[[Rh\(^{II}\)(L\(_m\))\(_2\)Cl]] than for Na[[Rh\(^{II}\)(L\(_m\))\(_2\)Cl](py)] in the presence of these reagents.
Na[[Rh^{II}(L_m)]_2(Cl)(py)] was stable for months in air in methanol-\textit{d}_4, and no changes were observed in the $^1$H NMR spectrum of this complex over this time. As was discussed briefly in Section 5.2.2.3, it is not immediately obvious why the rhodium-rhodium bond of the dimer remains intact in the presence of pyridine, whereas DMSO, DMF, triphenylphosphine, carbon monoxide, and acetylene all result in rhodium-rhodium bond cleavage and the formation of monomeric products. The much higher stability of the dimer in the presence of pyridine than in the presence of triphenylphosphine or carbon monoxide could be explained in terms of these latter ligands forming stronger donor bonds to the rhodium centre of Na[[Rh^{II}(L_m)]_2Cl], thereby weakening the rhodium-rhodium bond. However, this does not explain why rhodium-rhodium bond cleavage in the presence of acetylene, DMSO, or DMF is much faster than rhodium-rhodium bond cleavage in the presence of pyridine. Further experiments that provide more information about how the stability of the rhodium-rhodium bond changes in the presence of other donors, or with changes in the solvent dielectric constant will need to be carried out to help understand why this occurs.

5.3 Conclusions and future work

Na[[Rh^{II}(L_m)]_2Cl] was shown to react with a variety of substrates to produce various dimeric and monomeric products. These results are summarised in this section, and future work is discussed. In the experiments described in this chapter, it was shown that Na[[Rh^{II}(L_m)]_2Cl] and selected derivatives of this compound successfully activated the small molecules, carbon monoxide, acetylene, and methyl iodide, to form monomeric organometallic rhodium complexes. These rhodium complexes were found to react stoichiometrically but not catalytically with these small molecules. Further investigations into making these systems catalytic will be conducted in the near future, and some of the key future experiments will be discussed in this section. Possible reaction pathways for many of the reactions described in this chapter were also investigated, and the results (summarised below) were consistent with heterolytic cleavage of the rhodium-rhodium bond of Na[[Rh^{II}(L_m)]_2Cl].

Na[[Rh^{II}(L_m)]_2Cl] was found to be insoluble in most organic solvents and was also insoluble in water. However, this complex was slightly soluble in alcohols (around 0.1-0.3 mg mL$^{-1}$), and so
the reactions of Na[[RhII(Lm)]2Cl] in this chapter were only conducted in alcohol solvents. Although Na[[RhII(Lm)]2Cl] was also soluble in DMSO, DMF, pyridine, and 4-picoline (>50 mg mL⁻¹), this was because the former two reagents cleaved the rhodium-rhodium bond to form monomeric [RhIII(Lm)(DMSO)]²⁺ and [RhIII(Lm)(DMF)]²⁺ complexes, whereas the latter two reagents formed higher-solubility adducts of the dimer (Na[[RhII(Lm)]2(Cl)(py)] and Na[[RhII(Lm)]2(Cl)(4-picoline)]), where the rhodium-rhodium bond remained intact. Other potentially coordinating solvents (such as THF, acetone, and acetonitrile) did not appear to coordinate to Na[[RhII(Lm)]2Cl] to any important extent, and Na[[RhII(Lm)]2Cl] was insoluble in these solvents.

Na[[RhII(Lm)]2(Cl)(py)] was characterised by NMR spectroscopies and mass spectrometries (Section 5.2.2.3). Like the Na[[RhII(Lm)]2Cl] complex described in Section 3.2.6, the ¹H and ¹³C NMR spectra of Na[[RhII(Lm)]2(Cl)(py)] in methanol-d₄ revealed that each of the four “halves” of the Lₘ ligands (as per Figure 3.19) were inequivalent. This high degree of asymmetry was attributed to the presence of two different axial ligands on Na[[RhII(Lm)]2(Cl)(py)], along with hindered internal rotation of the Lₘ ligands about the rhodium-rhodium bond, which holds the Lₘ ligands in an asymmetric orientation. The hindered rotation perhaps arises from buckling of the Lₘ ligands, which restricts rotation of the two Lₘ ligands about the rhodium-rhodium bond. Unlike Na[[RhII(Lm)]2Cl], Na[[RhII(Lm)]2(Cl)(py)] was high enough in solubility and stability that good ¹³C and 2D NMR spectra could be obtained, and by analysing these spectra, the ¹H and ¹³C NMR chemical shifts of each position of the Lₘ and pyridine ligands could be determined (Figure 5.17).

An elementally-pure sample of Na[[RhII(Lm)]2(Cl)(py)] was not obtained because studies suggested that this complex is in equilibrium with Na[[RhII(Lm)]2Cl]. Thus, whenever the free pyridine was removed from the Na[[RhII(Lm)]2(Cl)(py)] sample, a mixture of Na[[RhII(Lm)]2Cl] and Na[[RhII(Lm)]2(Cl)(py)] was observed by ¹H NMR spectroscopy in methanol-d₄. Therefore, Na[[RhII(Lm)]2(Cl)(py)] had to be isolated in the presence of a small amount of free pyridine to prevent partial reversion back to Na[[RhII(Lm)]2Cl].

Although Na[[RhII(Lm)]2(Cl)(4-picoline)] was not characterised as extensively as Na[[RhII(Lm)]2(Cl)(py)], ¹H NMR spectroscopy showed that the four “halves” of the Lₘ ligands were also inequivalent, suggesting that the structures of the two adducts are similar, with only
one 4-picoline/pyridine axial ligand. Preliminary studies also suggested that, like Na[\(\text{Rh}^\text{II}(\text{L}_m)\text{Cl}(\text{py})]\), Na[\(\text{Rh}^\text{II}(\text{L}_m)\text{Cl}(4\text{-picoline})]\] is in equilibrium with Na[\(\text{Rh}^\text{II}(\text{L}_m)\text{Cl}\)] in solution.

Rhodium(III)-hydride complexes can be synthesised from [\(\text{Rh}^\text{II}(\text{porphyrin})\text{Cl}_2\) and [\(\text{Rh}^\text{II}(\text{TMTAA})\text{Cl}_2\) dimers either by adding dihydrogen gas, or by reducing the dimer with sodium borohydride, followed by the addition of acetic acid. Both routes were investigated using Na[\(\text{Rh}^\text{II}(\text{L}_m)\text{Cl}\)] (Section 5.2.3). In the first route, Na[\(\text{Rh}^\text{II}(\text{L}_m)\text{Cl}\)] did not react using one atmosphere of dihydrogen in sealed NMR tubes, while in the second route, decomposition occurred upon addition of acetic acid, forming a large number of major products. It is possible that Na[\(\text{Rh}^\text{II}(\text{L}_m)\text{Cl}\)] did not react with dihydrogen because the equilibrium reaction expected between the Na[\(\text{Rh}^\text{II}(\text{L}_m)\text{Cl}\)] and rhodium(III)-hydride complexes in the presence of dihydrogen may lie far to the reactants side of the reaction under one atmosphere of dihydrogen gas. An important future experiment is therefore to repeat these reactions in sealed thick-walled NMR tubes using dihydrogen pressures much greater than one atmosphere.

Although Na[\(\text{Rh}^\text{II}(\text{L}_m)\text{Cl}\)] did not appear to react with dihydrogen, it did react with triphenylphosphine in methanol at room temperature in air to form a stable [\(\text{Rh}^\text{III}(\text{L}_m)(\text{PPh}_3)][\text{PF}_6\)] complex in good yield after anion exchange with NH\(_4\)PF\(_6\) (Section 5.2.4). Like triarylphosphine complexes of rhodium(III)-corroles published in the literature (for example, \(\text{Rh}^\text{III}(\text{omc})(\text{PPh}_3)\), [\(\text{Rh}^\text{III}(\text{L}_m)(\text{PPh}_3)][\text{PF}_6\)] was air-stable, with a single axial phosphine ligand. It was postulated that the five-coordinate geometry of [\(\text{Rh}^\text{III}(\text{L}_m)(\text{PPh}_3)][\text{PF}_6\)] is due to the rather strongly coordinated triphenylphosphine ligand, which pulls the rhodium centre out of the plane defined by the four nitrogen donors of the \(\text{L}_m\) ligand, on the side towards the triphenylphosphine ligand, thus making coordination of a ligand to the second axial site unfavourable. This contrasts with [\(\text{Rh}^\text{III}(\text{L}_m)(\text{DMSO})_2\)]\(^+\) and [\(\text{Rh}^\text{III}(\text{L}_m)(\text{DMF})_2\)]\(^+\), where a six-coordinate geometry is probably due to the much weaker coordination of the DMSO/DMF ligands than the triphenylphosphine ligand. Thus, the rhodium centre of the former complexes is expected to be pulled less out of the tetra-nitrogen plane of the \(\text{L}_m\) ligand than in [\(\text{Rh}^\text{III}(\text{L}_m)(\text{PPh}_3)\)]\(^+\), and so the coordination of a second axial ligand becomes much more favourable for [\(\text{Rh}^\text{III}(\text{L}_m)(\text{DMSO})_2\)]\(^+\) and [\(\text{Rh}^\text{III}(\text{L}_m)(\text{DMF})_2\)]\(^+\).
Na[[Rh^{III}(L_m)]_2Cl] was successfully reduced to Na[Rh^{I}(L_m)] using sodium borohydride in ethanol (Section 5.2.5.1). Reactivity studies suggested that, like similar Na[Rh^{I}(porphyrin)] and Na[Rh^{I}(TMTAA)] complexes,\textsuperscript{15,231} Na[Rh^{I}(L_m)] is highly air-sensitive and oxidises rapidly to a rhodium(III) complex upon exposure to air. Due to the high air-sensitivity of Na[Rh^{I}(L_m)], this complex was not characterised. However, the rhodium(III) complex formed in high yield upon aerial oxidation of Na[Rh^{I}(L_m)] in methanol-\textit{d}_4 was characterised. Although it was not possible to distinguish between formulations of Rh^{III}(L_m)(OCD\textsubscript{3})(CD\textsubscript{3}OD) and [Rh^{III}(L_m)(CD\textsubscript{3}OD)]\textsuperscript{+} based on the spectroscopic data of this complex, the former formulation was used for consistency throughout this thesis. More studies need to be conducted to determine the nature of the axial ligands on this complex. Although the formulation of Rh^{III}(L_m)(OCD\textsubscript{3})(CD\textsubscript{3}OD) has two different axial ligands, the equivalence of the two geminal-C-methyl groups in the \textit{1}H NMR spectrum of Rh^{III}(L_m)(OCD\textsubscript{3})(CD\textsubscript{3}OD) could be ascribed to rapid exchange of the axial ligands with the methanol-\textit{d}_4 solvent on the NMR timescale. In reality, there is probably rapid exchange of the axial ligands on the NMR timescale between CD\textsubscript{3}OD and CD\textsubscript{3}O\textsuperscript{−} axial ligands (or counteranions) in solution, and there is possibly also rapid exchange with H\textsubscript{2}O and OH\textsuperscript{−} axial ligands/counteranions that arise from traces of water in the methanol-\textit{d}_4 solvent. In the literature, the mesityl \textit{ortho}-methyl groups of the TMP ligand of a Rh^{III}(TMP)(OCH\textsubscript{3})(CH\textsubscript{3}OH) complex (TMP = tetramesitylporphyrin) were also equivalent by \textit{1}H NMR spectroscopy in benzene-\textit{d}_6 in the presence of excess free methanol. It was postulated that this is due to rapid exchange between the OCH\textsubscript{3}/CH\textsubscript{3}OH ligands and free methanol in solution.\textsuperscript{245}

