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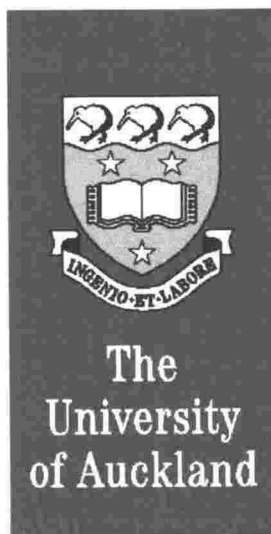
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**Studies of Osmium and Ruthenium Complexes with Ligands
Featuring Group 14 and 15 Donor Atoms**



A thesis presented to the University of Auckland in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry

FOR EXAMINATION PURPOSES ONLY

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ABSTRACT

This thesis examines the preparation and chemistry of osmium and ruthenium complexes with ligands featuring the group 14 donor atoms carbon and silicon, and the group 15 donor atom phosphorus.

Aryl, alkenyl, and alkynyl complexes of osmium and ruthenium, prepared via mercury reagents, are discussed in Chapter One. 5-Coordinate 2-halophenyl complexes $M(C_6H_4X-2)Cl(CE)(PPh_3)_2$ ($M = Os$; $X = Cl, Br$; $E = O, S$; $M = Os$; $X = I, E = O$; $M = Ru$; $X = Cl, Br, E = O$) were synthesised by reaction of organomercury reagents $Hg(C_6H_4X-2)_2$ ($X = Cl, I, Br$) with $MHCl(CO)(PPh_3)_3$ ($M = Os, Ru$). $Os(C_6H_4X-2)Cl(CO)(PPh_3)_2$ ($M = Os$; $X = Cl, I, Br$) were characterised structurally and the interaction between X and M examined. Attempted benzyne syntheses using these complexes were not successful.

6-Coordinate complexes $M(C_6H_4X-2)Cl(CO)(CE)(PPh_3)_2$ ($M = Os, X = Cl, E = O, S$; $Br, E = O, S$; $M = Os, E = O, X = I$; $M = Ru, E = O, X = Cl, Br$) were prepared by the addition of carbon monoxide to the corresponding 5-coordinate precursors. Approaches towards reduction of these complexes are discussed.

The structure of $Os(C_6H_4Cl-2)Cl(CS)(CO)(PPh_3)_2$ revealed that the thiocarbonyl and the aryl halide ligands were *cis* and therefore in an ideal geometry to rearrange and form a substituted thioacyl ligand. Indeed, on heating $Os(C_6H_4X-2)Cl(CS)(CO)(PPh_3)_2$ ($X = Cl, Br$) the corresponding thioacyl complexes $Os(\eta^2-CS\{C_6H_4X-2\})Cl(CO)(PPh_3)_2$ ($X = Cl, Br$) were formed.

The decreased electron density in the halo aryl rings of these thioacyl complexes, combined with the fact that the halide substituents were no longer bonded to the metal, enabled facile lithiation of the aryl rings, even at low temperature. Quenching the appropriate lithiated intermediate with Bu_3SnCl gave $Os(\eta^2-CS\{C_6H_4SnBu_3-2\})Cl(CO)(PPh_3)_2$.

These results suggested that $M(C_6H_4\{CH_2X\}-2)Cl(CO)(PPh_3)_2$ ($M = Os, Ru$) were worthwhile target complexes for lithiation studies. To this end, $Hg(C_6H_4\{CH_2OH\}-2)Cl$ was prepared but attempts to convert the alcohol into a tosylate (for subsequent reaction with LiX) were unsuccessful and so this chemistry was not pursued further.

$\text{Hg}(\text{C}_6\text{H}_4\{\text{CH}_2\text{OH}\}-2)\text{Cl}$ transferred the benzylic alcohol groups to osmium and ruthenium, albeit in low yields. Oxidation of $\text{Hg}(\text{C}_6\text{H}_4\{\text{CH}_2\text{OH}\}-2)\text{Cl}$ with PCC provided the benzaldehyde-containing mercury complex $\overline{\text{Hg}(\text{C}_6\text{H}_4\{\overline{\text{CHO}}\}-2)\text{Cl}}$, symmetrization of which gave $\text{Hg}(\text{C}_6\text{H}_4\{\text{CHO}\}-2)_2$. The latter compound was used to prepare aldehyde complexes of osmium and ruthenium, as well as mercury(II) benzaldoxime and benzaldimines. The aldehyde oxygen atoms in the osmium and ruthenium complexes were bound to the metals and were unaffected by amines, and by attempts to displace them from the metals. The addition of dimethyldithiocarbamate to $\overline{\text{Ru}(\text{C}_6\text{H}_4\{\overline{\text{CHO}}\}-2)\text{Cl}(\text{CO})(\text{PPh}_3)_2}$ displaced a triphenylphosphine ligand and $\text{Ru}(\text{C}_6\text{H}_4\{\text{CHO}\}-2)(\text{CO})((\text{CH}_3)_2\text{NCS}_2)(\text{PPh}_3)$ was formed.

