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Metal Complexes of Acyclic and Macrocyclic Multifunctional Ligands

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Abstract

This thesis describes the design, synthesis and study of metal derivatives of new acyclic and macrocyclic ligands containing pyridine and amide groups.

Chapter 1 provides an overview of metal-carboxamide and pyridinamide chemistry including a number of important pincer compounds, macrocyclic involvement in formation of metal-templated rotaxanes and catenanes, oxidation catalysts, anion receptors and bimetallic complexes.

Chapter 2 discusses new palladium(II) complexes of an acyclic ligand bearing pendant 2-pyridyl-6-methyl arms, *N,N'*-bis(6-methyl-2-pyridinyl)-2,6-pyridinedicarboxamide (H_2L_{Me}). H_2L_{Me} formed a dimer $[Pd(L_{Me})]_2$ when treated with palladium(II) salts and non-ligating bases, but in the presence of DBU the palladium-DBU adduct, $Pd(L_{Me})(DBU)$, was formed. Reaction of $Pd(L_{Me})(DBU)$ with methyl iodide resulted in the displacement of the DBU ligand and the concomitant formation of cationic monomeric complex, $[PdI(L_{Me}\{Me\}_2)]I$ and dimeric *N*-methylpyridinium complex, $[Pd(L_{Me}\{Me\})]_2I_2$. A series of ligands, *N,N'*-bis(*x*-tolyl)-2,6-pyridinedicarboxamide ($x = 2, 3, 4$) (H_2L_{xtol}), bearing *ortho*-, *meta*- and *para*-tolyl groups, was prepared and these were coordinated to palladium(II) in their deprotonated form so that the effect of the pendant pyridine rings and steric environment around the metal on the reactivity of metal derivatives could be investigated. Stable palladium(II) derivatives of the deprotonated H_2L_{xtol} ligands, $Pd(L_{xtol})(E)$ ($E = DBU, n$ -butylamine, *p*-tolylisocyanide) were prepared. The *p*-tolylisocyanide adducts reacted with pyrrolidine or *p*-toluidine to afford the stable bis(amino)carbene complexes, $Pd(L_{xtol})(=C(NH-p-tolyl)(pyrl))$ and $Pd(L_{xtol})(=C(NH-p-tolyl)_2)$, respectively. The coordinated DBU ligands in $Pd(L_{xtol})(DBU)$ and $Pd(L_{Me})(DBU)$ were displaced by *n*-butylamine to afford the corresponding *n*-butylamine adducts, and their relative rates of exchange were determined by 1H NMR spectroscopy.

Chapter 3 discusses palladium(II) complexes of dicationic *N*-methylpyridinium ligands prepared by treating H_2L_{Me} or the series of ligands, *N,N'*-bis(*x*-pyridinyl)-2,6-pyridinedicarboxamide ($x = 2, 3, 4$) (H_2L_{xpy}) that contain pendant 2-, 3-, or 4-pyridyl groups, with methyl triflate to form $[H_2L_{Me}\{Me\}_2][OTf]_2$ or $[H_2L_{xpy}\{Me\}_2][OTf]_2$,

respectively. These ligands were coordinated in their deprotonated forms to palladium(II) to give $[\text{PdCl}(\text{L}_{\text{xpy}}\{\text{Me}\}_2)]\text{OTf}$. The chloro ligands in these metallated complexes were displaced on treatment with silver triflate in acetonitrile or water to afford the corresponding solvent adducts. The coordinated solvent molecules in $[\text{Pd}(\text{L}_{\text{Me}}\{\text{Me}\}_2)(\text{NCCH}_3)]\text{[OTf]}_2$ and $[\text{Pd}(\text{L}_{\text{opy}}\{\text{Me}\}_2)(\text{OH}_2)]\text{[OTf]}_2$ could in turn be displaced by *p*-tolylisocyanide to form isocyanide adducts, $[\text{Pd}(\text{L}_{\text{Me}}\{\text{Me}\}_2)(\text{CN-}p\text{-tolyl})]\text{[OTf]}_2$ and $[\text{Pd}(\text{L}_{\text{opy}}\{\text{Me}\}_2)(\text{CN-}p\text{-tolyl})]\text{[OTf]}_2$. Dicationic bis(amino)carbene complexes $[\text{Pd}(\text{L}_{\text{Me}}\{\text{Me}\}_2)(=\text{C}(\text{NH-}p\text{-tolyl})_2)]\text{[OTf]}_2$ and $[\text{Pd}(\text{L}_{\text{opy}}\{\text{Me}\}_2)(=\text{C}(\text{NH-}p\text{-tolyl})_2)]\text{[OTf]}_2$ were prepared by treating the corresponding isocyanide precursors with *p*-toluidine. A ^1H NMR spectroscopic study was performed to compare the relative rates of reaction of *p*-toluidine with the neutral tolyl isocyanide complexes $\text{Pd}(\text{L}_{\text{xtol}})(\text{CN-}p\text{-tolyl})$ and the dicationic isocyanide complexes $[\text{Pd}(\text{L}_{\text{Me}}\{\text{Me}\}_2)(\text{CN-}p\text{-tolyl})]\text{[OTf]}_2$ and $[\text{Pd}(\text{L}_{\text{opy}}\{\text{Me}\}_2)(\text{CN-}p\text{-tolyl})]\text{[OTf]}_2$ to determine the influence of the steric and electronic environments on the reactivity of the isocyanide ligand. On deprotonation of the amide groups in $[\text{H}_2\text{L}_{\text{Me}}\{\text{Me}\}_2]\text{[OTf]}_2$ and $[\text{H}_2\text{L}_{\text{opy}}\{\text{Me}\}_2]\text{[OTf]}_2$ the neutral free bis(imine) compounds $\text{L}_{\text{Me}}\{\text{Me}\}_2$ and $\text{L}_{\text{opy}}\{\text{Me}\}_2$ could be isolated.

Chapter 4 discusses extended acyclic ligands $\text{H}_4\text{L}_{\text{pdnA}}$ and $\text{H}_4\text{L}_{\text{SpyA}}$ ($\text{H}_4\text{L}_{\text{xA}}$) that were derived from the precursor *N,N'*-bis(6-acrylamido-2-pyridinyl)pyridine-2,6-dicarboxamide ($\text{H}_4\text{L}_{\text{acrA}}$) through Michael addition of pyrrolidine or 2-mercaptopyridine, respectively, to the acrylyl groups. The double-helical dimers $[\text{M}(\text{H}_2\text{L}_{\text{xA}})]_2$ were formed when these ligands were treated with palladium(II) or mercury(II) acetate, and in the presence of DBU the adducts $\text{Pd}(\text{H}_2\text{L}_{\text{xA}})(\text{DBU})$ were formed. In the absence of added base, palladium(II) acetate coordinated between the tail amine groups of the ligand $\text{H}_4\text{L}_{\text{pdnA}}$ which bears terminal pyrrolidyl groups.

Chapter 5 discusses complexes of macrocycles formed from double Michael-type addition of the amines *n*-butylamine, 2-(aminomethyl)pyridine, 2-(aminoethyl)pyridine, *N,N*-dimethylethylenediamine and *N,N'*-bis(2-pyridylmethyl)ethylenediamine to the pendant acrylyl groups of $\text{H}_4\text{L}_{\text{acrA}}$. The macrocycle synthesised from addition of *n*-butylamine, $\text{H}_4\text{L}_{\text{nBu}}$, reacted with palladium(II) acetate and DBU to form a complex in which palladium was coordinated in the macrocycle headgroup and an aminolactam resulting from hydrolysis of DBU was coordinated on the fourth site of the metal, $\text{Pd}(\text{H}_2\text{L}_{\text{nBu}})(\text{NH}_2\text{Lac}[7])$. A palladium derivative of $\text{H}_4\text{L}_{\text{nBu}}$ with a labile water ligand, $\text{Pd}(\text{H}_2\text{L}_{\text{nBu}})(\text{OH}_2)$, was prepared and used for subsequent syntheses of *n*-butylamine,

DBU and *p*-tolylisocyanide adducts. When treated with *p*-toluidine, the isocyanide ligand of the macrocyclic *p*-tolylisocyanide adduct was displaced to form a *p*-toluidine adduct. Modified macrocycles with other amine donors incorporated into the tail were prepared in order to provide an additional site for metal complexation. The macrocycle with an additional *N,N*-dimethylamino group, H_4L_{dmen} , reacted with metal salts to form complexes where metallation had taken place at the tail amide groups and the tail amine group interacted with the metal.