Rh^{III}(L_m)(OR)(ROH) complexes where R = CH\textsubscript{3} or Et were also synthesised by dissolving the isolated complex, Na[Rh^{I}(L_m)], in air in methanol or ethanol, respectively. After removing the solvent under vacuum, the residue was dissolved in methanol-\textit{d}_4. The \textit{1}H NMR spectra of these complexes were identical to the \textit{1}H NMR spectrum of the Rh^{III}(L_m)(OCD\textsubscript{3})(CD\textsubscript{3}OD) complex that was prepared by dissolving Na[Rh^{I}(L_m)] directly in methanol-\textit{d}_4 in air, except that the corresponding free alcohol solvent (ROH) was also observed in the former spectra. This suggested that the OR/ROH axial ligands of Rh^{III}(L_m)(OR)(ROH) rapidly exchange on the NMR timescale for OCD\textsubscript{3}/CD\textsubscript{3}OD ligands upon dissolution in methanol-\textit{d}_4. Attempts were made to purify Rh^{III}(L_m)(OR)(ROH) (R = CH\textsubscript{3} or Et) by column chromatography and by recrystallisations, but these resulted in large increases in the relative amount of impurities, suggesting that these rhodium(III) compounds are rather reactive. Indeed, as summarised below, these Rh^{III}(L_m)(OR)(ROH) complexes also react readily with many other reagents, such as carbon monoxide and acetylene, to give new rhodium(III) products in high yield. Attempts to isolate the Rh^{III}(L_m)(OR)(ROH) complexes in a single product form are ongoing.
Further reactivity studies (Section 5.2.5) also confirmed that Na[Rh\(^I\)(L\(_m\))] was formed when Na[[Rh\(^II\)(L\(_m\))]\(_2\)Cl] was reduced with sodium borohydride in ethanol. In these studies, alkyl halides were added \textit{in situ} to Na[Rh\(^I\)(L\(_m\))] in ethanol under air-free conditions. A variety of Rh\(^{III}\)(L\(_m\))(alkyl) complexes were successfully synthesised in these reactions, including Rh\(^{III}\)(L\(_m\))Me, Rh\(^{III}\)(L\(_m\))Et, and Rh\(^{III}\)(L\(_m\))Bn. These reactions indirectly confirmed that Na[Rh\(^I\)(L\(_m\))] was synthesised, because the rhodium(I) metal centre is expected to be nucleophilic, and therefore reacts with the electrophilic alkyl group from the alkyl halide.

Rh\(^{III}\)(L\(_m\))Me was synthesised by adding methyl iodide to Na[Rh\(^I\)(L\(_m\))]. The methyl ligand was identified by the presence of an upfield doublet at 0.12 ppm (\(J_{\text{1H-103Rh}} = 3.0\) Hz) in the \(^1\text{H}\) NMR spectrum, and by an upfield doublet at -6.0 ppm (\(J_{\text{13C-103Rh}} = 35.6\) Hz) in the \(^{13}\text{C}\) NMR spectrum. The coupling constants were similar to reported Rh\(^{III}\)(porphyrin)Me and Rh\(^{III}\)(TMTAA)Me complexes.\(^{15,232}\) Only one major signal was observed in the positive ion mass spectrum of Rh\(^{III}\)(L\(_m\))Me, which corresponded to a [Rh\(^{III}\)(L\(_m\))]\(^+\) species, where the methyl ligand is probably weakly coordinated and consequently easily lost during the electrospray ionisation process. This contrasted with Rh\(^{III}\)(porphyrin)Me and Rh\(^{III}\)(TMTAA)Me complexes, where the methyl ligand was not lost in the mass spectrum.\(^{15,232}\) It was speculated that this difference may be due to the stronger donating properties of the L\(_m\) ligand than for the porphyrin and TMTAA ligands, which would cause greater labilisation of axial ligands in the rhodium(III)-L\(_m\) complexes.

Although the crude Rh\(^{III}\)(L\(_m\))Me complex was stable for weeks in methanol-\(d_4\) in air, after removal of the sodium borate salts and other by-products using column chromatography on neutral alumina, Rh\(^{III}\)(L\(_m\))Me began to decompose. Over one day at room temperature in air in methanol-\(d_4\), Rh\(^{III}\)(L\(_m\))Me completely decomposed to form Rh\(^{III}\)(L\(_m\))(OCD\(_3\))(CD\(_3\)OD) and free CH\(_3\)OD as the only major products. This decomposition was studied by \(^1\text{H}\) NMR spectroscopy (in Section 5.2.5.5), and the results from these studies strongly suggested that dioxygen plays a crucial role in loss of the methyl ligand. A possible reaction pathway was also proposed.

Unlike Rh\(^{III}\)(L\(_m\))Me, Rh\(^{III}\)(L\(_m\))Et and Rh\(^{III}\)(L\(_m\))Bn (synthesised using ethyl iodide or benzyl chloride, respectively) were unstable in methanol-\(d_4\) prior to purification (Section 5.2.5.4), and decomposed over hours to form Rh\(^{III}\)(L\(_m\))(OCD\(_3\))(CD\(_3\)OD). It was proposed that this is due to the rhodium-ethyl and rhodium-benzyl bonds being weaker than the rhodium-methyl bond. In contrast to these Rh\(^{III}\)(L\(_m\))(alkyl) complexes, analogous Rh\(^{III}\)(porphyrin)(alkyl) and
Rh^{III}(TMTAA)(alkyl) complexes are usually highly air-stable after purification.\textsuperscript{15,204,232} These differences may again be due to greater axial ligand labilisation by the strongly donating L_{m} ligand. Important future work for the Rh^{III}(L_{m})(alkyl) complexes is to purify and characterise these complexes under air-free conditions to minimise loss of the axial ligands.

The reaction of Na[\text{Rh}^{II}(L_{m})_{2}Cl] with carbon monoxide in alcohols under aerobic conditions gave the corresponding Rh^{III}(L_{m})(C(=O)OR) metalloesters in high yield (Section 5.2.6), where the OR group depended on the alcohol solvent that was used. Complexes with OCD_{3}, OCH_{3}, OEt, O'Pr, and O'Pr groups were synthesised. All of these complexes were air-stable, and the Rh^{III}(L_{m})(C(=O)OCH_{3}) complex was purified by recrystallisation from methanol/water. Elemental analysis of this complex was consistent with a formulation of Rh^{III}(L_{m})(C(=O)OCH_{3})\cdot H_{2}O in the solid state. Although it is currently unknown whether this water molecule is present as an axial ligand or as a water of crystallisation, it was postulated that the latter seems more likely. This is because the relatively strongly coordinated C(=O)OCH_{3} ligand is expected to pull the rhodium atom out of the plane defined by the four nitrogen donor atoms of the L_{m} ligand, on the side towards the C(=O)OCH_{3} ligand, which consequently makes coordination of a second axial ligand unfavourable. Despite many attempts, crystals of Rh^{III}(L_{m})(C(=O)OCH_{3})\cdot H_{2}O suitable for X-ray structure determination could not be obtained, which would shed light on the coordination geometry of this complex. These attempts are ongoing.

The OR groups of the Rh^{III}(L_{m})(C(=O)OR) complexes were identified by upfield OR protons in the $^{1}H$ and $^{13}C$ NMR spectra in methanol-$d_{4}$. In the $^{1}H$ NMR spectra, these OR groups had the expected splitting patterns and integrations. Furthermore, in the $^{13}C$ NMR spectra, the carbonyl carbon of the C(=O)OR ligands was identified by the presence of doublets with $^{13}C$-$^{103}$Rh coupling constants of 50-60 Hz. All of the Rh^{III}(L_{m})(C(=O)OR) complexes were stable over weeks in methanol-$d_{4}$ at room temperature in air, except for slow exchange of the OR group for OCD_{3} over weeks, which produced ROD as a by-product.

The C(=O)OR ligands of the Rh^{III}(L_{m})(C(=O)OR) complexes were also observed in the high resolution positive ion mass spectra, where the highest intensity signals in these spectra corresponded to the ions [Rh^{III}(L_{m})(C(=O)OR) + Na\textsuperscript{+}]. This suggested that the rhodium-carbon bond in these complexes is stronger than the rhodium-carbon bond in the Rh^{III}(L_{m})(alkyl)
complexes, because only [Rh\textsuperscript{III}(L\textsubscript{m})\textsuperscript{+}] species were observed in the mass spectra of the latter complexes, where any axial ligands were lost in the electrospray ionisation process.

Compared to the literature, the reactions of rhodium(II) dimers with carbon monoxide usually gives carbon monoxide adducts of these dimers, dimetal ketones, dimetal diketones, or metalloformyl complexes (see Section 5.1.5 for the structure of these complexes).\textsuperscript{15,236,237} None of these complexes were observed in the reaction of Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}Cl] with carbon monoxide in alcohols. One paper has been published which describes the formation of a metalloester complex from a rhodium(II) dimer.\textsuperscript{228} This metalloester complex, Rh\textsuperscript{III}(OEP)(C(=O)OEt), was synthesised from [Rh\textsuperscript{II}(OEP)]\textsubscript{2} and carbon monoxide in ethanol/CD\textsubscript{2}Cl\textsubscript{2}. Unlike Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OR), the synthesis of Rh\textsuperscript{III}(OEP)(C(=O)OEt) was not carried out in a neat alcohol, and consequently a mixture of products (including Rh\textsuperscript{III}(OEP)(CHO) and Rh\textsuperscript{III}(OEP)Cl) was synthesised. However, like the Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OR) complexes, Rh\textsuperscript{III}(OEP)(C(=O)OEt) was air-stable and could be isolated from the reaction mixture. Rh\textsuperscript{III}(OEP)(C(=O)OEt) was characterised by NMR spectroscopy. The C(=O)OEt ligand of Rh\textsuperscript{III}(OEP)(C(=O)OEt) was significantly upfield of the C(=O)OEt ligand of Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OEt), due to the ring-current effect of the OEP ligand. Despite this difference, the \textsuperscript{13}C-\textsuperscript{103}Rh coupling constants for the C(=O)OEt carbonyl groups in the \textsuperscript{13}C NMR spectra of both complexes were similar.\textsuperscript{228}

The reaction of acetylene with Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}Cl] in alcohols under aerobic conditions gave the corresponding trans-Rh\textsuperscript{III}(L\textsubscript{m})(CH=CHOR) metalloalkoxyvinyl complexes in high yield (Section 5.2.7). Yields were higher for the reactions in methanol and methanol-\textit{d}\textsubscript{4} than in ethanol, isopropanol, and \textit{n}-propanol. Mass spectrometry and NMR spectroscopies were consistent with the expected formulations. Vicinal coupling constants indicated that the CH=CH protons were mutually trans, which minimises steric strain of the OR group with the L\textsubscript{m} ligand. This was achieved by comparing the vicinal coupling constants of the trans-Rh\textsuperscript{III}(L\textsubscript{m})(CH=CHOR) complexes to reported cis- and trans-Rh\textsuperscript{III}(porphyrin)(CH=CHR) complexes.\textsuperscript{243}

Like the Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OR) complexes, the Rh\textsuperscript{III}(L\textsubscript{m})(CH=CHOR) complexes did not rearrange or lose their CH=CHOR axial ligands over weeks in methanol-\textit{d}\textsubscript{4} at room temperature in air, although very slow exchange of the OR group for OCD\textsubscript{3} did occur over this time, producing ROD as a by-product. Also like the Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OR) complexes, the presence of
a major [Rh\textsuperscript{III}(L\textsubscript{m})(CH=CHOR) + Na\textsuperscript{+}] species in the mass spectra of these complexes suggested that the rhodium-carbon bond in these complexes is reasonably strong, and is stronger than the rhodium-carbon bond in the Rh\textsuperscript{III}(L\textsubscript{m})(alkyl) complexes. This was also used to explain why negligible loss of the CH=CHOR axial ligand occurs in alcohol solutions over months at room temperature.