Transfer of the benzaldoxime ligand, and various benzaldimine ligands [$\text{C}_6\text{H}_4\{\text{C}[\text{H}]=\text{NR}\}$ R = Me, $\text{CH}_2\text{CH}_2\text{NEt}_2$, $\text{CH}_2\text{CH}_2\text{NMe}_2$], to osmium or ruthenium gave $\overline{\text{M}(\text{C}_6\text{H}_4\{\text{C}[\text{H}]=\overline{\text{NR}}\}-2)\text{Cl}(\text{CO})(\text{PPh}_3)_2}$ (M = Ru, R = OH; M = Os, Ru; R = Me, $\text{CH}_2\text{CH}_2\text{NEt}_2$; M = Ru, R = $\text{CH}_2\text{CH}_2\text{NMe}_2$). The derived cationic complexes $\overline{\text{Ru}(\text{C}_6\text{H}_4\{\text{C}[\text{H}]=\overline{\text{NCH}_2\text{CH}_2\text{NHR}_2}\}-2)\text{Cl}(\text{CO})(\text{PPh}_3)_2]\text{BF}_4$ (R = Me, Et) were prepared by protonation of the benzaldimine complexes with HBF_4 and $[\overline{\text{Ru}(\text{C}_6\text{H}_4\{\text{C}[\text{H}]=\overline{\text{NCH}_2\text{CH}_2\text{NR}_2}\}-2)(\text{CO})(\text{PPh}_3)_2]\text{BF}_4$ (R = Me, Et) were prepared by addition of AgBF_4 . Bromination of $\overline{\text{Ru}(\text{C}_6\text{H}_4\{\text{C}[\text{H}]=\overline{\text{NMe}}\}-2)\text{Cl}(\text{CO})(\text{PPh}_3)_2}$ gave $\overline{\text{Ru}(\text{C}_6\text{H}_3\{\text{C}[\text{H}]=\overline{\text{NMe}}\}-2,\text{Br}-4)\text{Cl}(\text{CO})(\text{PPh}_3)_2}$ which was lithiated at low temperature. The aryllithium was quenched with Bu_3SnCl to give $\overline{\text{Ru}(\text{C}_6\text{H}_3\{\text{C}[\text{H}]=\overline{\text{NMe}}\}-2,\text{SnBu}_3-4)\text{Cl}(\text{CO})(\text{PPh}_3)_2}$.

The reaction of alkynylmercury reagents with osmium and ruthenium complexes are discussed in the following sections. Treatment of $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ with $\text{Hg}(\text{C}\equiv\text{CPh})_2$ has been reported previously, the result being formation of an α -phenylethynyl-*trans*- β -styryl ligand. However, the corresponding reaction with $\text{OsHCl}(\text{CO})(\text{PPh}_3)_3$ resulted in catalysed coupling of the alkyne. This reaction was re-examined and the 6-coordinate α -phenylethynyl-*trans*- β -styryl osmium complex was prepared by direct reaction of the 5-coordinate complex with acetate ion. A dicarbonyl complex containing the α -phenylethynyl-*trans*- β -styryl ligand, $\text{Os}(\text{C}\{\text{C}\equiv\text{CPh}\}=\text{CHPh})\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$, was prepared by the addition of carbon monoxide in the presence of LiCl to the acetate complex. Thiocarbonyl complexes

containing an α -phenylethynyl-*trans*- β -styryl ligand were prepared. Addition of carbon monoxide to solutions containing these complexes gave the thioacyl analogues $M(\eta^2\text{-CS}\{\text{C}[\text{C}\equiv\text{CPh}]=\text{CHPh}\})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ ($M = \text{Os}, \text{Ru}$).