For my parents Graeme and Robyn and my wife Anna –

This thesis is as much a product of your work as it is of mine.

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“To him who is able to keep you from falling and to present you before his glorious presence without fault and with great joy – to the only God our Saviour be glory, majesty, power and authority, through Jesus Christ our Lord, before all ages, now and forevermore! Amen.” – Jude 1 v 24-25 (NIV)

Table of Contents

Abstract.....	ii
Acknowledgements	vi
Table of Contents	vii
List of Figures	x
List of Schemes.....	xviii
List of Tables	xxii
List of Charts.....	xxiii
List of Equations	xxiii
List of Abbreviations.....	xxiv
Chapter One - Introduction	1
1.1 Scope of current work	1
1.2 Background.....	1
1.3 Metal-carboxamide chemistry	6
1.4 Pyridinamide chemistry	6
1.4.1 Substituted pyridines	6
1.4.2 Bispyridylamide chemistry	8
1.5 Pincer ligands	9
1.5.1 Catalytic applications of pincer ligands	13
1.6 Pincer ligands based on 2,6-pyridinedicarboxylic acid	17
1.6.1 Complexes of 2,6-pyridinedicarboxamide pincers bearing pendant phenyl arms	20
1.6.2 Complexes of 2,6-pyridinedicarboxamide pincers bearing pendant pyridyl arms	24
1.7 Macrocyclic complexes.....	34
1.7.1 Rotaxanes and catenanes	35
1.7.2 Oxidation catalysts	38
1.7.3 Anion receptors	39
1.7.4 Binucleating macrocycles.....	42
1.7.5 Previous work	47
1.7.6 Goals of the current project	49
Chapter 2 - New Palladium(II) Complexes of Acyclic Carboxamide Ligands	51
2.1 New palladium complexes of H ₂ L _{Me}	51

2.1.1	Pd(L _{Me})(DBU).....	52
2.1.2	Pd(L _{Me})(NH ₂ ⁿ Bu).....	65
2.1.3	[Pd(L _{Me} {Me})] ₂ I ₂ and [PdI(L _{Me} {Me}) ₂]I.....	67
2.1.4	Discussion.....	73
2.2	Neutral tolyl complexes.....	74
2.2.1	New H ₂ L _{mtol} derivatives.....	74
2.2.2	<i>para</i> -Tolyl ligand, H ₂ L _{ptol}	93
2.2.3	<i>ortho</i> -Tolyl ligand, H ₂ L _{otol}	106
2.3	DBU displacement study.....	120
2.3.1	Method.....	120
2.3.2	Results.....	121
2.4	Summary.....	122
Chapter 3 - Complexes of New Cationic Ligands.....		124
3.1	Free-base cationic ligand.....	124
3.1.1	Synthesis of the free dicationic ligand, [H ₂ L _{Me} {Me}] ₂ [OTf] ₂	126
3.1.2	[PdCl(L _{Me} {Me}) ₂][OTf].....	130
3.1.3	[Pd(L _{Me} {Me}) ₂](NCCH ₃)[OTf] ₂	132
3.1.4	[Pd(L _{Me} {Me}) ₂](NH ₃)[OTf] ₂	144
3.1.5	[Pd(L _{Me} {Me}) ₂](CN- <i>p</i> -tolyl)[OTf] ₂	145
3.1.6	[Pd(L _{Me} {Me}) ₂](=C(NH- <i>p</i> -tolyl) ₂)[OTf] ₂	146
3.1.7	Summary.....	148
3.2	New cationic complexes.....	148
3.2.1	<i>o</i> -Pyridinium ligand, [H ₂ L _{opy} {Me}] ₂ [OTf] ₂	150
3.2.2	<i>m</i> -Pyridinium ligand, [H ₂ L _{mpy} {Me}] ₂ [OTf] ₂	159
3.2.3	<i>p</i> -Pyridinium ligand, [H ₂ L _{ppy} {Me}] ₂ [OTf] ₂	167
3.3	Neutral imine derivatives of cationic ligands.....	179
3.3.1	Bis(imine) ligand, L _{Me} {Me}] ₂	180
3.3.2	Bis(imine) ligand, L _{opy} {Me}] ₂	181
3.3.3	Bond length analysis of pyridinium and bis(imine) compounds.....	185
3.4	Addition of <i>p</i> -toluidine to coordinated isocyanide.....	189
3.4.1	Method.....	190
3.4.2	Results.....	190
3.4.3	Discussion.....	191
3.5	Summary.....	193
Chapter 4 - Complexes of Extended Acyclic Ligands.....		196
4.1	New complexes of H ₄ L _{acrA}	196
4.1.1	[Pd(H ₂ L _{acrA})] ₂	198
4.1.2	Pd(H ₂ L _{acrA})(DBU).....	202
4.1.3	[Hg(H ₂ L _{acrA})] ₂	204
4.1.4	Reactivity of metallated L _{acrA} complexes.....	205
4.2	Synthesis of extended acyclic ligands.....	207
4.3	Bis(pyrrolidyl) ligand, H ₄ L _{pdnA}	208
4.3.1	Pd(OAc) ₂ (H ₄ L _{pdnA}).....	212

4.3.2	$[\text{Pd}(\text{H}_2\text{L}_{\text{pdnA}})]_2$	217
4.3.3	$\text{Pd}(\text{H}_2\text{L}_{\text{pdnA}})(\text{DBU})$	220
4.3.4	$[\text{Hg}(\text{H}_2\text{L}_{\text{pdnA}})]_2 \cdot 2\text{CH}_3\text{COOH}$	225
4.3.5	Other reactions of $\text{H}_4\text{L}_{\text{pdnA}}$	230
4.3.6	Discussion	233
4.4	Bis(2-mercaptopyridyl) ligand, $\text{H}_4\text{L}_{\text{SpyA}}$	234
4.4.1	$[\text{Pd}(\text{H}_2\text{L}_{\text{SpyA}})]_2$	236
4.4.2	$\text{Pd}(\text{H}_2\text{L}_{\text{SpyA}})(\text{DBU})$	238
4.4.3	$[\text{Hg}(\text{H}_2\text{L}_{\text{SpyA}})]_2$	239
4.4.4	Other reactions of $\text{H}_4\text{L}_{\text{SpyA}}$	240
4.4.5	Discussion	242
4.5	Summary	243
Chapter 5 - Complexes of Macrocyclic Ligands		245
5.1	Macrocyclic ligands	245
5.2	New complexes of $\text{H}_4\text{L}_{\text{nBu}}$	246
5.2.1	$\text{PdCl}(\text{H}_3\text{L}_{\text{nBu}})$	247
5.2.2	$\text{Pd}(\text{H}_2\text{L}_{\text{nBu}})(\text{NH}_2\text{Lac}[7])$	252
5.2.3	$\text{Pd}(\text{H}_2\text{L}_{\text{nBu}})(\text{NH}_2\text{Lac}[5])$	259
5.2.4	DBU hydrolysis investigation	260
5.2.5	$\text{Pd}(\text{H}_2\text{L}_{\text{nBu}})(\text{OH}_2)$	261
5.2.6	$\text{Pd}(\text{H}_2\text{L}_{\text{nBu}})(\text{NH}_2''\text{Bu})$	267
5.2.7	$\text{Pd}(\text{H}_2\text{L}_{\text{nBu}})(\text{DBU})$	269
5.2.8	$\text{Pd}(\text{H}_2\text{L}_{\text{nBu}})(\text{CN-}p\text{-tolyl})$	273
5.2.9	$\text{Pd}(\text{H}_2\text{L}_{\text{nBu}})(\text{NH}_2\text{-}p\text{-tolyl})$	274
5.3	Complexes of new “scorpion-tail” macrocyclic ligands	277
5.3.1	$\text{H}_4\text{L}_{\text{dmen}}$	277
5.3.2	$\text{H}_4\text{L}_{\text{amp}}$	287
5.3.3	$\text{H}_4\text{L}_{\text{aep}}$	290
5.3.4	$\text{H}_4\text{L}_{\text{msamp}}$	292
5.4	Summary	298
Experimental		300
Data for compounds in Chapter 2		302
Data for compounds in Chapter 3		348
Data for compounds in Chapter 4		393
Data for compounds in Chapter 5		432
References		462