Rh\textsuperscript{III}(L\textsubscript{m})(CH=CHOCH\textsubscript{3}) was purified by column chromatography on neutral alumina, and elemental analysis of the thoroughly-dried sample was consistent with a formulation of Rh\textsuperscript{III}(L\textsubscript{m})(CH=CHOCH\textsubscript{3})\cdot H\textsubscript{2}O in the solid state. It was proposed that the water ligand is more likely to exist as a water of crystallisation rather than as an axial ligand, due to the relatively strongly coordinated CH=CHOCH\textsubscript{3} ligand. Thus, the CH=CHOCH\textsubscript{3} ligand is expected to pull the rhodium atom out of the plane defined by the four nitrogen donor atoms (on the side towards the CH=CHOCH\textsubscript{3} ligand), making coordination of a second axial ligand unfavourable. Attempts to grow X-ray quality crystals to confirm this postulate are ongoing.

For both the Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OR) and Rh\textsuperscript{III}(L\textsubscript{m})(CH=CHOR) complexes, changing the OR group had very little effect on the chemical shift of the L\textsubscript{m} ligand, suggesting that different OR groups do not change the donating strength of the C(=O)OR/CH=CHOR ligand significantly, and therefore do not significantly change the electronic environment of the L\textsubscript{m} ligand.

Reactivity studies were carried out to determine the possible reaction pathway in the synthesis of Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OCH\textsubscript{3}) from Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}Cl] and carbon monoxide in methanol (Section 5.2.6.2). Based on the products formed in these reactions, it was concluded that reaction pathways involving heterolytic cleavage of the rhodium-rhodium bond are much more likely than homolytic cleavage pathways. It was also concluded that similar heterolytic reaction pathways probably occur in the synthesis of [Rh\textsuperscript{III}(L\textsubscript{m})(PPh\textsubscript{3})]\textsuperscript{+}, Rh\textsuperscript{III}(L\textsubscript{m})(CH=CHOR), and [Rh\textsuperscript{III}(L\textsubscript{m})(L)\textsubscript{2}]\textsuperscript{+} (L = DMSO or DMF) from Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}Cl] (Sections 5.2.2.2, 5.2.4, and 5.2.7). However, further reactivity studies need to be carried out in the near future to confirm that heterolytic reaction pathways are indeed occurring in these reactions. Furthermore, the methyl iodide trapping experiment described in Section 5.2.6.2 for the synthesis of Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OCH\textsubscript{3}) from Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}Cl] and carbon monoxide in degassed methanol will be repeated, using the modifications that were suggested in that section.
From the aforementioned reactivity studies, possible reaction pathways were postulated for the synthesis of [Rh\textsuperscript{III}(L\textsubscript{m})(PPh\textsubscript{3})\textsuperscript{+}], Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OR), Rh\textsuperscript{III}(L\textsubscript{m})(CH=CHOR), and [Rh\textsuperscript{III}(L\textsubscript{m})(L)\textsubscript{2}]\textsuperscript{+} (L = DMSO or DMF). These postulated reaction pathways begin with coordination of the reagent (triphenylphosphine, carbon monoxide, acetylene, DMSO, or DMF) to the vacant axial site of Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}]Cl]. The axial chloride ligand may be lost in this step, or it may be lost in the subsequent rhodium-rhodium bond cleavage step. Coordination of the reagent to Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}]Cl] results in weakening of the rhodium-rhodium bond, which then breaks heterolytically to form a rhodium(I) and a rhodium(III) intermediate. Because the reaction of Na[Rh\textsuperscript{I}(L\textsubscript{m})] with carbon monoxide in an alcohol was shown to be negligible (Section 5.2.6.2), it was concluded that the rhodium(I) intermediate does not react with the reagent, but instead oxidises under the aerobic conditions used in the reaction to form another rhodium(III) intermediate. Depending on the reagent, these rhodium(III) products are either in the final product form (for [Rh\textsuperscript{III}(L\textsubscript{m})(PPh\textsubscript{3})\textsuperscript{+}], [Rh\textsuperscript{III}(L\textsubscript{m})(DMSO)\textsubscript{2}]\textsuperscript{+}, and [Rh\textsuperscript{III}(L\textsubscript{m})(DMF)\textsubscript{2}]\textsuperscript{+}), or undergo nucleophilic attack of the axial ligand by the alcohol solvent (for Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OR) and Rh\textsuperscript{III}(L\textsubscript{m})(CH=CHOR)). Therefore, only one product was formed in high yield in each of these reactions.

In the literature, it was demonstrated that homolytic reaction pathways usually operate when low polarity aprotic solvents are used to synthesise monomeric rhodium(III) complexes from Rh\textsuperscript{II}(porphyrin)\textsubscript{2} and [Rh\textsuperscript{II}(TMTAA)]\textsubscript{2} dimers. In contrast, it was shown that heterolytic pathways occurred when similar reactions were carried out in pyridine-\textit{d}\textsubscript{5}. These differences were ascribed to the higher polarity of the pyridine-\textit{d}\textsubscript{5} solvent, which supports ionic reaction pathways and lowers the energy of heterolytic reactions compared to homolytic reactions.\textsuperscript{24,225} This may also explain why heterolytic reaction pathways appear to occur in the reactions of Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}]Cl] with various reagents in alcohols.

Triphenylphosphine, carbon monoxide, or acetylene were also added to Rh\textsuperscript{III}(L\textsubscript{m})(OCD\textsubscript{3})(CD\textsubscript{3}OD) in methanol-\textit{d}\textsubscript{4}, using similar conditions to the corresponding reactions of Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}]Cl] with these reagents. Although the same [Rh\textsuperscript{III}(L\textsubscript{m})(PPh\textsubscript{3})\textsuperscript{+}], Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OCD\textsubscript{3}), and Rh\textsuperscript{III}(L\textsubscript{m})(CH=CHOCD\textsubscript{3}) products were synthesised in high yield starting from either Rh\textsuperscript{III}(L\textsubscript{m})(OCD\textsubscript{3})(CD\textsubscript{3}OD) or Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}]Cl], the reactions starting from the former complex were much faster. It was proposed that this is because coordination of the reagent to Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}]Cl] and/or cleavage of rhodium-rhodium bond of these dimeric intermediates are the slowest step(s) in the synthesis of these products from Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}]Cl].
Reactions of Na[[Rh^{II}(L_m)]_2(Cl)(py)] with carbon monoxide, acetylene, and triphenylphosphine in methanol-d_4 (Section 5.2.8) were also explored. Using similar conditions to the corresponding reactions of Na[[Rh^{II}(L_m)]_2Cl] with these reagents, the same [Rh^{III}(L_m)(PPh_3)]^+, Rh^{III}(L_m)(C(=O)OCH_3), and Rh^{III}(L_m)(CH=CHOCH_3) products were synthesised in high yield, suggesting that pyridine does not coordinate appreciably to these products. This was not surprising, considering that there was also no spectroscopic evidence for the coordination of chloride to the second axial site of these products when they were synthesised from Na[[Rh^{II}(L_m)]_2Cl]. It was postulated that neither chloride nor pyridine coordinates to the second axial site of these products, because the relative strongly coordinated PPh_3, C(=O)OCH_3, and CH=CHOCH_3 axial ligands pull the rhodium centre out of the plane defined by the four nitrogen donor atoms of the L_m ligand (on the side towards these axial ligands), making the coordination of a second axial ligand unfavourable. The reactions of Na[[Rh^{II}(L_m)]_2(Cl)(py)] with these reagents was found to be considerably slower than the corresponding reactions of Na[[Rh^{II}(L_m)]_2Cl] with these reagents. It was postulated that this is because the reagent has to displace the axial pyridine ligand of Na[[Rh^{II}(L_m)]_2(Cl)(py)] before the rhodium-rhodium bond can break, whereas in Na[[Rh^{II}(L_m)]_2Cl], the reagent can coordinate much more readily to the vacant coordination site. Alternatively, an axial alcohol or water ligand might be weakly coordinated in the second axial site of Na[[Rh^{II}(L_m)]_2Cl] in solution, which would also be much more readily displaced than an axial pyridine ligand.

As was summarised in Section 5.2.8, it is not immediately obvious why the rhodium-rhodium bond of Na[[Rh^{II}(L_m)]_2Cl] remains intact after the addition of pyridine to form a Na[[Rh^{II}(L_m)]_2(Cl)(py)] adduct that is stable for months in methanol-d_4, whereas the addition of DMSO, DMF, triphenylphosphine, carbon monoxide, or acetylene to Na[[Rh^{II}(L_m)]_2Cl] all result in cleavage of the rhodium-rhodium bond to form monomeric products. Although the differences between the reaction with pyridine and the reactions with triphenylphosphine or carbon monoxide could be due to the stronger donation of the latter reagents to the rhodium centre of Na[[Rh^{II}(L_m)]_2Cl], this does not explain why rhodium-rhodium bond cleavage in the presence of DMSO, DMF, or acetylene is much faster than rhodium-rhodium bond cleavage in the presence of pyridine. Further experiments that provide more information about how the stability of the rhodium-rhodium bond changes in the presence of other donors or with changes in the solvent dielectric constant will be carried out in future to help understand why this occurs.
Although the aforementioned reactions demonstrated that Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}]Cl] and its dimeric and monomeric derivatives successfully activated small molecules such as carbon monoxide, acetylene, and methyl iodide to form organometallic rhodium complexes, in none of these reactions was the catalytic synthesis of organic molecules observed. In other words, although these rhodium complexes did activate various small molecules, these reactions were not catalytic. Due to time constraints, it was not possible to investigate various methods that could be used to make these systems catalytic. This remains as important future work that will be carried out in future. Some of the key future experiments are described below. Achieving catalytic reaction conditions for the activation of small organic molecules in these rhodium-\textsubscript{L\textit{m}} systems may enable the catalytic synthesis of organic products from cheap and abundant feedstocks that may otherwise be formed via laborious synthetic routes.