The remaining sections in Chapter One examine the reactions of mercury(II) reagents with the osmium(0) complexes $\text{Os}(\text{CO})_2(\text{PPh}_3)_3$ and $\text{OsCl}(\text{NO})(\text{PPh}_3)_3$. Oxidative addition of the mercury-carbon bond of HgR_2 ($R = \text{C}_6\text{H}_4\text{CH}_3$ -4, $\text{C}\equiv\text{CPh}$, *trans*- $\text{CH}=\text{CHPh}$) to $\text{Os}(\text{CO})_2(\text{PPh}_3)_3$ gave $\text{OsR}(\text{HgR})(\text{CO})_2(\text{PPh}_3)_2$. Reaction of the acetylide or styryl complexes with iodine resulted in cleavage of the osmium-mercury bond and yielded either $\text{Os}(\text{C}\equiv\text{CPh})\text{I}(\text{CO})_2(\text{PPh}_3)_2$ or $\text{Os}(\textit{trans}\text{-CH}=\text{CHPh})\text{I}(\text{CO})_2(\text{PPh}_3)_2$. Similar complexes were not accessible from reaction of the osmium(II) complex $\text{OsHCl}(\text{CO})(\text{PPh}_3)_3$ with the appropriate mercury reagent.

Whereas the mercury reagents reacted with $\text{Os}(\text{CO})_2(\text{PPh}_3)_3$ to give the simple oxidative addition products, the corresponding reactions of $\text{OsCl}(\text{NO})(\text{PPh}_3)_3$ with HgR_2 did not always give the analogous products $\text{OsR}(\text{HgR})\text{Cl}(\text{NO})(\text{PPh}_3)_2$. Addition of $\text{Hg}(\text{C}_6\text{H}_4\text{CH}_3$ -4)₂ to $\text{OsCl}(\text{NO})(\text{PPh}_3)_3$ gave a mixture of the bis(*p*-tolyl) complex $\text{Os}(\text{C}_6\text{H}_4\text{CH}_3$ -4)₂ $\text{Cl}(\text{NO})(\text{PPh}_3)_2$ and the mono(*p*-tolyl) complex $\text{Os}(\text{C}_6\text{H}_4\text{CH}_3$ -4)₂ $\text{Cl}_2(\text{NO})(\text{PPh}_3)_2$. The structure of the bis(*p*-tolyl) complex revealed that the *p*-tolyl ligands were *trans* and the metal-carbon(aryl) bond lengths were extremely long. Addition of pyridine to the bis(*p*-tolyl) complex gave $\text{Os}(\text{C}_6\text{H}_4\text{CH}_3$ -4)₂($\text{C}_5\text{H}_5\text{N}$) $\text{Cl}(\text{NO})(\text{PPh}_3)$, which contained two *cis* *p*-tolyl ligands. The reactions of $\text{Hg}(\text{C}_6\text{H}_4\text{Cl}$ -2)₂ and $\text{Hg}(\text{C}\equiv\text{CPh})\text{Ph}$ with $\text{OsCl}(\text{NO})(\text{PPh}_3)_3$ gave complexes containing a single organic ligand. In contrast, treatment of $\text{OsCl}(\text{NO})(\text{PPh}_3)_3$ with either $\text{Hg}(\{\text{C}_4\text{H}_4\text{S}-2\})_2$ or $\text{Hg}(\{\text{C}_4\text{H}_4\text{SMe}-5\}-2)_2$ gave the dithienyl complexes $\text{OsR}_2\text{Cl}(\text{NO})(\text{PPh}_3)_2$ [$R = (\text{C}_4\text{H}_4\text{S})-2, (\{\text{C}_4\text{H}_4\text{SMe}-5\})-2$]. Furthermore, the reaction of $\text{Hg}(\text{CF}_3)_2$ with $\text{OsCl}(\text{NO})(\text{PPh}_3)_3$ gave $\text{Os}(\text{CF}_3)(\text{Hg}\{\text{CF}_3\})\text{Cl}(\text{NO})(\text{PPh}_3)_2$.

Treatment of $\text{OsCl}(\text{NO})(\text{PPh}_3)_3$ with $\text{Hg}(\textit{trans}\text{-CH}=\text{CHPh})_2$ gave $\text{Os}(\textit{trans}\text{-CH}=\text{CHPh})\text{Cl}_2(\text{NO})(\text{PPh}_3)_2$ and an osmaidene complex, $\text{Os}(\overline{\text{C}_6\text{H}_4\text{CH}=\text{CH}})\text{H}(\text{NO})(\text{PPh}_3)_2$, which in turn gave $\text{Os}(\overline{\text{C}_6\text{H}_4\text{CH}=\text{CH}})\text{Cl}(\text{NO})(\text{PPh}_3)_2$ on treatment with HCl.