List of Figures

Figure 1.1: Metal-hydroxo species stabilised by intramolecular hydrogen bonding.	3
Figure 1.2: Iron hangman porphyrin complex.	3
Figure 1.3: Pseudomacrocyclic phenolic oxime complex.	4
Figure 1.4: Nicotinamide-based anion receptors.	5
Figure 1.5: Cooperative molecular recognition processes in a macrocyclic organopalladium-adenine complex.	5
Figure 1.6: Examples of 2-substituted pyridines.	7
Figure 1.7: 2,2'-Bipyridine, 1,10-phenanthroline and di(2-pyridyl)methane.	7
Figure 1.8: Generic bispyridylamide.	8
Figure 1.9: General structures of metal complexes with bispyridylamides.	9
Figure 1.10: Free and metallated pincer ligands.	10
Figure 1.11: Examples of functionalized pincer complexes.	10
Figure 1.12: Coordination modes of NCN pincer ligands.	11
Figure 1.13: Brookhart-Gibson-Dupont alkene polymerisation catalyst.	12
Figure 1.14: Structures of some NHC-containing pincer ligands.	13
Figure 1.15: Palladium(II) complexes of phosphine and phosphite PCP ligands used in Heck transformations.	14
Figure 1.16: Palladium complex of a modified phosphinite ligand.	14
Figure 1.17: Palladium complexes of aminophosphine pincer ligands.	15
Figure 1.18: Water soluble palladacyclic aqua catalysts.	15
Figure 1.19: Nickel NCN catalysts for Kharasch addition.	16
Figure 1.20: Iridium hydride PCP dehydrogenation catalysts.	16
Figure 1.21: Ruthenium PNN catalyst.	17
Figure 1.22: Free and metallated ON'O, SN'S and NN'N ligands.	18
Figure 1.23: Square pyramidal nickel(II) and copper(II) complexes with 2,6-pyridinedicarboxamide ligand behaving as a neutral ON'O donor.	19
Figure 1.24: Copper(II) and cobalt(II) complexes with tridentate and bidentate <i>N,N,N'</i> -tetraethylpyridine-2,6-dicarboxamide.	19
Figure 1.25: Free and metallated diphenyl amide pincer ligand.	20
Figure 1.26: μ -Hydroxo bridged copper dimer.	21
Figure 1.27: Carboxamide ligands used in oxidation catalysis.	21
Figure 1.28: Chiral copper(II) complexes of bis(imazolyl) ligand.	22
Figure 1.29: Palladium complexes of ligands containing the 2,6-pyridinedicarboxamide headgroup and η^1 -acetonitrile.	22

Figure 1.30: Homobimetallic complex of a quinonediimine ligand.	23
Figure 1.31: 2,6-Pyridinedicarboxamide tectons bearing pendant pyridyl groups.	25
Figure 1.32: Palladium-containing metallamacrocycles based on H ₂ L _{mpy} and H ₂ L _{ppy}	26
Figure 1.33: Anion recognition by self-complimentary metallamacrocycle.	28
Figure 1.34: Porphyrin-containing metallamacrocycles based on H ₂ L _{ppy} derivatives.	29
Figure 1.35: Luminescent anion receptor.	29
Figure 1.36: Ruthenium complex of 1,10-phenanthrolyl bispyridyl ligand.	32
Figure 1.37: [Hg(L _{Me}) ₂] structure and ORTEP depiction of the crystal structure.	32
Figure 1.38: Octahedral iron(III) and cobalt(III) complexes of H ₂ L _{Me}	33
Figure 1.39: Structure of palladium and nickel derivatives of H ₂ L _{Me}	33
Figure 1.40: Copper and lanthanide complexes of H ₂ L _{opy}	34
Figure 1.41: Structures of free and metallated TAML ligands.	38
Figure 1.42: 2,6-Pyridinedicarboxamide-containing macrocyclic anion receptor and acyclic counterpart.	40
Figure 1.43: Cofacial porphyrins and spacer groups.	45
Figure 1.44: Macrocyclic Schiff base calixpyrrole ligand and crystal structure of cofacial dicobalt-peroxo complex.	46
Figure 1.45: Complex formed between dicopper macrocyclic complex and β-phenylalanine.	46
Figure 1.46: Tetraamide macrocycles prepared by Horner.	47
Figure 1.47: Unsymmetrical palladium(II) complex of H ₄ L _{nBu}	48
Figure 2.1: ORTEP depictions of [Pd(L _{Me}) ₂] showing left- and right-handed helices. Hydrogen atoms and solvent removed for clarity. Ellipsoids shown at 50% probability level.	52
Figure 2.2: [Pd(L _{Me} {H}) ₂]Cl ₂	52
Figure 2.3: ¹ H NMR spectrum of Pd(L _{Me})(DBU) (300 MHz, CDCl ₃ , 300 K).	54
Figure 2.4: ORTEP depiction of Pd(L _{Me})(DBU) (Molecule B). Hydrogen atoms removed for clarity. Ellipsoids shown at 50% probability level.	55
Figure 2.5: ORTEP depiction of Pd(L _{Me})(DBU) viewed along plane of headgroup (Molecule B). Hydrogen atoms removed for clarity. Ellipsoids shown at 50% probability level.	57
Figure 2.6: Re ₂ (μ-H)(μ-C ₂ Ph)(CO) ₇ (DBU).	59
Figure 2.7: NiOC(O)CH ₂ CH ₂ (DBU) ₂	60
Figure 2.8: Al(SiMe ₃) ₃ (DBU).	61
Figure 2.9: RhCl(COD)(DBU).	61
Figure 2.10: <i>trans</i> -[Rh(CO)(DBU)(PPh ₃) ₂]ClO ₄ (ClO ₄ ⁻ counterion and Ph groups in crystal structure removed for clarity).	62
Figure 2.11: ¹ H NMR spectrum of Pd(L _{Me})(NH ₂ ⁿ Bu) (400 MHz, CDCl ₃ , 300 K).	66