A possible reason why catalytic small molecule activation was not observed in the aforementioned reactions could be because catalytic turnover is hindered by the relatively strong rhodium-carbon bond of the organometallic rhodium products, which prevents the axial organometallic ligand from being released to form organic products. If a suitable electrophilic reagent is added to these reactions, it may react with the organometallic ligand to form organic products. Provided that this reagent (or by-products formed from this reagent) does not coordinate strongly to the rhodium centre of the resting catalyst, and can be displaced readily by carbon monoxide or acetylene, this reaction may undergo further turnovers. Thus, in the presence of excess reagents, organic products may be synthesised catalytically. As an example of this approach, excess methyl iodide could be added to the reaction used to synthesise Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OR) from Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}]Cl] and carbon monoxide in an alcohol. The methyl iodide may then cleave the rhodium-carbon bond of Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OR) to form MeC(=O)OR esters and the rhodium complex probably becomes ligated by the iodide by-product. Provided that the iodide axial ligand can be displaced by carbon monoxide, another catalytic turnover may ensue. Strong coordination of the iodide ligand from the methyl iodide reagent seems unlikely, considering that the strongly donating L\textsubscript{m} ligand is expected to labilise axial ligands to a significant extent, as was shown in many experiments described in this chapter and in Chapter 3. In this reaction, it may be possible to produce different R’C(=O)OR esters by using different alkyl halides (R’X) and different alcohols (ROH). Similar reactions may be possible with acetylene, to produce R’CH=CHOR vinyl alcohols. The use of suitable acids instead of alkyl halides may form HC(=O)OR and CH\textsubscript{2}=CHOR products.
Further investigations with the Rh\text{III}(L_m)(alkyl) complexes described in Section 5.2.5 will also be carried out to see whether these reactions can be made catalytic. It was already shown that the alkyl ligand is readily lost from these complexes in air, and it may be possible to exploit this property to produce organic products catalytically. Further studies into the reaction pathway for the decomposition of these Rh\text{III}(L_m)(alkyl) complexes in air (postulated in Figure 5.22) will be conducted in the near future. Using this information, it may be possible to synthesise various organic products catalytically, for example, by adding suitable reagents to these reactions, perhaps under air-free conditions.

Another method that could be used to make these small molecule activation reactions catalytic is to increase the reaction temperature. All the reactions described in the chapter were conducted at room temperature, and increasing the reaction temperature will make loss of the organometallic axial ligand more facile. Different products may also be synthesised at higher temperatures by thermally-induced rearrangements of the intermediates or products.

Yet another method for making these systems catalytic is to irradiate the reactions with UV or visible light. In a related reaction reported in the literature, [Rh\text{II}(OEP)]_2 was found to react with carbon monoxide and dihydrogen to produce formaldehyde and methanol catalytically when the reaction was irradiated with UV light (300 nm) in a sealed NMR tube in benzene-\text{d}_6. However, when irradiation was terminated, the methanol and formaldehyde reacted with the rhodium complexes in solution to form Rh\text{III}(OEP)(CHO) and Rh\text{III}(OEP)(H) (see Section 5.1.5.2 for a summary of these results). Although a homolytic reaction pathway was postulated, and although the methanol and formaldehyde products reacted back with the rhodium(III) complexes in the absence of irradiation,\textsuperscript{242} it may be possible to produce organic products irreversibly via heterolytic reaction pathways upon irradiating the reaction of Na[[Rh\text{II}(L_m)]_2Cl] with carbon monoxide or alkynes in alcohols. One of the advantages of the rhodium-L_m complexes over similar rhodium-porphyrin and rhodium-TMTAA complexes is that ligand donating strength is expected to be higher for the L_m ligand than for the porphyrin and TMTAA ligands. Therefore, axial ligands are expected to be lost more readily in the rhodium-L_m complexes, which may aid in catalytic turnovers in these systems.

Other research that will be conducted in future includes continuing the attempts to grow X-ray quality crystals of these rhodium-L_m complexes, and investigating the reaction of rhodium-L_m
complexes with carbon dioxide and ethylene. The latter reagent has been shown to react with [Rh\textsuperscript{II}(porphyrin)]\textsubscript{2} dimers to produce various rhodium(III) products via homolytic reaction pathways in low polarity solvents.\textsuperscript{24,221}

Because Na[[Rh\textsuperscript{II}(L\textsubscript{m})]\textsubscript{2}Cl] was shown to react via heterolytic reaction pathways in alcohols, and because nucleophilic attack of coordinated acetylene and coordinated carbon monoxide by these alcohols are known to occur in these rhodium-L\textsubscript{m} systems, interesting new organometallic complexes may be produced when Na[[Rh\textsuperscript{II}(L\textsubscript{m})]\textsubscript{2}Cl] reacts with ethylene in alcohols. The reaction of Na[[Rh\textsuperscript{II}(L\textsubscript{m})]\textsubscript{2}(Cl)(py)] and Rh\textsuperscript{III}(L\textsubscript{m})(OCD\textsubscript{3})(CD\textsubscript{3}OD) with various reagents in solvents other than alcohols will also be investigated in future, because (unlike Na[[Rh\textsuperscript{II}(L\textsubscript{m})]\textsubscript{2}Cl]), these complexes are slightly soluble in some aprotic solvents, such as THF. These reactions will be conducted in future once pure samples of Na[[Rh\textsuperscript{II}(L\textsubscript{m})]\textsubscript{2}(Cl)(py)] and Rh\textsuperscript{III}(L\textsubscript{m})(OCD\textsubscript{3})(CD\textsubscript{3}OD) are obtained. These complexes also have a slight solubility in water and so, like similar reactions in the literature,\textsuperscript{228,241} it may be possible to synthesise Rh\textsuperscript{III}(L\textsubscript{m})(CHO) complexes in this solvent.
5.4 Experimental

5.4.1 General procedures

See Section 2.5.1 for general synthetic and spectroscopic procedures and instrumentation.

5.4.2 Synthesis of Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}(Cl)(py)]

[Chemical structure diagram]

Figure 5.25: Chemical structure of Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}(Cl)(py)]. The rhodium-rhodium, rhodium-chlorine, and rhodium-pyridine bonds have been lengthened considerably in this figure to show the L\textsubscript{m} ligands more clearly

Pyridine (40 \textmu L, 0.495 mmol) was added to a suspension of Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}(Cl)] (0.105 g, 0.096 mmol) in methanol (50 mL). After 40 minutes at room temperature, once the solution had changed to clear yellow-orange, the solvent was removed under vacuum. The orange solid was purified by column chromatography on alumina (12 x 2.5 cm column, 19 : 1: 0.02 dichloromethane/methanol/pyridine), collecting the yellow-orange band. The solvent was then removed under vacuum to yield Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}(Cl)(py)] as an orange solid. Yield: 0.103 g (92%).
$^1$H NMR (500 MHz, methanol-$d_4$, $\delta$): 9.41 (d, $J = 1.9$ Hz, 1H, pyridinium CH), 9.10 (d, $J = 1.8$ Hz, 1H, pyridinium CH), 8.52-8.54 (m, 0.75 eq. (1.5 H) free pyridine, ortho-CH), 7.83-7.86 (m, 0.75 eq. (0.75 H) free pyridine, para-CH), 7.68 (dd, $J_1 = 7.2$ Hz, $J_2 = 1.9$ Hz, 1H, pyridinium CH), 7.65-7.67 (m, 3H, coordinated pyridine, ortho- and para-CH), 7.63 (d, $J = 7.8$ Hz, 1H, phenyl CH), 7.57 (dd, $J_1 = 7.3$ Hz, $J_2 = 1.8$ Hz, 1H, pyridinium CH), 7.49 (d, $J = 7.2$ Hz, 1H, pyridinium CH), 7.47 (d, $J = 8.0$ Hz, 1H, phenyl CH), 7.43-7.45 (m, 0.75 eq. (1.5 H) free pyridine, meta-CH), 7.41 (dd, $J_1 = 7.4$ Hz, $J_2 = 1.6$ Hz, 1H, pyridinium CH), 7.35 (d, $J = 8.0$ Hz, 1H, phenyl CH), 7.28 (d, $J = 7.4$ Hz, 1H, pyridinium CH), 7.26 (d, $J = 7.3$ Hz, 1H, pyridinium CH), 7.24 (d, $J = 1.8$ Hz, 1H, pyridinium CH), 7.22 (d, $J = 7.8$ Hz, 1H, phenyl CH), 7.18 (dd, $J_1 = 7.3$ Hz, $J_2 = 1.8$ Hz, 1H, pyridinium CH), 7.15 (t, $J = 7.1$ Hz, 2H, coordinated pyridine, meta-CH), 7.04 (t, $J = 8.0$ Hz, 1H, phenyl CH), 6.97 (t, $J = 8.0$ Hz, 1H, phenyl CH), 6.68 (t, $J = 7.8$ Hz, 1H, phenyl CH), 6.63 (d, $J = 1.6$ Hz, 1H, pyridinium CH), 3.91 (s, 3H, N-CH$_3$), 3.86 (s, 3H, N-CH$_3$), 3.68 (s, 3H, N-CH$_3$), 1.32 (s, 3H, C-CH$_3$), 1.05 (s, 3H, C-CH$_3$), 0.87 (s, 3H, C-CH$_3$), 0.48 (s, 3H, C-CH$_3$).

$^{13}$C NMR (125.7 MHz, methanol-$d_4$, $\delta$): 227.6 (C=O), 184.4 (C=O), 179.6 (C=O), 178.5 (C=O), 159.5 (pyridinium C=NR), 158.6 (pyridinium C=NR), 153.7 (pyridinium C=NR), 153.2 (pyridinium C=NR), 151.4 (coordinated pyridine, CH), 151.0 (pyridinium C-N-C(O)R), 150.1 (free pyridine, ortho-CH), 147.0 (phenyl C), 146.5 (pyridinium C-N-C(O)R), 146.3 (phenyl C), 145.4 (phenyl C), 145.3 (pyridinium C-N-C(O)R), 144.8 (phenyl C), 144.6 (pyridinium C-N-C(O)R), 139.8 (coordinated pyridine, CH), 139.5 (pyridinium CH), 138.4 (2 x pyridinium CH), 138.4 (free pyridine, para-CH), 137.4 (pyridinium CH), 135.6 (pyridinium CH), 134.9 (pyridinium CH), 134.5 (pyridinium CH), 133.0 (pyridinium CH), 126.8 (coordinated pyridine, meta-CH), 125.6 (free pyridine, meta-CH), 123.6 (phenyl CH), 123.1 (phenyl CH), 122.8 (phenyl CH), 122.7 (phenyl CH), 120.7 (phenyl CH), 120.5 (phenyl CH), 120.3 (phenyl CH), 119.7 (phenyl CH), 110.8 (pyridinium CH), 110.4 (pyridinium CH), 108.1 (phenyl CH), 106.8 (pyridinium CH), 69.5 (C-CH$_3$), 63.1 (C-CH$_3$), 45.3 (N-CH$_3$), 45.2 (N-CH$_3$), 44.7 (N-CH$_3$), 44.2 (N-CH$_3$), 30.0 (C-CH$_3$), 26.2 (C-CH$_3$), 25.4 (C-CH$_3$), 22.6 (C-CH$_3$).

IR (cm$^{-1}$): 3376 (br, s), 1670 (m), 1613 (m), 1576 (s), 1514 (s), 1473 (m), 1435 (s), 1377 (s), 1342 (w), 1301 (w), 1268 (w), 1249 (w), 1190 (s), 1048 (w), 872 (w), 849 (w), 778 (w), 742 (m), 684 (m), 611 (w), 555 (w), 511 (w), 477 (w).

UV-vis (CH$_3$OH) $\lambda_{max}$, nm ($\epsilon$, L mol$^{-1}$ cm$^{-1}$): 253 (sh, 45,400), 333 (sh, 22,900), 415 (41,400), 472 (sh, 20,800).
ESI-MS $m/z$ (positive ion mode): $(M^- - Cl^- - py + H^+)$: calcd for $C_{46}H_{45}N_{12}O_4Rh_2$, 1035.1791; found, 1035.1828 (100%, $z = +1$).