Chapter Two examines osmabenzene chemistry. Spectroscopic data were collected for the known complexes $\text{Os}(\eta^2\text{-C[S]CH=CHCH=CH})(\text{CO})(\text{PPh}_3)_2$, and $\text{Os}(\text{C[SH]CH=CHCH=CH})(\text{cis-Cl})(\text{CO})(\text{PPh}_3)_2$. Oxidation of the osmabenzene thiol to a sulfinic acid was attempted. Methylation of the parent complex, $\text{Os}(\eta^2\text{-C[S]CH=CHCH=CH})(\text{CO})(\text{PPh}_3)_2$, gave the product of kinetic control as $\text{Os}(\text{C[SMe]CH=CHCH=CH})(\text{cis-I})(\text{CO})(\text{PPh}_3)_2$, reported previously, which rearranged on heating to give the *trans* isomer, $\text{Os}(\text{C[SMe]CH=CHCH=CH})(\text{trans-I})(\text{CO})(\text{PPh}_3)_2$. Approaches to auration of the sulfur in $\text{Os}(\eta^2\text{-C[S]CH=CHCH=CH})(\text{CO})(\text{PPh}_3)_2$ are described.

Although the metallabenzenes reported previously have physical properties comparable with those of benzene itself, little evidence has been reported to suggest that the chemical reactivity of metallabenzenes is similar to that of benzene. The research described in this chapter provides the first example of a metallabenzene complex that undergoes aromatic electrophilic substitution. Thus, the metallabenzene complex $\text{Os}(\text{C[SMe]CH=CHCH=CH})(\text{cis-I})(\text{CO})(\text{PPh}_3)_2$ was brominated, chlorinated, and even iodinated. Crystal structure determinations and NMR studies showed that C5, which was activated by the thioether functionality, was the preferred site of electrophile attack. Even more significantly, $\text{Os}(\text{C[SMe]CH=CHCH=CH})(\text{cis-I})(\text{CO})(\text{PPh}_3)_2$ was nitrated with either $\text{Cu}(\text{NO}_3)_2/\text{acetic anhydride}$, or with the more potent reagent $\text{NO}_2\text{CF}_3\text{SO}_3.\text{CF}_3\text{SO}_3\text{H}$. The site of nitration was identical with that of halogenation, namely, C5.

Previous syntheses of metallabenzenes had reported the use of the simplest alkyne, ethyne. This chapter describes the first metallabenzene complex prepared from propyne, giving the metallabenzene $\text{Os}(\eta^2\text{-C[S]C\{CH}_3\}=\text{CHCH}=\text{C\{CH}_3\}) (\text{CO})(\text{PPh}_3)_2$ and the oxidative addition product $\text{Os}(\text{C}\equiv\text{CCH}_3)\text{H}(\text{CO})(\text{CS})(\text{PPh}_3)_2$.

Ten of the metallabenzene complexes were characterised structurally and the significance of the carbon-carbon bond lengths in the metallacyclic rings are discussed.

The complete characterisation of these complexes by NMR spectroscopy revealed that the ring protons in the metallabenzene complexes, excepting H6, were at chemical shifts similar to those expected for normal aromatic carbons.

Chapter Three examines the coordination of the strongly π -accepting tris(*N*-pyrrolyl)phosphine ligand to osmium. Two tris(*N*-pyrrolyl)phosphine complexes of Os(II), $\text{OsHCl}(\text{CO})(\text{PPh}_3)_2(\text{P}\{\text{NC}_4\text{H}_4\}_3)$ and $\text{OsH}(\text{C}_6\text{H}_4\text{CH}_3\text{-4})(\text{CO})(\text{PPh}_3)_2(\text{P}\{\text{NC}_4\text{H}_4\}_3)$, were prepared. Both of these showed significantly higher infrared carbonyl stretching absorptions than the analogous triphenylphosphine complexes, reflecting the π -acceptor nature of the tris(*N*-pyrrolyl)phosphine ligand.

The osmium(0) complexes $\text{Os}(\text{CE})(\text{CO})(\text{PPh}_3)_2\text{P}(\text{NC}_4\text{H}_4)_3$ (E = O, S) were prepared and the carbonyl complex was characterised structurally. The osmium-phosphorus(pyrrrolyl) bond length of this complex was relatively short. The tris(*N*-pyrrolyl)phosphine ligand was in the equatorial plane as were the two carbonyl ligands.