Figure 2.12: Proposed intramolecular hydrogen bonding interactions in Pd(L _{Me})(NH ₂ ^{<i>n</i>} Bu).	67
Figure 2.13: [Ru(L _{Me} {Me})(PPh ₃) ₂ (CO)] ⁺	69
Figure 2.14: ¹ H NMR spectrum (aromatic region) and structure of [PdI(L _{Me} {Me}) ₂]I (300 MHz, DMSO- <i>d</i> ₆ , 300 K). Atom numbers in blue indicate nitrogen atoms.	70
Figure 2.15: Possible rotamers of [PdI(L _{Me} {Me}) ₂] ⁺	70
Figure 2.16: ORTEP depiction of [PdI(L _{Me} {Me}) ₂] ⁺ cation. Hydrogen atoms, solvent and iodide counterion removed for clarity. Ellipsoids shown at 50% probability level.	72
Figure 2.17: ORTEP depiction of Pd(L _{mtol})(CN- <i>p</i> -tolyl) (Molecule A). Hydrogen atoms removed for clarity. Ellipsoids shown at 50% probability level.....	76
Figure 2.18: ORTEP depiction of Pd(L _{mtol})(CN- <i>p</i> -tolyl) (Molecule B). Hydrogen atoms removed for clarity. Ellipsoids shown at 50% probability level.....	76
Figure 2.19: Molecule A viewed along L _{mtol} headgroup. Hydrogen atoms removed for clarity. Ellipsoids shown at 50% probability level.....	78
Figure 2.20: Molecule B viewed along L _{mtol} headgroup. Hydrogen atoms removed for clarity. Ellipsoids shown at 50% probability level.....	78
Figure 2.21: Possible conformers of Pd(L _{mtol})(=C(NH- <i>p</i> -tolyl)(pyrl)).	80
Figure 2.22: ORTEP depiction of Pd(L _{mtol})(=C(NH- <i>p</i> -tolyl)(pyrl)). Hydrogen atoms apart from toluidyl NH removed for clarity. Ellipsoids shown at 50% probability level.	81
Figure 2.23: A section of the hydrogen bonding network found in the solid state structure of Pd(L _{mtol})(=C(NH- <i>p</i> -tolyl)(pyrl)).	82
Figure 2.24: COSY NMR spectrum (aromatic region) of Pd(L _{mtol})(=C(NH- <i>p</i> -tolyl) ₂) (600 MHz, CDCl ₃ , 300K). Labels in blue refer to nitrogen atoms.	84
Figure 2.25: Possible conformers of Pd(L _{mtol})(=C(NH- <i>p</i> -tolyl) ₂).....	85
Figure 2.26: ORTEP depiction of Pd(L _{mtol})(=C(NH- <i>p</i> -tolyl) ₂) (Molecule A). Hydrogen atoms apart from toluidyl NH groups removed for clarity. Ellipsoids shown at 50% probability level.	86
Figure 2.27: ORTEP depiction of Pd(L _{mtol})(=C(NH- <i>p</i> -tolyl) ₂) (Molecule B). Hydrogen atoms apart from toluidyl NH groups removed for clarity. Ellipsoids shown at 50% probability level.	86
Figure 2.28: Intermolecular hydrogen bonding between molecule A (green) and molecule B (blue) in Pd(L _{mtol})(=C(NH- <i>p</i> -tolyl) ₂).	88
Figure 2.29: A section of the extended intermolecular hydrogen bonding network between molecule A (green) and molecule B (blue) in Pd(L _{mtol})(=C(NH- <i>p</i> -tolyl) ₂).	89
Figure 2.30: ORTEP depiction of Pd(L _{mtol})(DBU) (molecule A). Hydrogen atoms removed for clarity. Ellipsoids shown at 50% probability level.....	90
Figure 2.31: Crystal structure of Pd(L _{mtol})(DBU) showing co-planar arrangement of molecules (A = green, B = blue, C = red, D = purple).	91
Figure 2.32: ORTEP depiction of Pd(L _{ptol})(NCCH ₃). Hydrogen atoms and solvent removed for clarity. Ellipsoids shown at 50% probability level.....	96

Figure 2.33: Co-planar stacking of Pd(L _{ptol})(NCCH ₃). Adventitious acetonitrile shown in blue.	97
Figure 2.34: ORTEP depiction of Pd(L _{ptol})(DMSO- <i>d</i> ₆). Hydrogen atoms and solvent removed for clarity. Ellipsoids shown at 50% probability level.	99
Figure 2.35: Proposed (<i>Z</i> , <i>E</i>) conformation of Pd(L _{ptol})(=C(NH- <i>p</i> -tolyl) ₂).	101
Figure 2.36: ORTEP depiction of Pd(L _{ptol})(DBU) (Molecule A). Hydrogen atoms and solvent removed for clarity. Ellipsoids shown at 50% probability level.	103
Figure 2.37: ORTEP depiction of H ₂ L _{otol} . Hydrogen atoms apart from NH groups removed for clarity. Ellipsoids shown at 50% probability level.	107
Figure 2.38: ORTEP depiction of Pd(L _{otol})(CN- <i>p</i> -tolyl). Hydrogen atoms removed for clarity. Ellipsoids shown at 50% probability level.	109
Figure 2.39: Stacked ¹ H VT NMR spectra of Pd(L _{otol})(=C(NH- <i>p</i> -tolyl) ₂) (aromatic region) (300 MHz, DMSO- <i>d</i> ₆).	111
Figure 2.40: Stacked ¹ H VT NMR spectra of Pd(L _{otol})(=C(NH- <i>p</i> -tolyl) ₂) (aliphatic region) (300 MHz, DMSO- <i>d</i> ₆). Peak at 2.50 ppm is the residual DMSO protio signal.	112
Figure 2.41: Stacked ¹ H VT NMR spectra of Pd(L _{otol})(DBU) showing detail of headgroup proton resonances (300 MHz, DMSO- <i>d</i> ₆).	114
Figure 2.42: Stacked ¹ H VT NMR spectra of Pd(L _{otol})(DBU) showing detail of pendant tolyl methyl group resonances (300 MHz, DMSO- <i>d</i> ₆).	115
Figure 2.43: Possible rotamers of Pd(L _{otol})(DBU).	116
Figure 2.44: ORTEP depiction of Pd(L _{otol})(DBU). Hydrogen atoms removed for clarity. Ellipsoids shown at 50% probability level.	118
Figure 2.45: Stacked ¹ H VT NMR spectra of Pd(L _{otol})(NH ₂ ^{<i>n</i>} Bu) showing coalescence of <i>C</i> -methyl resonances (300 MHz, DMSO- <i>d</i> ₆). Signal at 2.50 is residual DMSO protio resonance.	120
Figure 3.1: ORTEP depiction of [H ₂ L _{Me} {Me} ₂] ²⁺ dication. Hydrogen atoms (apart from NH groups) and triflate counterions removed for clarity. Ellipsoids shown at 50% probability level.	129
Figure 3.2: ORTEP depiction of [H ₂ L _{Me} {Me} ₂][OTf] ₂ viewed along the plane of the headgroup. Hydrogen atoms apart from NH groups removed for clarity. Ellipsoids shown at 50% probability level.	130
Figure 3.3: Crystal structure of [PdCl(L _{Me} {Me} ₂)]OTf.	132
Figure 3.4: The aromatic region of the ¹ H NMR DMSO- <i>d</i> ₆ spectrum of [Pd(L _{Me} {Me} ₂)(NCCH ₃)] ₂ [OTf] ₂ (300 MHz, 300 K). Atom numbers in blue indicate nitrogen atoms.	134
Figure 3.5: The aromatic region of the ¹ H NMR of [Pd(L _{Me} {Me} ₂)(NCCH ₃)] ₂ [OTf] ₂ in CD ₃ CN (300 MHz, 300 K).	135
Figure 3.6: ORTEP depiction of [Pd(L _{Me} {Me} ₂)(NCCH ₃)] ²⁺ dication. Hydrogen atoms and triflate counterions removed for clarity. Ellipsoids shown at 50% probability level.	136