ESI-MS $m/z$ (negative ion mode): $(M^- - Cl^- - py + 2HCOO^- + H^+)$, calcd for $C_{46}H_{47}N_{12}O_4Rh_2$, 1125.1755; found, 1125.1739 (100%, $z = -1$). $(M^- - Cl^- - py + HCOO^- + H^+)$, calcd for $C_{47}H_{45}N_{12}O_4Rh_2$, 1079.1701; found, 1079.1688 (30%, $z = -1$). $(M^- - py + HCOO^- + H^+)$, calcd for $C_{47}H_{46}ClN_{12}O_4Rh_2$, 1115.1462; found, 1115.1466 (30%, $z = -1$). $(M^- - py)$, calcd for $C_{46}H_{44}ClN_{12}O_4Rh_2$, 1069.1413; found, 1069.1439 (10%, $z = -1$). $(M^- - py + Cl^- + H^+)$, calcd for $C_{46}H_{45}Cl_2N_{12}O_4Rh_2$, 1105.1179; found, 1105.1217 (5%, $z = -1$).

5.4.3 Synthesis of $[\text{Rh}^{III}(L_m)(\text{PPh}_3)][\text{PF}_6]$  

![Chemical structure of $[\text{Rh}^{III}(L_m)(\text{PPh}_3)][\text{PF}_6]$]

Figure 5.26: Chemical structure of $[\text{Rh}^{III}(L_m)(\text{PPh}_3)][\text{PF}_6]$  

Triphenylphosphine (0.0760 g, 0.290 mmol) was added to a suspension of $\text{Na}[[\text{Rh}^{II}(L_m)]_2\text{Cl}]$ (0.098 g, 0.0896 mmol) in methanol (100 mL). After 20 minutes at room temperature, the solvent was removed under vacuum. The residue was suspended in toluene (40 mL) and was then extracted into deionised water (3 x 40 mL). The combined aqueous phases were washed with toluene (3 x 120 mL). The aqueous phase was then filtered and the filtrate was concentrated to about 50 mL under vacuum. To this solution was added ammonium hexafluorophosphate (0.310 g, 1.898 mmol, dissolved in 5 mL of deionised water). After stirring this suspension for 1 hour at room temperature, the green precipitate was collected by filtration and was washed with deionised water (5 mL). After drying the collected precipitate under vacuum for 2 hours, it was purified by column chromatography on alumina (12 x 2 cm column, 19:1 dichloromethane/methanol), collecting the green band. Upon evaporating the solvent under reduced pressure, a pure sample of green-brown $[\text{Rh}^{III}(L_m)(\text{PPh}_3)][\text{PF}_6]$ precipitated from solution and was collected by filtration (yield: 0.116 g, 71%).
$^1$H NMR (500 MHz, methanol-$d_4$, $\delta$): 9.14 (d, $J = 2.0$ Hz, 2H, pyridinium CH), 7.67 (dd, $J_1 = 7.3$ Hz, $J_2 = 2.0$ Hz, 2H, pyridinium CH), 7.51-7.53 (m, 2H, phenyl CH), 7.39-7.42 (m, 3H, PPh$_3$ ortho CH), 7.40 (d, $J = 7.3$ Hz, 2H, pyridinium CH), 7.17-7.22 (m, 6H, PPh$_3$ meta CH), 7.14-7.17 (m, 6H, PPh$_3$ para CH), 7.02-7.04 (m, 2H, phenyl CH), 3.94 (s, 6H, N-CH$_3$), 1.51 (br s, 3H, C-CH$_3$), 1.17 (br s, 3H, C-CH$_3$).

$^{13}$C NMR (125.7 MHz, methanol-$d_4$, $\delta$): 180.5 (C=O), 154.7 (pyridinium C=N=NR), 145.8 (phenyl C), 145.2 (pyridinium C-N-C(O)R), 137.9 (pyridinium CH), 136.1 (pyridinium CH), 135.2 (PPh$_3$ ortho CH), 135.1 (PPh$_3$ ortho CH), 132.6 (PPh$_3$ para CH), 129.3 (PPh$_3$, meta CH), 129.2 (PPh$_3$, meta CH), 124.0 (phenyl CH), 121.9 (phenyl CH), 109.9 (pyridinium CH), 61.3 (C-CH$_3$), 29.0 (C-CH$_3$), 28.3 (C-CH$_3$).

$^{31}$P NMR (202.4 MHz, methanol-$d_4$, $\delta$): 41.2 (d, $J_{31P-103Rh} = 175$ Hz).

IR (cm$^{-1}$): 3420 (br, m), 2928 (br, m), 1614 (m), 1575 (m), 1507 (s), 1464 (m), 1433 (s), 1376 (s), 1336 (w), 1302 (w), 1253 (w), 841 (m), 785 (w), 740 (m), 685 (s), 612 (w), 558 (m), 529 (m), 511 (m).

UV-vis (CH$_3$OH) $\lambda_{max}$, nm ($\varepsilon$, L mol$^{-1}$ cm$^{-1}$): 251 (sh, 36,300), 308 (sh, 10,500), 382 (26,000), 417 (28,100), 439 (sh, 23,100).

ESI-MS $m/z$: (M$^+$), calcd for C$_{41}$H$_{37}$N$_6$O$_2$PRh, 779.1765; found, 779.1788 (100%, z = +1). (M$^+$ – PPh$_3$), calcd for C$_{23}$H$_{22}$N$_6$O$_2$Rh, 517.0854; found, 517.0863 (12%, z = +1).

Anal. Calcd for C$_{41}$H$_{37}$F$_6$N$_6$O$_2$P$_2$Rh: C, 53.26; H, 4.03; N, 9.09. Found: C, 53.61; H, 4.13; N, 8.79.
5.4.4 Synthesis of Rh\textsuperscript{III}(L\textsubscript{m})(Me)

Sodium borohydride (0.186 g, 4.92 mmol) was added to a suspension of Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}Cl] (0.255 g, 0.233 mmol) in ethanol (100 mL). After 35 minutes at room temperature, methyl iodide (0.92 mL, 14.8 mmol) was added and the solution was stirred for a further 45 minutes at room temperature. The solvent was then removed under vacuum and the red-orange solid was purified by column chromatography on alumina (10 x 3 cm column, 19:1 dichloromethane/methanol), collecting the orange band. Upon evaporation of the solvent under reduced pressure, Rh\textsuperscript{III}(L\textsubscript{m})Me precipitated as a red-orange solid (yield: 0.212 g, 85%).

\textsuperscript{1}H NMR (500 MHz, methanol-\textit{d}_4, \delta): 9.02 (d, \textit{J} = 1.9 Hz, 2H, pyridinium CH), 7.70-7.73 (m, 2H, phenyl CH), 7.48 (dd, \textit{J}_1 = 7.4 Hz, \textit{J}_2 = 1.9 Hz, 2H, pyridinium CH), 7.30 (d, \textit{J} = 7.4 Hz, 2H, pyridinium CH), 6.97-7.00 (m, 2H, phenyl CH), 3.78 (N-CH\textsubscript{3}), 1.64 (C-CH\textsubscript{3}), 1.54 (C-CH\textsubscript{3}), 0.12 (d, \textit{J}_{1H-103Rh} = 3.0 Hz, 3H, Rh-CH\textsubscript{3}).

\textsuperscript{13}C NMR (125.7 MHz, methanol-\textit{d}_4, \delta): 180.8 (C=O), 153.7 (pyridinium C=NR), 147.2 (phenyl C), 146.0 (pyridinium C-NC(O)R), 136.1 (pyridinium CH), 133.3 (pyridinium CH), 122.6 (phenyl CH), 120.9 (phenyl CH), 109.0 (pyridinium CH), 62.4 (C-CH\textsubscript{3}), 44.6 (N-CH\textsubscript{3}), 28.9 (C-CH\textsubscript{3}), 28.7 (C-CH\textsubscript{3}), -6.0 (d, \textit{J}_{13C-103Rh} = 35.6 Hz, Rh-CH\textsubscript{3}).

IR (cm\textsuperscript{-1}): 3420 (br, s), 2880 (br, s), 1616 (s), 1565 (w), 1514 (s), 1463 (w), 1441 (m), 1380 (s), 1346 (w), 1249 (w), 1191 (s), 1114 (w), 1077 (m), 996 (m), 932 (w), 867 (m), 776 (w), 742 (m), 683 (m), 559 (w), 511 (w), 435 (w).

ESI-MS \textit{m}/\textit{z}: (M – Me), calcd for C\textsubscript{23}H\textsubscript{22}N\textsubscript{6}O\textsubscript{2}Rh, 517.0854; found, 517.0862 (100%, \textit{z} = +1).
5.4.5 Synthesis of Rh$^{III}$(L$_m$)(OCH$_3$)(CH$_3$OH)

![Chemical structure of Rh$^{III}$(L$_m$)(OCH$_3$)(CH$_3$OH)](image)

$L = \text{OCH}_3$
$L' = \text{CH}_3\text{OH}$

Figure 5.28: Chemical structure of Rh$^{III}$(L$_m$)(OCH$_3$)(CH$_3$OH)

The alumina columned Rh$^{III}$(L$_m$)(Me) complex (0.212 g, 0.398 mmol) prepared in Section 5.4.4 was dissolved in methanol (25 mL). After 2 days at room temperature in air, the solvent was removed under vacuum, giving the Rh$^{III}$(L$_m$)(OCH$_3$)(CH$_3$OH) complex as a brown solid in approximately stoichiometric yield. Note that upon dissolution in methanol-$d_4$, the axial ligands rapidly exchange to give a Rh$^{III}$(L$_m$)(OCD$_3$)(CH$_3$OD) complex.

$^1$H NMR (500 MHz, methanol-$d_4$, $\delta$): 9.28 (d, $J = 1.9$ Hz, 2H, pyridinium CH), 7.85-7.87 (m, 2H, phenyl CH), 7.58 (dd, $J_1 = 7.4$ Hz, $J_2 = 1.9$ Hz, 2H, pyridinium CH), 7.47 (d, $J = 7.4$ Hz, 2H, pyridinium CH), 7.06-7.08 (m, 2H, phenyl CH), 3.86 (s, 6H, N-CH$_3$), 1.69 (s, 6H, C-CH$_3$).

$^{13}$C NMR (125.7 MHz, methanol-$d_4$, $\delta$): 180.5 (C=O), 154.7 (pyridinium C=NR), 146.7 (phenyl C), 145.8 (pyridinium C-NC(O)R), 137.0 (pyridinium CH) 133.7 (pyridinium CH), 123.2 (phenyl CH), 121.2 (phenyl CH), 109.4 (pyridinium CH), 63.2 (C-CH$_3$), 44.8 (N-CH$_3$), 29.0 (C-CH$_3$).

IR (cm$^{-1}$): 3364 (br, s), 2926 (br, w), 1615 (m), 1567 (m), 1508 (s), 1464 (m), 1438 (s), 1380 (s), 1345 (m), 1299 (w), 1179 (s), 1083 (w), 1049 (w), 1003 (w), 959 (w), 867 (m), 781 (w), 737 (m), 684 (m), 611 (w), 555 (w).

UV-vis (CH$_3$OH) $\lambda_{\text{max}}$, nm ($\varepsilon$, L mol$^{-1}$ cm$^{-1}$): 402 (18,900), 432 (19,100), 459 (14,800).