Chapter Four examines silyl and siloxane complexes of osmium and ruthenium. Although triethoxysilyl complexes of ruthenium have been prepared previously through ethanolysis of the coordinated SiCl_3 group, the osmium analogues could not be prepared this way. It was found that $\text{Os}(\text{Si}\{\text{OEt}\}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ could be prepared successfully by direct treatment of $\text{Os}(\text{Ph})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ with triethoxysilane. Addition of carbon monoxide to the 5-coordinate triethoxysilyl complex afforded the dicarbonyl complex. The triethoxysilyl nitrosyl complex, $\text{OsH}(\text{Si}\{\text{OEt}\}_3)\text{Cl}(\text{NO})(\text{PPh}_3)_2$, was prepared by oxidative addition of triethoxysilane to $\text{OsCl}(\text{NO})(\text{PPh}_3)_3$, and the siloxane nitrosyl complex, $\text{Os}(\text{O}[\text{Si}\{\text{OEt}\}_3])\text{Cl}_2(\text{NO})(\text{PPh}_3)_2$ was also characterised fully.

Prior to this work only a single silatranyl complex was known. This chapter reports fifteen new silatranyl complexes and examines the unique properties conferred upon the silatrane by coordination to the metal. The silatranyl-containing complexes $\text{OsH}(\overline{\text{Si}}\{\overline{\text{OCH}_2\text{CH}_2}\}_3\overline{\text{N}})\text{Cl}(\text{NO})(\text{PPh}_3)_2$ and $\text{OsH}(\overline{\text{Si}}\{\overline{\text{OCH}_2\text{CH}_2}\}_3\overline{\text{N}})(\text{CO})_2(\text{PPh}_3)_2$ were formed by oxidative addition of silatrane to the appropriate osmium(0) complex. Neither was suitable for further research because the chloro nitrosyl complex ejected silatrane in the presence of oxygen, and the dicarbonyl complex was isolated as a mixture of three isomers. In contrast, the unsaturated complexes $\text{M}(\overline{\text{Si}}\{\overline{\text{OCH}_2\text{CH}_2}\}_3\overline{\text{N}})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ (M = Os, Ru) were excellent materials for further study. The crystal structures of both of these complexes reveal typical metal-silyl distances with atypical silatranyl $\text{N}\rightarrow\text{Si}$ bond lengths. In both cases the $\text{N}\rightarrow\text{Si}$ bond length is elongated, the nitrogen is planar, and the cage is best described as

quasi-silatranyl. The unsaturated nature of the metal in $\text{Os}(\overline{\text{Si}}\{\overline{\text{OCH}_2\overline{\text{CH}_2}\overline{\text{CH}_2}\overline{\text{CH}_2}\}_3\overline{\text{N}})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ offered access to derived complexes. The π -acid carbon monoxide added to the vacant site forming $\text{Os}(\overline{\text{Si}}\{\overline{\text{OCH}_2\overline{\text{CH}_2}\overline{\text{CH}_2}\overline{\text{CH}_2}\}_3\overline{\text{N}})\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$.

Methylation of the 5-coordinate silatranyl complexes, gave $[\text{M}(\text{Si}\{\text{OCH}_2\text{CH}_2\}_3\text{NMe})\text{Cl}(\text{CO})(\text{PPh}_3)_2]\text{CF}_3\text{SO}_3$ ($\text{M} = \text{Os}, \text{Ru}$). This reaction has not been achieved previously for silatrane derivatives. These methylated complexes have the longest recorded $\text{N}\rightarrow\text{Si}$ distances for any silatrane derivatives, and display a tetrahedral bridgehead nitrogen which points out of the cage at the methyl substituent.