Figure 3.7: Close approach between neighbouring $[\text{Pd}(\text{L}_{\text{Me}}\{\text{Me}\}_2)(\text{NCCH}_3)][\text{OTf}]_2$ molecules.	137
Figure 3.8: ORTEP depiction of $[\text{Pd}(\text{L}_{\text{Me}}\{\text{Me}\}_2)(\text{OH}_2)]^{2+}$ dication. Hydrogen atoms (apart from OH_2 group), triflate counterions and solvent removed for clarity. Ellipsoids shown at 50% probability level.	139
Figure 3.9: A section of the hydrogen bonding network in $[\text{Pd}(\text{L}_{\text{Me}}\{\text{Me}\}_2)(\text{OH}_2)][\text{OTf}]_2$. Adventitious water shown in purple, triflate counterions in red and blue.	140
Figure 3.10: $\text{Pd}(\text{L}_{\text{Me}}\{\text{Me}\}_2)(\text{maleate})$ 1:1 complex.	141
Figure 3.11: 1:1 and 2:1 palladium-oxalate complexes.	142
Figure 3.12: Sterically analogous dicationic (top) and neutral (bottom) ligands.	149
Figure 3.13: ORTEP depiction of $[\text{H}_2\text{L}_{\text{opy}}\{\text{Me}\}_2]^{2+}$ dication (molecule B). Hydrogen atoms (apart from NH groups) and triflate counterions removed for clarity. Ellipsoids shown at 50% probability level.	152
Figure 3.14: ORTEP depiction of $[\text{Pd}(\text{L}_{\text{opy}}\{\text{Me}\}_2)(\text{OH}_2)]^{2+}$ dication. Hydrogen atoms, triflate counterions and solvent removed for clarity. Ellipsoids shown at 50% probability level.	156
Figure 3.15: A section of the hydrogen bonding network found in $[\text{Pd}(\text{L}_{\text{opy}}\{\text{Me}\}_2)(\text{OH}_2)][\text{OTf}]_2$. Water of crystallization shown in purple, triflate counterions in red and blue.	157
Figure 3.16: ORTEP depiction of $\text{H}_2\text{L}_{\text{mpy}}$. Hydrogen atoms apart from NH groups removed for clarity. Ellipsoids shown at 50% probability level.	160
Figure 3.17: A section of the intermolecular hydrogen bonding network found in $\text{H}_2\text{L}_{\text{mpy}}$	161
Figure 3.18: ORTEP depiction of $[\text{H}_2\text{L}_{\text{mpy}}\{\text{Me}\}_2]^{2+}$ dication (molecule A). Hydrogen atoms (apart from NH groups), triflate counterions and solvent removed for clarity. Ellipsoids shown at 50% probability level.	162
Figure 3.19: Intermolecular hydrogen bonding interactions between triflate and ligand molecules in $[\text{H}_2\text{L}_{\text{mpy}}\{\text{Me}\}_2][\text{OTf}]_2$. Molecule A shown in green, molecule B in dark blue.	164
Figure 3.20: ORTEP depiction of $[\text{H}_2\text{L}_{\text{ppy}}\{\text{Me}\}_2]^{2+}$ dication. Hydrogen atoms (apart from NH groups) and triflate counterions removed for clarity. Ellipsoids shown at 50% probability level.	168
Figure 3.21: Close approaches and hydrogen bonding interactions in $[\text{H}_2\text{L}_{\text{ppy}}\{\text{Me}\}_2][\text{OTf}]_2$. Carboxamide ligand shown in red, triflate counterions in green and blue.	170
Figure 3.22: X-ray crystal structure of $[\text{Pd}(\text{OAc})(\text{L}_{\text{ppy}}\{\text{Me}\}_2)]^+$ cation. Hydrogen atoms and triflate counterion removed for clarity. Ellipsoids shown at 50% probability level.	174
Figure 3.23: $\text{CH}\cdots\text{O}$ close approaches in $[\text{Pd}(\text{OAc})(\text{L}_{\text{ppy}}\{\text{Me}\}_2)]\text{OTf}$	175
Figure 3.24: Comparison of aliphatic region of $\text{Pd}(\text{L}_{\text{ptol}})(\text{DBU})$ (top) and $[\text{Pd}(\text{L}_{\text{ppy}}\{\text{Me}\}_2)(\text{DBU})][\text{OTf}]_2$ (bottom) ^1H NMR spectra (400 MHz, $\text{DMSO}-d_6$, 300 K). Peak at 2.50 ppm is the residual DMSO protio signal.	178

Figure 3.25: Alternative representations of ligand behaviour in dicationic palladium complexes of $[\text{H}_2\text{L}_{\text{Me}}\{\text{Me}\}_2][\text{OTf}]_2$.	180
Figure 3.26: ORTEP depiction of $\text{L}_{\text{opy}}\{\text{Me}\}_2$.	182
Figure 3.27: Bond lengths (Å) for $\text{L}_{\text{opy}}\{\text{Me}\}_2$ with bond lengths for Molecule A of $[\text{H}_2\text{L}_{\text{opy}}\{\text{Me}\}_2][\text{OTf}]_2$ shown in red for comparison (atom numbers italicised).	183
Figure 3.28: Reported bond lengths for BTDP.	184
Figure 3.29: Resonance forms for 2- and 4- <i>N</i> -methylpyridinium urea derivatives.	185
Figure 3.30: Bond labelling scheme for ligands in crystallographic study.	186
Figure 4.1: $\text{H}_4\text{L}_{\text{acrA}}$.	196
Figure 4.2: COSY NMR spectrum of $[\text{Pd}(\text{H}_2\text{L}_{\text{acrA}})]_2$ (300 MHz, $\text{DMSO-}d_6$, 300 K).	200
Figure 4.3: Acrylyl proton numbering scheme.	201
Figure 4.4: Real (top) and simulated (bottom) 300MHz ^1H NMR spectra of $[\text{Pd}(\text{H}_2\text{L}_{\text{acrA}})]_2$ (vinyl region).	202
Figure 4.5: Potential monometallic binding modes of extended acyclic ligands.	208
Figure 4.6: Aliphatic region of $\text{H}_4\text{L}_{\text{pdnA}}$ ^1H NMR spectrum (400 MHz, CDCl_3 , 300 K).	210
Figure 4.7: ORTEP depiction of $\text{H}_4\text{L}_{\text{pdnA}}$. Hydrogen atoms apart from <i>NH</i> groups removed for clarity. Ellipsoids shown at 50% probability level.	211
Figure 4.8: Hydrogen bonding interactions in $\text{H}_4\text{L}_{\text{pdnA}}$.	212
Figure 4.9: ORTEP depiction of $\text{Pd}(\text{OAc})_2(\text{H}_4\text{L}_{\text{pdnA}})$. Hydrogen atoms (apart from <i>NH</i> and <i>OH</i> ₂ groups) and dichloromethane solvent removed for clarity. Ellipsoids shown at 50% probability level.	214
Figure 4.10: Alternative view of $\text{Pd}(\text{OAc})_2(\text{H}_4\text{L}_{\text{pdnA}})$. Hydrogen atoms (apart from <i>NH</i> and <i>OH</i> ₂ groups) and dichloromethane solvent removed for clarity. Ellipsoids shown at 50% probability level.	215
Figure 4.11: Hydrogen bonding interactions in $\text{Pd}(\text{OAc})_2(\text{H}_4\text{L}_{\text{pdnA}})$.	216
Figure 4.12: Crystal structure of $[\text{Pd}(\text{H}_2\text{L}_{\text{pdnA}})]_2$. Hydrogen atoms (apart from <i>NH</i> groups) and solvent removed for clarity. Ellipsoids shown at 50% probability level.	218
Figure 4.13: Dimeric copper complex of trimeric amide. Benzyloxy groups truncated on crystal structure for clarity.	220
Figure 4.14: Crystal structure of $\text{Pd}(\text{H}_2\text{L}_{\text{pdnA}})(\text{DBU})$. Hydrogen atoms (apart from <i>NH</i> groups) and solvent removed for clarity.	222
Figure 4.15: Alternative view of $\text{Pd}(\text{H}_2\text{L}_{\text{pdnA}})(\text{DBU})$. Hydrogen atoms (apart from <i>NH</i> groups) and solvent removed for clarity.	222
Figure 4.16: Expansion of aliphatic region of $[\text{Pd}(\text{H}_2\text{L}_{\text{pdnA}}\{\text{Me}\}_2)(\text{DBU})]_2$ HMBC NMR spectrum (400 MHz, $\text{DMSO-}d_6$, 300K).	225
Figure 4.17: ORTEP depiction of $[\text{Hg}(\text{H}_2\text{L}_{\text{pdnA}})]_2$. Hydrogen atoms (apart from <i>NH</i> groups), solvent molecules and acetic acid removed for clarity. Ellipsoids shown at 50% probability level.	227