ESI-MS $m/z$: (M – OCH$_3$ – CH$_3$OH): calcd for C$_{23}$H$_{22}$N$_6$O$_2$Rh, 517.0854; found, 517.0840 (100%, $z = +1$).
5.4.6 Synthesis of Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OR)

\begin{center}
\begin{tikzpicture}
  \node (A) at (0,0) {\includegraphics[width=0.5\textwidth]{structure.png}};
  \node at (A) [above] \text{L = C(=O)OR (R = CH\textsubscript{3}, CD\textsubscript{3}, Et, \text{^n}Pr, \text{^i}Pr)};
\end{tikzpicture}
\end{center}

Figure 5.29: Chemical structure of the Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OR) complexes

Carbon monoxide was bubbled gently through a suspension of Na[[Rh\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}Cl] (0.080 g, 0.0732 mmol) in an alcohol (50 mL) for 2 minutes. The suspension was then stirred at room temperature under an atmosphere of carbon monoxide (approx. 1 atmosphere in pressure) for 40 minutes. The flask was then vented for 5 minutes and the solvent was removed under vacuum, yielding the corresponding Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OR) complex as a yellow-brown solid. The R = CH\textsubscript{3} complex was purified by recrystallisation from water/methanol to yield Rh\textsuperscript{III}(L\textsubscript{m})(C(=O)OCH\textsubscript{3}) as a yellow-orange solid (0.068 g, 81%).

For R = CH\textsubscript{3}:

\textsuperscript{1}H NMR (500 MHz, methanol-\textit{d}_4, \delta): 9.09 (d, J = 2.0 Hz, 2H, pyridinium CH), 7.71-7.73 (m, 2H, phenyl CH), 7.54 (dd, J\textsubscript{1} = 7.6 Hz, J\textsubscript{2} = 2.0 Hz, 2H, pyridinium CH), 7.36 (d, J = 7.6 Hz, 2H, pyridinium CH), 6.98-7.01 (m, 2H, phenyl CH), 3.83 (s, 6H, N-CH\textsubscript{3}), 3.29 (s, 3H, Rh-C(=O)OCH\textsubscript{3}), 1.57 (s, 3H, C-CH\textsubscript{3}), 1.52 (s, 3H, C-CH\textsubscript{3}).

\textsuperscript{13}C NMR (125.7 MHz, methanol-\textit{d}_4, \delta): 183.0 (d, J\textsubscript{123C-103Rh} = 49.3 Hz, Rh-C(=O)OCH\textsubscript{3}), 180.3 (R-C(O)-NR\textsuperscript{’}), 154.6 (pyridinium C=NR), 147.0 (phenyl C), 146.3 (pyridinium C-N-C(O)R), 136.7 (pyridinium CH), 133.8 (pyridinium CH), 122.8 (phenyl CH), 120.6 (phenyl CH), 108.9 (pyridinium CH), 62.4 (C-CH\textsubscript{3}), 52.3 (Rh-C(=O)OCH\textsubscript{3}), 44.7 (N-CH\textsubscript{3}), 30.2 (C-CH\textsubscript{3}), 26.7 (C-CH\textsubscript{3}).

IR (cm\textsuperscript{-1}): 3203 (br, m), 2935 (br, m), 1726 (m), 1647 (s), 1613 (m), 1586 (s), 1511 (m), 1477 (m), 1439 (m), 1428 (m), 1378 (s), 1344 (w), 1299 (m), 1178 (s), 1125 (w), 1031 (s), 944 (w), 868 (m), 785 (m), 751 (m), 683 (s), 612 (w), 559 (w), 513 (m).
UV-vis (CH$_3$OH) $\lambda_{max}$, nm (ε, L mol$^{-1}$ cm$^{-1}$): 217 (29,700), 260 (18,100), 322 (8,600), 405 (22,200), 431 (28,200), 456 (22,300).

ESI-MS $m/z$: (M + Na$^+$), calcd for C$_{25}$H$_{25}$N$_6$NaO$_4$Rh, 599.0890; found, 599.0885 (100%, z = +1). (M – C(=O)OCH$_3$), calcd for C$_{23}$H$_{22}$N$_6$O$_2$Rh, 517.0854; found, 517.0848 (40%, z = +1).


For R = CD$_3$:

$^1$H NMR (300 MHz, methanol-$d_4$, δ): 9.09 (d, J = 1.8 Hz, 2H, pyridinium CH), 7.70-7.73 (m, 2H, phenyl CH), 7.54 (dd, $J_1 = 7.5$ Hz, $J_2 = 1.8$ Hz, 2H, pyridinium CH), 7.37 (d, J = 7.5 Hz, 2H, pyridinium CH), 6.98-7.01 (m, 2H, phenyl CH), 3.83 (s, 6H, N-CH$_3$), 1.57 (s, 3H, C-CH$_3$), 1.52 (s, 3H, C-CH$_3$).

ESI-MS $m/z$: (M + Na$^+$), calcd for C$_{25}$H$_{22}$D$_3$N$_6$NaO$_4$Rh, 602.1078; found, 602.1074 (100%, z = +1). (M – C(=O)OCD$_3$), calcd for C$_{23}$H$_{22}$N$_6$O$_2$Rh, 517.0854; found, 517.0883 (80%, z = +1).

For R = Et:

$^1$H NMR (500 MHz, methanol-$d_4$, δ): 9.09 (d, J = 1.9 Hz, 2H, pyridinium CH), 7.71-7.73 (m, 2H, phenyl CH), 7.53 (dd, $J_1 = 7.4$ Hz, $J_2 = 1.9$ Hz, 2H, pyridinium CH), 7.35 (d, J = 7.4 Hz, 2H, pyridinium CH), 6.98-7.00 (m, 2H, phenyl CH), 3.83 (s, 6H, N-CH$_3$), 3.76 (q, $J = 7.1$ Hz, 2H, Rh-C(=O)O(OCH$_2$)C$_2$H$_5$), 1.58 (s, 3H, C-CH$_3$), 1.55 (s, 3H, C-CH$_3$), 0.80 (t, $J = 7.1$ Hz, 3H, Rh-C(=O)O(OCH$_2$)C$_2$H$_5$).

$^{13}$C NMR (125.7 MHz, methanol-$d_4$, δ): 183.6 (d, $J_{13C-103Rh} = 58.1$ Hz, Rh-C(=O)OCH$_2$CH$_3$), 180.4 (R-C(=O)-NR'), 154.6 (pyridinium C=NR), 147.0 (phenyl C), 146.4 (pyridinium C-N-C(O)R), 136.0 (pyridinium CH), 133.7 (pyridinium CH), 122.7 (phenyl CH), 120.6 (phenyl CH), 108.9 (pyridinium CH), 62.4 (C-CH$_3$), 61.0 (Rh-C(=O)OCH$_2$CH$_3$), 44.7 (N-CH$_3$), 30.2 (C-CH$_3$), 26.9 (C-CH$_3$), 14.4 (Rh-C(=O)OCH$_2$CH$_3$).

ESI-MS $m/z$: (M + Na$^+$), calcd for C$_{26}$H$_{27}$N$_6$NaO$_4$Rh, 613.1041; found, 613.1034 (95%, z = +1). (M – C(=O)OEt), calcd for C$_{23}$H$_{22}$N$_6$O$_2$, 517.0854; found, 517.0839 (100%, z = +1).
For $R = \text{"^{3}Pr}$:

$^1$H NMR (300 MHz, methanol-$d_4$, $\delta$): 9.10 (d, $J = 2.0$ Hz, 2H, pyridinium CH), 7.70-7.73 (m, 2H, phenyl CH), 7.53 (dd, $J_1 = 7.4$ Hz, $J_2 = 2.0$ Hz, 2H, pyridinium CH), 7.36 (d, $J = 7.4$ Hz, 2H, pyridinium CH), 6.98-7.00 (m, 2H, phenyl CH), 3.83 (s, 6H, N-CH$_3$), 3.68 (t, $J = 6.0$ Hz, 2H, Rh-C(=O)OCH$_2$CH$_2$CH$_3$), 1.58 (s, 3H, C-CH$_3$), 1.54 (s, 3H, C-CH$_3$), 1.16-1.21 (m, 2H, Rh-C(=O)OCH$_2$CH$_2$CH$_3$), 0.58 (t, $J = 7.5$ Hz, 3H, Rh-C(=O)OCH$_2$CH$_2$CH$_3$).

ESI-MS m/z: (M + Na$^+$), calcd for C$_{27}$H$_{29}$N$_6$NaO$_4$Rh, 627.1203; found, 627.1156 (15%, $z = +1$). (M – C(=O)O$i^{3}$Pr), calcd for C$_{23}$H$_{22}$N$_6$O$_2$Rh, 517.0854; found, 517.0872 (100%, $z = +1$).

For $R = \text{"^{3}Pr}$:

$^1$H NMR (300 MHz, methanol-$d_4$, $\delta$): 9.09 (d, $J = 2.1$ Hz, 2H, pyridinium CH), 7.70-7.73 (m, 2H, phenyl CH), 7.53 (dd, $J_1 = 7.5$ Hz, $J_2 = 2.1$ Hz, 2H, pyridinium CH), 7.35 (d, $J = 7.5$ Hz, 2H, pyridinium CH), 6.98-7.01 (m, 2H, phenyl CH), 4.67 (septet, $J = 6.3$ Hz, 1H, Rh-C(=O)OCH(CH$_3$)$_2$), 3.83 (s, 6H, N-CH$_3$), 1.58 (s, 3H, C-CH$_3$), 1.56 (s, 3H, C-CH$_3$), 0.76 (d, $J = 6.3$ Hz, 6H, Rh-C(=O)OCH(CH$_3$)$_2$).

ESI-MS m/z: (M + Na$^+$), calcd for C$_{27}$H$_{29}$N$_6$NaO$_4$Rh, 627.1203; found, 627.1220 (100%, $z = +1$). (M – C(=O)O$i^{3}$Pr), calcd for C$_{23}$H$_{22}$N$_6$O$_2$Rh, 517.0854; found, 517.0864 (90%, $z = +1$).