Protonation of the 5-coordinate silatranyl complexes gave $[\text{M}(\text{Si}\{\text{OCH}_2\text{CH}_2\}_3\text{NH})\text{Cl}(\text{CO})(\text{PPh}_3)_2]\text{CF}_3\text{SO}_3$ ($\text{M} = \text{Os}, \text{Ru}$). The thiocarbonyl-containing derivatives $\text{Os}(\overline{\text{Si}}\{\overline{\text{OCH}_2\overline{\text{CH}_2}\overline{\text{CH}_2}\overline{\text{CH}_2}\}_3\overline{\text{N}})\text{Cl}(\text{CS})(\text{PPh}_3)_2$ and $[\text{Os}(\text{Si}\{\text{OCH}_2\text{CH}_2\}_3\text{NMe})\text{Cl}(\text{CS})(\text{PPh}_3)_2]\text{CF}_3\text{SO}_3$ were prepared and these complexes showed spectroscopic properties similar to those observed for the carbonyl-containing analogues. The 5-coordinate silatranyl-thiocarbonyl complex rearranged in the presence of carbon monoxide to form $\text{Os}(\eta^2\text{-C}\{\text{S}\}\overline{\text{Si}}\{\overline{\text{OCH}_2\overline{\text{CH}_2}\overline{\text{CH}_2}\overline{\text{CH}_2}\}_3\overline{\text{N}})\text{Cl}(\text{CO})(\text{PPh}_3)_2$, which did not contain a metal-silicon bond. The silatranyl cage in the structure of this complex showed a very short $\text{N}\rightarrow\text{Si}$ bond with the nitrogen centre tetrahedral and pointing into the cage and towards the silicon atom.

The osmium(IV) complex $\text{OsH}_3(\overline{\text{Si}}\{\overline{\text{OCH}_2\overline{\text{CH}_2}\overline{\text{CH}_2}\overline{\text{CH}_2}\}_3\overline{\text{N}})(\text{PPh}_3)_3$ was prepared from $\text{OsH}_4(\text{PPh}_3)_3$ and silatrane. The structure of this complex showed that the hydride ligands were oriented *trans* to a single triphenylphosphine in each case. Treatment of this complex with methyl iodide gave the quaternary salt $[\text{OsH}_3(\text{Si}\{\text{OCH}_2\text{CH}_2\}_3\text{NMe})(\text{PPh}_3)_3]\text{I}$, and protonation gave $[\text{OsH}_3(\text{Si}\{\text{OCH}_2\text{CH}_2\}_3\text{NH})(\text{PPh}_3)_3]\text{CF}_3\text{SO}_3$.

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LIST OF ABBREVIATIONS

Anal.	microanalytic data
av.	average
aq	aqueous
atm.	atmosphere(s)
Ar	aryl
bcat	1,3,2-benzodioxaborole (catecholboron)
BDA	PhCH=CHCOMe
bipy	2,2'-bipyridyl
bs	broad singlet
ⁿ Bu	n-butyl
^t Bu	t-butyl
<i>ca.</i>	approximately
calc	calculated
cm	centimetre
conc.	concentrated
COSY	[¹ H- ¹ H]/[¹³ C- ¹ H] correlation spectroscopy
Cp	η ⁵ -cyclopentadienyl
C _q	quaternary carbon
Cy	cyclohexyl
d	doublet
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DEI	desorption electron impact
dmsO	dimethyl sulphoxide
DEPT	distortionless enhancement by polarisation transfer
EPTO	4-ethyl-2,6,7-trioxa-1-phospha-bicyclo [2.2.2]octane
esd	estimated standard deviation
<i>et al</i>	and others
Et	ethyl

equiv.	equivalent(s)
FAB	fast atom bombardment
Fc	ferrocene
HMBC	heteronuclear multiple bond coherence
HMQC	heteronuclear multiple quantum coherence
HSQC	heteronuclear single quantum coherence
IR	infrared
In	indenyl
<i>i</i>	ipso
<i>J</i>	coupling constant
<i>m</i>	meta
m.p.	melting point
m	multiplet
min.	minute(s)
Hz	hertz
MHz	mega hertz
NBS	N-bromosuccinimide
NMR	nuclear magnetic resonance
<i>o</i>	ortho
OAc	acetate
<i>o</i> -phen	1,10-phenanthroline
ORTEP	Oak Ridge Thermal Ellipsoid Plot
<i>p</i>	para
ppm	parts per million
<i>i</i> Pr	<i>i</i> -propyl
PPN	bis(triphenylphosphoranylidene) ammonium
Pyr	pyrrolyl
OTf	triflate
q	quartet
rms	root mean square
R _f	fluoroalkyl
s	singlet

ss	solid state splitting
sol/soln	solution
t	triplet
t'	pseudo triplet
thf	tetrahydrofuran
tms	tetramethylsilane
VT	variable temperature

For clarity, non-IUPAC notation is used in this thesis for the formulae of transition metal silyl complexes which are written with the silyl group directly following the transition metal.