Figure 4.18: Hydrogen bonding interactions in $[\text{Hg}(\text{H}_2\text{L}_{\text{pdnA}})]_2$. Solvent molecules not involved in hydrogen bonding interactions removed for clarity.....	229
Figure 4.19: Synthesis of $\text{OsCl}_2(\text{H}_4\text{L}_{\text{pdnA}})(\text{PPh}_3)_2$	230
Figure 4.20: Potential chelates formed by coordination of palladium(II) to $\text{H}_4\text{L}_{\text{pdnA}}$	234
Figure 4.21: ORTEP depiction of $\text{H}_4\text{L}_{\text{SpyA}}$. Hydrogen atoms apart from <i>NH</i> groups removed for clarity. Ellipsoids shown at 50% probability level.....	236
Figure 4.22: Comparison of aromatic region of $[\text{Pd}(\text{H}_2\text{L}_{\text{pdnA}})]_2$ (400 MHz, CDCl_3 , 300 K) (top) and $[\text{Pd}(\text{H}_2\text{L}_{\text{SpyA}})]_2$ (600 MHz, CDCl_3 , 300 K) (bottom) ^1H NMR spectra. Peak at 7.26 ppm is the residual CHCl_3 protio signal. Mid-ligand pyridyl resonances are highlighted in blue.....	238
Figure 5.1: ORTEP depiction of $\text{H}_4\text{L}_{\text{nBu}}$ (molecule A). Hydrogen atoms apart from <i>NH</i> groups removed for clarity. Ellipsoids shown at 50% probability level.	246
Figure 5.2: Hydrogen bonding interactions in $\text{H}_4\text{L}_{\text{nBu}}$ (molecule A).	247
Figure 5.3: ORTEP depiction of $\text{PdCl}(\text{H}_3\text{L}_{\text{nBu}})$. Hydrogen atoms (apart from <i>NH</i> groups) and solvent removed for clarity. Ellipsoids shown at 50% probability level.	249
Figure 5.4: Alternative view of $\text{PdCl}(\text{H}_3\text{L}_{\text{nBu}})$. Hydrogen atoms (apart from <i>NH</i> groups) and solvent removed for clarity. Ellipsoids shown at 50% probability level.	249
Figure 5.5: $\text{Pd}(\text{H}_2\text{L}_{\text{nBu}})(\text{NH}_2\text{Lac}[7])$	252
Figure 5.6: ORTEP depiction of $\text{Pd}(\text{H}_2\text{L}_{\text{nBu}})(\text{NH}_2\text{Lac}[7])$. Hydrogen atoms (apart from <i>NH</i> and NH_2 groups) and solvent removed for clarity. Ellipsoids shown at 50% probability level.	255
Figure 5.7: Alternative view of $\text{Pd}(\text{H}_2\text{L}_{\text{nBu}})(\text{NH}_2\text{Lac}[7])$. Hydrogen atoms (apart from <i>NH</i> and NH_2 groups) and solvent removed for clarity. Ellipsoids shown at 50% probability level.	256
Figure 5.8: Intramolecular hydrogen bonding interactions in $\text{Pd}(\text{H}_2\text{L}_{\text{nBu}})(\text{NH}_2\text{Lac}[7])$	257
Figure 5.9: A section of the two-dimensional sheet formed by the intermolecular hydrogen bonding network in $\text{Pd}(\text{H}_2\text{L}_{\text{nBu}})(\text{NH}_2\text{Lac}[7])$. Water of crystallization shown in green.	258
Figure 5.10: ORTEP depiction of $\text{Pd}(\text{H}_2\text{L}_{\text{nBu}})(\text{OH}_2)$. Hydrogen atoms (apart from <i>NH</i> and OH_2 groups) and solvent removed for clarity. Ellipsoids shown at 50% probability level.	263
Figure 5.11: Alternative view of $\text{Pd}(\text{H}_2\text{L}_{\text{nBu}})(\text{OH}_2)$. Hydrogen atoms (apart from <i>NH</i> and OH_2 groups) and solvent removed for clarity. Ellipsoids shown at 50% probability level.	264
Figure 5.12: Intramolecular hydrogen bonding interactions in $\text{Pd}(\text{H}_2\text{L}_{\text{nBu}})(\text{OH}_2)$	265
Figure 5.13: A section of the intermolecular hydrogen bonding network in $\text{Pd}(\text{H}_2\text{L}_{\text{nBu}})(\text{OH}_2)$	266
Figure 5.14: Aliphatic region of $\text{Pd}(\text{H}_2\text{L}_{\text{nBu}})(\text{NH}_2^{\text{n}}\text{Bu})$ COSY NMR spectrum. Resonances attributable to coordinated <i>n</i> -butylamine highlighted in red, macrocyclic <i>n</i> -butyl tail highlighted in green. Resonance at 2.50 ppm is the residual protio DMSO, resonance at 3.32 ppm is water.	268

Figure 5.15: Potential mono- and bimetallic complexes of scorpion-tail ligands.	277
Figure 5.16: Stacked ^1H VT NMR spectra of $\text{H}_4\text{L}_{\text{dmen}}$ (aromatic region) (300 MHz, $\text{DMSO-}d_6$).	279
Figure 5.17: Aliphatic region of $[\text{Pd}(\text{H}_3\text{L}_{\text{dmen}})]\text{OAc}$ Edited-HSQC NMR spectrum (400 MHz, $\text{DMSO-}d_6$, 300 K). CH_2 peaks shown in blue, CH_3 peaks shown in red. Peak at 2.50 ppm is residual DMSO protio signal, multiplet at 3.31-3.27 ppm overlaps with water.	281
Figure 5.18: Methylene region of $\text{Hg}(\text{H}_2\text{L}_{\text{dmen}})$ HSQC NMR spectrum (400 MHz, CDCl_3 , 300 K).	283
Figure 5.19: ORTEP depiction of $\text{Hg}(\text{H}_2\text{L}_{\text{dmen}})$. Hydrogen atoms (apart from <i>NH</i> groups) and solvent removed for clarity. Ellipsoids shown at 50% probability level.	284
Figure 5.20: ORTEP depiction of $\text{H}_4\text{L}_{\text{aep}}$. Hydrogen atoms (apart from <i>NH</i> groups) and solvent removed for clarity. Ellipsoids shown at 50% probability level.	291
Figure 5.21: Intermolecular hydrogen bonding between $\text{H}_4\text{L}_{\text{aep}}$ and $\text{DMSO-}d_6$	291
Figure 5.22: Amido-imine-type hybrid macrocyclic DMSO complex.	292
Figure 5.23: Proposed free (left) and bimetallic (right) twin-tailed ligand.	293
Figure 5.25: ORTEP depiction of $\text{H}_4\text{L}_{\text{msamp}}$. Hydrogen atoms apart from <i>NH</i> groups removed for clarity. Ellipsoids shown at 50% probability level.	295
Figure 5.26: Alternative view of $\text{H}_4\text{L}_{\text{msamp}}$. Hydrogen atoms apart from <i>NH</i> groups removed for clarity. Ellipsoids shown at 50% probability level.	296
Figure 5.27: Decyloxy-substituted acyclic ligand.	297