5.4.7 Synthesis of trans-Rh$^{\text{III}}$(L$_{\text{Me}}$)(CH=CHOCH$_3$)

![Chemical structure of trans-Rh$^{\text{III}}$(L$_{\text{Me}}$)(CH=CHOCH$_3$)](image)

$L = \text{trans-CH}=\text{CHOME}$

Figure 5.30: Chemical structure of trans-Rh$^{\text{III}}$(L$_{\text{Me}}$)(CH=CHOCH$_3$)

Acetylene was bubbled gently through a suspension of Na[[Rh$^{\text{II}}$(L$_{\text{Me}}$)]$_2$Cl] (0.092 g, 0.0813 mmol) in methanol (60 mL) for 3 minutes. The suspension was then stirred under an atmosphere
of acetylene (approximately 1 atmosphere in pressure) at room temperature for 2 days. The solvent was then removed under vacuum. The residue was purified by column chromatography on alumina (15 x 2 cm column, 19:1 dichloromethane/methanol), collecting the orange band. The solvent was then evaporated under reduced pressure and a pure sample of orange trans-Rh^{III}(L_m)(CH=CHOCH_3) crystallised from solution (yield: 0.0723 g, 77%).

\[ ^1H \text{ NMR (500 MHz, methanol-}d_4, \delta): \]
\[ 9.09 \text{ (d, } J = 1.8 \text{ Hz, 2H, pyridinium CH), 7.70-7.72 \text{ (m, 2H, phenyl CH), 7.47 (dd, } J_1 = 7.3 \text{ Hz, } J_2 = 1.8 \text{ Hz, 2H, pyridinium CH), 7.31 (d, } J = 7.3 \text{ Hz, 2H, pyridinium CH), 6.97-7.00 \text{ (m, 2H, phenyl CH), 4.95 (dd, } J_{1H-1H} = 12.6 \text{ Hz, } J_{1H-103Rh} = 1.1 \text{ Hz, 1H, Rh-CH=CH-OCCH}_3, 4.91 (dd, } J_{1H-1H} = 12.6 \text{ Hz, } J_{1H-103Rh} = 1.9 \text{ Hz, 1H, Rh-CH=CH-OCCH}_3, 3.79 \text{ (s, 6H, N-CH}_3, 3.15 \text{ (s, 3H, Rh-CH=CH-OCCH}_3, 1.61 \text{ (s, 3H, C-CH}_3, 1.59 \text{ (s, 3H, C-CH}_3). \]

\[ ^13C \text{ NMR (125.7 MHz, methanol-}d_4, \delta): \]
\[ 180.4 \text{ (C=O), 153.7 \text{ (pyridinium C=NR), 147.1 \text{ (phenyl C), 145.9 \text{ (pyridinium C-NC(O)R), 142.7 (d, } J_{13C-103Rh} = 11.9 \text{ Hz, Rh-CH=CH-OCCH}_3, 136.4 \text{ (pyridinium CH), 133.6 \text{ (pyridinium CH), 122.7 \text{ (phenyl CH), 120.8 \text{ (phenyl CH), 109.0 \text{ (pyridinium CH), 99.6 (d, } J_{13C-103Rh} = 46.0 \text{ Hz, Rh-CH=CH-OCCH}_3, 62.6 \text{ (C-CH}_3, 55.4 \text{ (Rh-CH=CH-OCCH}_3, 45.0 \text{ (N-CH}_3, 28.9 \text{ (C-CH}_3, 28.0 \text{ (C-CH}_3).} \]

\[ \text{IR (cm}^{-1}): 3373 \text{ (br, s), 2626 \text{ (br, m), 1613 \text{ (m), 1568 \text{ (s), 1510 \text{ (s), 1462 \text{ (w), 1439 \text{ (s), 1379 \text{ (s), 1343 \text{ (m), 1298 \text{ (w), 1251 \text{ (w), 1180 \text{ (s), 1084 \text{ (s), 1002 \text{ (w), 958 \text{ (w), 909 \text{ (w), 870 \text{ (m), 780 \text{ (w), 739 \text{ (m), 684 \text{ (m), 611 \text{ (w), 556 \text{ (w).} \]

\[ \text{UV-vis (CH}_3\text{OH) } \lambda_{max, \text{ nm (} \varepsilon, \text{ L mol}^{-1} \text{ cm}^{-1}): 441 \text{ (16,900), 468 (13,200).} \]

\[ \text{ESI-MS } m/z: (M + Na^+), \text{ calcd for } C_{26}H_{27}N_6NaO_3Rh, 597.1097; \text{ found, 597.1097 (45%, } z = +1). \]
\[ \text{(M – CH=CHOCH}_3), \text{ calcd for } C_{23}H_{22}N_6O_2Rh, 517.0854; \text{ found, 517.0864 (100%, } z = +1). \]

\[ \text{Anal. Calcd for } C_{26}H_{27}N_6O_3Rh \cdot H_2O: \text{ C, 52.71; H, 4.93; N, 14.19. Found: C, 52.35; H, 4.97; N, 14.00.} \]
Chapter 6: Conclusions and Future Work

The central goal of the research described in this thesis was to develop new macrocyclic ligands that contained both pyridinium amides and carboxamides as the primary donor groups, and to explore the structural, spectroscopic, and catalytic properties of the metal complexes of these ligands.

The target macrocycle, $\text{H}_2\text{L}_m$, was successfully synthesised and purified using the procedure described in Section 2.5.9. UV-visible absorption and NMR spectroscopies indicated that solvent polarity had a strong effect on the structure that $\text{H}_2\text{L}_m$ adopts in solution, and suggested that the zwitterionic resonance form becomes increasingly favoured over the imine resonance form with increasing solvent polarity (Chapter 2).

A number of transition metal complexes of the deprotonated $\text{H}_2\text{L}_m$ ligand were synthesised and purified, and their spectroscopic properties were studied (Chapter 3). These included $\text{Fe}^{\text{III}}(\text{L}_m)\text{Cl}$, $\text{Co}^{\text{III}}(\text{L}_m)\text{Br}$, $\text{Ni}^{\text{II}}(\text{L}_m)$, $\text{Cu}^{\text{III}}(\text{L}_m)(\text{OH})(\text{H}_2\text{O})$, $[\text{Ru}^{\text{III}}(\text{L}_m)]_2[\text{BF}_4]_2$, $\text{Na}[[\text{Rh}^{\text{II}}(\text{L}_m)]_2\text{Cl}]$, and $\text{Pd}^{\text{II}}(\text{L}_m)$. A manganese complex of the $\text{L}_m^{2-}$ ligand was also synthesised but was not successfully purified. Attempts to purify this complex always seemed to result in the formation of a mixture of manganese(II) and manganese(III) complexes, even after attempts were made to deliberately oxidise or reduce the crude product. A satisfactory explanation for this behaviour has not yet been found. $\text{Ni}^{\text{II}}(\text{L}_m)$, $[\text{Ru}^{\text{III}}(\text{L}_m)]_2[\text{BF}_4]_2$, $\text{Na}[[\text{Rh}^{\text{II}}(\text{L}_m)]_2\text{Cl}]$, and $\text{Pd}^{\text{II}}(\text{L}_m)$ were all diamagnetic, whereas manganese-$\text{L}_m$, $\text{Fe}^{\text{III}}(\text{L}_m)\text{Cl}$, $\text{Co}^{\text{III}}(\text{L}_m)\text{Br}$, and $\text{Cu}^{\text{III}}(\text{L}_m)(\text{OH})(\text{H}_2\text{O})$ were paramagnetic. With the exception of manganese-$\text{L}_m$ and $\text{Cu}^{\text{III}}(\text{L}_m)(\text{OH})(\text{H}_2\text{O})$, all of these complexes were fully characterised.

Spectroscopic studies described in Chapter 3 strongly suggested that $[\text{Ru}^{\text{III}}(\text{L}_m)]_2[\text{BF}_4]_2$ and $\text{Na}[[\text{Rh}^{\text{II}}(\text{L}_m)]_2\text{Cl}]$ are dimeric, with direct unsupported metal-metal bonds. Macrocyclic complexes with direct unsupported ruthenium-ruthenium or rhodium-rhodium bonds are rare in the literature. The asymmetry of the $\text{L}_m^{2-}$ ligands of $\text{Na}[[\text{Rh}^{\text{II}}(\text{L}_m)]_2\text{Cl}]$ observed in the $^1\text{H}$ NMR spectrum was unexpected, considering that $[\text{Ru}^{\text{III}}(\text{L}_m)]_2[\text{BF}_4]_2$ is symmetric and reported rhodium(II) dimers are usually symmetric, as determined by NMR spectroscopy. It was postulated that this asymmetry is due to the presence of only one axial ligand in
Na[[Rh^{II}(L_m)_2]Cl], which, along with buckling of the L_m^2- ligands, holds the two L_m^2- ligands in a locked asymmetric orientation in such a way that the molecule contains no effective horizontal or vertical mirror planes (see Figure 3.19). Despite many attempts, none of the metal-L_m complexes described in Chapter 3 crystallised to produce crystals suitable for X-ray structural studies. Attempts to grow suitable crystals of these complexes are ongoing.

Fe^{III}(L_m)Cl and Co^{III}(L_m)Br were tested as catalysts for the oxidation of dye substrates by hydrogen peroxide (Chapter 4). Despite their very poor performance as catalysts for the oxidation of Orange II dye with hydrogen peroxide, Fe^{III}(L_m)Cl and Co^{III}(L_m)Br were robust and were good catalysts for the disproportionation of hydrogen peroxide to water and dioxygen. These complexes may be useful in industrial applications where hydrogen peroxide removal is desired. This is because the Fe^{III}(L_m)Cl and Co^{III}(L_m)Br complexes would be cheaper alternatives to the catalase enzymes that are often used in these applications. The catalysis of hydrogen peroxide disproportionation by these complexes became more dominant over the catalysis of dye oxidation at less basic pH values (around pH 7.5) for the Co^{III}(L_m)Br complex and at more basic pH values (around pH 10.8) for the Fe^{III}(L_m)Cl complex.

Kinetic data was not used to determine TONs or the mechanism of the very weak catalytic dye oxidation observed for the complexes Fe^{III}(L_m)Cl and Co^{III}(L_m)Br described in Chapter 4, because the rate of dye oxidation by unactivated hydrogen peroxide was close to the rate of dye oxidation in the presence of Fe^{III}(L_m)Cl or Co^{III}(L_m)Br. Therefore, both processes would play a significant role in the analysis of the kinetic data. The much more rapid catalytic disproportionation of hydrogen peroxide would also interfere with the analysis of the kinetic data.

Future work that will be conducted to attempt to increase the catalytic dye oxidation in these systems include investigating reactions at pH values outside of the range used in these studies (pH 7.5 to 10.8); designing and testing new pyridinium amide macrocyclic ligands that will enable structure/activity relationships to be determined for this class of ligands; investigating the catalysis of dye oxidation by the manganese-L_m complex, once a pure sample of this complex is obtained; using dye substrates such as Pinacyanol chloride that are faster to oxidise, so that the rate of dye oxidation is larger than the rate of hydrogen peroxide disproportionation; and
using organic peroxides (for example, tert-butyl hydroperoxide), which are unlikely to undergo disproportionation.

The ability of Na[[Rh\text{II}(L_m)]_2Cl] and its dimeric and monomeric derivatives to catalyse the activation of small molecules are reported in Chapter 5. Although none of the rhodium-L\text{m} complexes were shown to catalyse reactions with dihydrogen, carbon monoxide, acetylene, alkyl halides, or triphenylphosphine to produce organic products, a number of interesting organometallic and coordination complexes were synthesised. These included: Na[[Rh\text{II}(L_m)]_2(4-picoline)], [Rh\text{III}(L_m)(PPh_3)][PF_6], Na[Rh\text{I}(L_m)], Rh\text{III}(L_m)Me, Rh\text{III}(L_m)Et, Rh\text{III}(L_m)Bn, Rh\text{III}(L_m)(C(=O)OR) and Rh\text{III}(L_m)(CH=CHOR). For the latter two complexes, the OR group depended on the alcohol solvent that was used. Many of these complexes were purified and characterised. However, crystals suitable for X-ray structural studies were not successfully obtained and attempts to grow suitable crystals of these complexes are ongoing. Further reactions will be conducted in the near future in attempts to make these systems catalytic. Some of these key future reactions were discussed in Section 5.3, such as adding electrophiles (for example, alkyl halides or acids) to the reactions in order to cleave the organometallic ligand and so produce organic products; increasing the reaction temperature; and irradiating the reactions.