List of Schemes

Scheme 1.1: Complexation of nickel sulfate by a salen-based ligand.	4
Scheme 1.2: Amide coordination modes.	6
Scheme 1.3: Solvent-dependent equilibrium between η^1 -acetonitrile compound and tetrameric species.	23
Scheme 1.4: Redox behaviour of quinonediimine complex.	24
Scheme 1.5: Self-assembly of a [2]rotaxane.	27
Scheme 1.6: Synthesis of H_2L_{Me}	30
Scheme 1.7: Syntheses of ruthenium derivatives of H_2L_{Me}	31
Scheme 1.8: Template synthesis of [2]rotaxane <i>via</i> RCM pathway.	36
Scheme 1.9: Palladium(II)-mediated active-metal template synthesis of [2]rotaxanes.	37
Scheme 1.10: Anion-templated rotaxane synthesis.	40
Scheme 1.11: Oxidation and reduction of 2,6-pyridinedicarboxamide dipyrromethane hybrid macrocycles.	41
Scheme 1.12: Discrimination of enantiomeric anions by a macrocycle containing a chiral cavity.	42
Scheme 1.13: Synthesis of homodinuclear compartmental macrocyclic complex.	43
Scheme 1.14: Synthesis of unsymmetrical homo/heterodinuclear compartmental macrocyclic complexes.	43
Scheme 1.15: Synthesis of bimetallic imino and amino compartmental macrocycles with 6- and 4-coordinate pockets.	44
Scheme 1.16: Synthesis of symmetrical and unsymmetrical palladium-containing 2,6-pyridinedicarboxamide dipyrromethane hybrid macrocycles.	49
Scheme 2.1: Synthesis of $[Pd(L_{Me})]_2$	51
Scheme 2.2: Synthesis of $Pd(L_{Me})(DBU)$	53
Scheme 2.3: Synthesis of $PtCl_2(PEt_3)(DBU)$	58
Scheme 2.4: Synthesis and reactions of $(OC)_3(DBU)Ru(\mu-PPh_2)Co(CO)_3$	58
Scheme 2.5: Synthesis of $(DBU)(DPPB)Ru(\mu-Cl)_3RuCl(DPPB)$	59
Scheme 2.6: Synthesis of $[CpRu(PPh_3)(CH_3CN)(DBU)]PF_6$	59
Scheme 2.7: Synthesis of $Mo(DBU)_2(CO)_4$	60
Scheme 2.8: <i>N</i> -Arylation of imidazole promoted by copper catalysts.	62
Scheme 2.9: Synthesis of magnesium diamide with DBN acting as a ligand.	63
Scheme 2.10: DBU as a ligand in the synthesis of η^3 -allylpalladium complexes.	64
Scheme 2.11: Synthesis of $Pd(L_{Me})(NH_2^tBu)$	65

Scheme 2.12: Reaction of Pd(L _{Me})(DBU) with methyl iodide.....	68
Scheme 2.13: Synthesis of [Pd(L _{Me} {Me}) ₂]I ₂ from [Pd(L _{Me}) ₂].....	69
Scheme 2.14: Synthesis of H ₂ L _{mtol}	74
Scheme 2.15: Synthesis of [Pd(L _{mtol}) ₄] and Pd(L _{mtol})(CN- <i>p</i> -tolyl).....	75
Scheme 2.16: Synthesis of Pd-L _{mtol} carbenes.	79
Scheme 2.17: Synthesis of Pd(L _{mtol})(=C(NH- <i>p</i> -tolyl)(pyrl)).....	80
Scheme 2.18: Synthesis of Pd(L _{mtol})(=C(NH- <i>p</i> -tolyl) ₂).	83
Scheme 2.19: Synthesis of Pd(L _{mtol})(DBU).....	89
Scheme 2.20: Synthesis of Pd(L _{mtol})(NH ₂ ⁿ Bu).	92
Scheme 2.21: Synthesis of H ₂ L _{ptol} reported by Horino <i>et al.</i>	93
Scheme 2.22: Synthesis of H ₂ L _{ptol} reported by Qi <i>et al.</i>	94
Scheme 2.23: Synthesis of H ₂ L _{ptol}	94
Scheme 2.24: Synthesis of Pd(L _{ptol})(NCCH ₃)-CH ₃ CN.....	95
Scheme 2.25: Pd(L _{ptol})(NCCH ₃) ligand exchange processes.....	98
Scheme 2.26: Synthesis of Pd(L _{ptol})(CN- <i>p</i> -tolyl).....	100
Scheme 2.27: Synthesis of Pd(L _{ptol})(=C(NH- <i>p</i> -tolyl) ₂).	101
Scheme 2.28: Synthesis of Pd(L _{ptol})(DBU).	102
Scheme 2.29: Proposed reaction of Pd(L _{ptol})(DBU) with methyl iodide.	104
Scheme 2.30: Synthesis of Pd(L _{ptol})(NH ₂ ⁿ Bu).....	106
Scheme 2.31: Synthesis of H ₂ L _{otol}	106
Scheme 2.32: Synthesis of [Pd(L _{otol}) ₄].....	108
Scheme 2.33: Synthesis of Pd(L _{otol})(CN- <i>p</i> -tolyl).....	109
Scheme 2.34: Synthesis of Pd(L _{otol})(=C(NH- <i>p</i> -tolyl) ₂).	111
Scheme 2.35: Synthesis of Pd(L _{otol})(DBU).	113
Scheme 2.36: Synthesis of Pd(L _{otol})(NH ₂ ⁿ Bu).....	119
Scheme 3.1: Nucleophilic attack at coordinated isocyanide on [Pt(CNR)(C ₅ H ₄ NMe- C ²)(dppe)][ClO ₄] ₂	124
Scheme 3.2: Proposed 2-pyridyl mediated reaction mechanism.	125
Scheme 3.3: Migratory insertion of CNR into Pd-C σ-bond.....	125
Scheme 3.4: Proposed synthetic routes to [H ₂ L _{Me} {Me} ₂]I ₂ and [PdX(L _{Me} {Me} ₂)X]. .	126
Scheme 3.5: Synthesis of [H ₂ L _{Me} {Me} ₂][OTf] ₂	127
Scheme 3.6: Synthesis of [PdCl(L _{Me} {Me} ₂)]OTf.....	131
Scheme 3.7: Synthesis of [Pd(L _{Me} {Me} ₂)(NCCH ₃)] [OTf] ₂	133
Scheme 3.8: Synthesis of [Pd(L _{Me} {Me} ₂)(OH ₂)] [OTf] ₂	140
Scheme 3.9: Postulated carbon monoxide-mediated β-hydride elimination mechanism.	143