Reactivity studies were conducted to determine the reaction pathway involved in the synthesis of [Rh\text{III}(L_m)(PPh_3)]^+, Rh\text{III}(L_m)(C(=O)OR), and Rh\text{III}(L_m)(CH=CHOR) from the reaction of Na[[Rh\text{II}(L_m)]_2Cl] with triphenylphosphine, carbon monoxide, or acetylene, respectively, in alcohol solvents in air (Chapter 5). These studies were consistent with reaction pathways where the rhodium-rhodium bond of Na[[Rh\text{II}(L_m)]_2Cl] breaks heterolytically. The postulated reaction pathways began with coordination of the reagent (triphenylphosphine, carbon monoxide, or acetylene) to Na[[Rh\text{II}(L_m)]_2Cl], which weakens the rhodium-rhodium bond, causing it to break heterolytically. A rhodium(I) and a rhodium(III) complex are formed in this process, and aerial oxidation of the rhodium(I) complex then formed more rhodium(III) complex. Therefore, only one product was synthesised in these reactions, even though the rhodium-rhodium bond of Na[[Rh\text{II}(L_m)]_2Cl] breaks heterolytically to form rhodium(I) and rhodium(III) complexes. For Rh\text{III}(L_m)(C(=O)OR) and Rh\text{III}(L_m)(CH=CHOR), the final step of the reaction pathway involves nucleophilic attack by the alcohol solvent at the coordinated rhodium(III)-carbonyl or rhodium(III)-acetylene complexes, respectively. Based on similar reactions reported in the literature,\cite{24,225} it was proposed that the high polarity of the alcohol solvents used in these
reactions promote ionic reaction pathways and therefore favour heterolytic cleavage of Na[[Rh^{II}(L_m)]_2Cl] over homolytic reaction pathways.

Therefore, in summary, a number of metal complexes of a new macrocyclic ligand (L_m) were synthesised and characterised, and the ability of some of these complexes to catalyse the oxidation of dye substrates and the activation of small molecules were investigated. Although these studies suggested that the complexes investigated were poor oxidation catalysts and did not catalyse the activation of small molecules, they did show promise as catalysts for the disproportionation of hydrogen peroxide, and could activate carbon monoxide and acetylene stoichiometrically. A significantly amount of future work will focus on improving the behaviour of these complexes as catalysts for these reactions.
Appendix A: X-ray crystal structure of 3,3’-(oxalylbis(azanediyl))bis(2-chloro-1-methylpyridin-1-ium) triflate (B)

As described in further detail in Section 2.5.3, X-ray quality crystals of 3,3’-(oxalylbis(azanediyl))bis(2-chloro-1-methylpyridin-1-ium) triflate were grown by slow vapour diffusion of chloroform into a saturated solution of this compound in ethanol. This section provides details about this crystal structure, including details about crystal parameters and data collection details (Table A-1), a table of selected bond lengths (Table A-2 and Figure A-1), and a table of selected bond angles (Table A-3 and Figure A-1). Section 2.5.1 provides more detail about the X-ray crystallography instrumentation.

Figure A-1: Numbering scheme for the atoms in the X-ray crystal structure of 3,3’-(oxalylbis(azanediyl))bis(2-chloro-1-methylpyridin-1-ium) triflate (B). The two triflate counteranions have been omitted for clarity.
Table A-1: Crystal parameters and data collection details for the X-ray crystal structure of 3,3’-(oxalylbis(azanediyl))bis(2-chloro-1-methylpyridin-1-ium) triflate

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Title</td>
<td>bdh194a_0m</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C₈H₇ClF₃N₂O₄S</td>
</tr>
<tr>
<td>Formula weight</td>
<td>319.67 g mol⁻¹</td>
</tr>
<tr>
<td>Temperature</td>
<td>99</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Monoclinic, P2(1)/n</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 8.339(5) Å, α = 90.000(5)°</td>
</tr>
<tr>
<td></td>
<td>b = 11.720(5) Å, β = 101.743(5)°</td>
</tr>
<tr>
<td></td>
<td>c = 11.925(5) Å, γ = 90.000(5)°</td>
</tr>
<tr>
<td>Volume</td>
<td>1141.1(10) Å³</td>
</tr>
<tr>
<td>Z, calculated density</td>
<td>4, 1.861 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.571 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>644</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.44 x 0.14 x 0.14 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.46° to 27.98°</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-10 ≤ h ≤ 10, -15 ≤ k ≤ 15, -15 ≤ l ≤ 14</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>20541 / 2714 [R(int) = 0.0306]</td>
</tr>
<tr>
<td>Completeness to theta = 27.98</td>
<td>99.0%</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>2714 / 0 / 173</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.060</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0252, wR2 = 0.0672</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0272, wR2 = 0.0686</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.459 and -0.404 e.A⁻³</td>
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</table>
Table A-2: Selected bond lengths obtained from the X-ray crystal structure of 3,3’-(oxalylbis(azanediyl))bis(2-chloro-1-methylpyridin-1-ium) triflate

<table>
<thead>
<tr>
<th>Bond $^a$</th>
<th>Bond length (Å) $^b$</th>
<th>Bond $^a$</th>
<th>Bond length (Å) $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)-O(1)</td>
<td>1.2154(16)</td>
<td>C(6)-H(6A)</td>
<td>0.9600</td>
</tr>
<tr>
<td>C(1)-N(1)</td>
<td>1.3617(16)</td>
<td>C(6)-H(6B)</td>
<td>0.9600</td>
</tr>
<tr>
<td>C(1)-C(1’)</td>
<td>1.538(2)</td>
<td>C(6)-H(6C)</td>
<td>0.9600</td>
</tr>
<tr>
<td>C(2)-C(3)</td>
<td>1.3912(18)</td>
<td>C(7)-N(2)</td>
<td>1.3526(17)</td>
</tr>
<tr>
<td>C(2)-C(7)</td>
<td>1.3946(17)</td>
<td>C(7)-Cl(1)</td>
<td>1.6978(13)</td>
</tr>
<tr>
<td>C(2)-N(1)</td>
<td>1.4070(17)</td>
<td>C(8)-F(3)</td>
<td>1.3377(15)</td>
</tr>
<tr>
<td>C(3)-C(4)</td>
<td>1.3855(19)</td>
<td>C(8)-F(2)</td>
<td>1.3400(14)</td>
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<tr>
<td>C(3)-H(3)</td>
<td>0.9300</td>
<td>C(8)-F(1)</td>
<td>1.3421(15)</td>
</tr>
<tr>
<td>C(4)-C(5)</td>
<td>1.3742(19)</td>
<td>C(8)-S</td>
<td>1.8261(14)</td>
</tr>
<tr>
<td>C(4)-H(4)</td>
<td>0.9300</td>
<td>N(1)-H(1)</td>
<td>0.8600</td>
</tr>
<tr>
<td>C(5)-N(2)</td>
<td>1.3515(17)</td>
<td>O(2)-S</td>
<td>1.4418(11)</td>
</tr>
<tr>
<td>C(5)-H(5)</td>
<td>0.9300</td>
<td>O(3)-S</td>
<td>1.4440(11)</td>
</tr>
<tr>
<td>C(6)-N(2)</td>
<td>1.4905(16)</td>
<td>O(4)-S</td>
<td>1.4482(11)</td>
</tr>
</tbody>
</table>

$^a$ See Figure A-1 for numbering scheme. The hydrogen atoms have been given the same number as the carbon or nitrogen atom they are directly attached to. The atoms C(8), F(1-3), O(2-4) and S are from the triflate counteranions.

$^b$ The values in brackets indicate the calculated errors for last decimal place(s) of the bond length values.
Table A-3: Selected bond angles obtained from the X-ray crystal structure of 3,3’-(oxalylbis(azanediyl))bis(2-chloro-1-methylpyridin-1-ium) triflate

<table>
<thead>
<tr>
<th>Bond angle $^a$</th>
<th>Angle (degrees) $^b$</th>
<th>Bond angle $^a$</th>
<th>Angle (degrees) $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1)-C(1)-N(1)</td>
<td>126.27(12)</td>
<td>N(2)-C(7)-C(2)</td>
<td>121.18(11)</td>
</tr>
<tr>
<td>O(1)-C(1)-C(1’)</td>
<td>121.93(14)</td>
<td>N(2)-C(7)-Cl(1)</td>
<td>117.86(9)</td>
</tr>
<tr>
<td>N(1)-C(1)-C(1’)</td>
<td>111.79(13)</td>
<td>C(2)-C(7)-Cl(1)</td>
<td>120.95(10)</td>
</tr>
<tr>
<td>C(3)-C(2)-C(7)</td>
<td>118.60(12)</td>
<td>F(3)-C(8)-F(2)</td>
<td>107.29(10)</td>
</tr>
<tr>
<td>C(3)-C(2)-N(1)</td>
<td>121.74(11)</td>
<td>F(3)-C(8)-F(1)</td>
<td>107.63(11)</td>
</tr>
<tr>
<td>C(7)-C(2)-N(1)</td>
<td>119.64(11)</td>
<td>F(2)-C(8)-F(1)</td>
<td>106.89(10)</td>
</tr>
<tr>
<td>C(4)-C(3)-C(2)</td>
<td>119.01(12)</td>
<td>F(3)-C(8)-S</td>
<td>111.62(9)</td>
</tr>
<tr>
<td>C(4)-C(3)-H(3)</td>
<td>120.5</td>
<td>F(2)-C(8)-S</td>
<td>111.78(9)</td>
</tr>
<tr>
<td>C(2)-C(3)-H(3)</td>
<td>120.5</td>
<td>F(1)-C(8)-S</td>
<td>111.38(9)</td>
</tr>
<tr>
<td>C(5)-C(4)-C(3)</td>
<td>120.31(12)</td>
<td>C(1)-N(1)-C(2)</td>
<td>122.69(11)</td>
</tr>
<tr>
<td>C(5)-C(4)-H(4)</td>
<td>119.8</td>
<td>C(1)-N(1)-H(1)</td>
<td>118.7</td>
</tr>
<tr>
<td>C(3)-C(4)-H(4)</td>
<td>119.8</td>
<td>C(2)-N(1)-H(1)</td>
<td>118.7</td>
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<tr>
<td>N(2)-C(5)-C(4)</td>
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<td>C(5)-N(2)-C(7)</td>
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<tr>
<td>C(2)-C(5)-H(5)</td>
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<td>C(5)-N(2)-C(6)</td>
<td>118.81(11)</td>
</tr>
<tr>
<td>C(4)-C(5)-H(5)</td>
<td>119.7</td>
<td>C(7)-N(2)-C(6)</td>
<td>121.04(10)</td>
</tr>
<tr>
<td>N(2)-C(6)-H(6A)</td>
<td>109.5</td>
<td>O(2)-S-O(3)</td>
<td>114.96(7)</td>
</tr>
<tr>
<td>N(2)-C(6)-H(6B)</td>
<td>109.5</td>
<td>O(2)-S-O(4)</td>
<td>114.75(6)</td>
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<tr>
<td>H(6A)-C(6)-H(6B)</td>
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<td>O(3)-S-O(4)</td>
<td>115.12(7)</td>
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<tr>
<td>N(2)-C(6)-H(6C)</td>
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<td>O(2)-S-C(8)</td>
<td>103.15(7)</td>
</tr>
<tr>
<td>H(6A)-C(6)-H(6C)</td>
<td>109.5</td>
<td>O(3)-S-C(8)</td>
<td>103.47(6)</td>
</tr>
<tr>
<td>H(6B)-C(6)-H(6C)</td>
<td>109.5</td>
<td>O(4)-S-C(8)</td>
<td>102.98(7)</td>
</tr>
</tbody>
</table>

$^a$ See Figure A-1 for numbering scheme. The hydrogen atoms have been given the same number as the carbon or nitrogen atom they are directly attached to. The atoms C(8), F(1-3), O(2-4) and S are from the triflate counteranions.

$^b$ The values in brackets indicate the calculated errors for last decimal place(s) of the bond angle values.
References