Scheme 3.10: Synthesis of $[\text{Pd}(\text{L}_{\text{Me}}\{\text{Me}\}_2)(\text{NH}_3)][\text{OTf}]_2$.	144
Scheme 3.11: Synthesis of $[\text{Pd}(\text{L}_{\text{Me}}\{\text{Me}\}_2)(\text{CN-}i>p\text{-tolyl})][\text{OTf}]_2$.	145
Scheme 3.12: Synthesis of $[\text{Pd}(\text{L}_{\text{Me}}\{\text{Me}\}_2)(=\text{C}(\text{NH-}i>p\text{-tolyl})_2)][\text{OTf}]_2$.	147
Scheme 3.13: Ligand substitution reactions of $[\text{Pd}(\text{L}_{\text{Me}}\{\text{Me}\}_2)(\text{NCCH}_3)][\text{OTf}]_2$ and the formation of the carbene complex $[\text{Pd}(\text{L}_{\text{Me}}\{\text{Me}\}_2)(=\text{C}(\text{NH-}i>p\text{-tolyl})_2)][\text{OTf}]_2$.	148
Scheme 3.14: Representative synthetic pathway for synthesis of dicationic <i>o</i> -pyridinium ligand.	150
Scheme 3.15: 3- <i>N</i> -methylquinolinium ligand acting as ONO donor.	150
Scheme 3.16: Synthesis of $\text{H}_2\text{L}_{\text{opy}}$.	151
Scheme 3.17: Synthesis of $[\text{H}_2\text{L}_{\text{opy}}\{\text{Me}\}_2][\text{OTf}]_2$.	151
Scheme 3.18: Synthesis of $[\text{PdCl}(\text{L}_{\text{opy}}\{\text{Me}\}_2)]\text{OTf}$.	154
Scheme 3.19: Synthesis of $[\text{Pd}(\text{L}_{\text{opy}}\{\text{Me}\}_2)(\text{OH}_2)][\text{OTf}]_2$.	155
Scheme 3.20: Synthesis of $[\text{Pd}(\text{L}_{\text{opy}}\{\text{Me}\}_2)(\text{CN-}i>p\text{-tolyl})][\text{OTf}]_2$.	157
Scheme 3.21: Synthesis of $[\text{Pd}(\text{L}_{\text{opy}}\{\text{Me}\}_2)(=\text{C}(\text{NH-}i>p\text{-tolyl})_2)][\text{OTf}]_2$.	158
Scheme 3.22: Synthesis of $\text{H}_2\text{L}_{\text{mpy}}$.	159
Scheme 3.23: Synthesis of $[\text{H}_2\text{L}_{\text{mpy}}\{\text{Me}\}_2][\text{OTf}]_2$.	162
Scheme 3.24: Synthesis of $[\text{PdCl}(\text{L}_{\text{mpy}}\{\text{Me}\}_2)]\text{OTf}$.	165
Scheme 3.25: Synthesis of $[\text{Pd}(\text{L}_{\text{mpy}}\{\text{Me}\}_2)(\text{OH}_2)][\text{OTf}]_2$.	166
Scheme 3.26: Synthesis of $\text{H}_2\text{L}_{\text{ppy}}$.	167
Scheme 3.27: Synthesis of $[\text{H}_2\text{L}_{\text{ppy}}\{\text{Me}\}_2][\text{OTf}]_2$.	168
Scheme 3.28: Synthesis of $[\text{PdCl}(\text{L}_{\text{ppy}}\{\text{Me}\}_2)]\text{OTf}$.	171
Scheme 3.29: Proposed synthetic routes to $[\text{Pd}(\text{L}_{\text{ppy}}\{\text{Me}\}_2)(\text{NCCH}_3)][\text{OTf}]_2$.	172
Scheme 3.30: Synthesis of $[\text{Pd}(\text{L}_{\text{ppy}}\{\text{Me}\}_2)(\text{OH}_2)][\text{OTf}]_2$.	176
Scheme 3.31: Synthesis of $[\text{Pd}(\text{L}_{\text{ppy}}\{\text{Me}\}_2)(\text{DBU})][\text{OTf}]_2$.	177
Scheme 3.35: Conversion of cationic amidopyridinium salt to a neutral imine.	179
Scheme 3.36: Potential mechanism of formation and resonance isomers of neutral <i>ortho</i> and <i>para</i> imine ligands.	179
Scheme 3.37: Synthesis of $\text{L}_{\text{Me}}\{\text{Me}\}_2$.	181
Scheme 3.38: Synthesis of $\text{L}_{\text{opy}}\{\text{Me}\}_2$.	181
Scheme 4.1: Syntheses of $\text{H}_2\text{L}_{\text{NH}_2}$ and $\text{H}_4\text{L}_{\text{acrA}}$.	197
Scheme 4.2: Proposed syntheses of catenanes and large macrocycles. Acrylyl ligand represented by curves.	198
Scheme 4.3: Synthesis of $[\text{Pd}(\text{H}_2\text{L}_{\text{acrA}})]_2$.	199
Scheme 4.4: Synthesis of $\text{Pd}(\text{H}_2\text{L}_{\text{acrA}})(\text{DBU})$.	203
Scheme 4.5: Synthesis of $[\text{Hg}(\text{H}_2\text{L}_{\text{acrA}})]_2$.	204
Scheme 4.6: $[\text{Co}(\text{H}_2\text{L}_{\text{acrA}})_2]^+$ and $[\text{Co}(\text{H}_2\text{L}_{\text{en}})_2]^+$.	205

Scheme 4.7: Attempted ring-closing reaction of Pd(H ₂ L _{acrA})(DBU) with <i>n</i> -butylamine.	206
Scheme 4.8: General synthesis of extended acyclic ligands.	207
Scheme 4.9: Synthesis of H ₄ L _{pdnA} .	209
Scheme 4.10: Synthesis of Pd(OAc) ₂ (H ₄ L _{pdnA}).	213
Scheme 4.11: Syntheses of [Pd(H ₂ L _{pdnA}) ₂].	217
Scheme 4.12: Synthesis of Pd(H ₂ L _{pdnA})(DBU).	221
Scheme 4.13: Synthesis of [PdCl ₂ (H ₄ L _{pdnA} {H} ₂)]Cl ₂ .	223
Scheme 4.14: Synthesis of [Pd(H ₂ L _{pdnA} {Me} ₂)(DBU)]I ₂ .	224
Scheme 4.15: Synthesis of [Hg(H ₂ L _{pdnA}) ₂ ·2CH ₃ COOH].	226
Scheme 4.16: Synthesis of [Co(H ₂ L _{pdnA}) ₂] ⁺ .	232
Scheme 4.17: Synthesis of [HDBU][Fe(H ₂ L _{pdnA}) ₂].	233
Scheme 4.18: Synthesis of H ₄ L _{SpyA} .	235
Scheme 4.19: Synthesis of [Pd(H ₂ L _{SpyA}) ₂].	237
Scheme 4.20: Synthesis of Pd(H ₂ L _{SpyA})(DBU).	239
Scheme 4.21: Synthesis of [Hg(H ₂ L _{SpyA}) ₂].	240
Scheme 4.22: Reaction of H ₄ L _{SpyA} with CoCl ₂ ·2H ₂ O.	242
Scheme 5.1: Syntheses of H ₄ L _{nBu} and H ₄ L _{en} .	245
Scheme 5.2: Synthesis of PdCl(H ₃ L _{nBu}).	248
Scheme 5.3: Synthesis of Pd(H ₂ L _{nBu})(NH ₂ Lac[7]).	253
Scheme 5.4: Synthesis of Pd(H ₂ L _{nBu})(NH ₂ Lac[5]).	260
Scheme 5.5: Proposed synthesis of palladium-DBU complex of H ₄ L _{nBu} .	261
Scheme 5.6: Synthesis of Pd(H ₂ L _{nBu})(NH ₂ ⁿ Bu).	267
Scheme 5.7: Synthesis of Pd(H ₂ L _{nBu})(DBU).	269
Scheme 5.8: Summary of synthetic approaches to Pd(H ₂ L _{nBu})(NH ₂ Lac[7]).	273
Scheme 5.9: Synthesis of Pd(H ₂ L _{nBu})(CN- <i>p</i> -tolyl).	274
Scheme 5.10: Synthesis of Pd(H ₂ L _{nBu})(NH ₂ - <i>p</i> -tolyl).	275
Scheme 5.11: Synthesis of H ₄ L _{dmen} .	278
Scheme 5.12: Synthesis of [Pd(H ₃ L _{dmen})]OAc.	280
Scheme 5.13: Synthesis of Hg(H ₂ L _{dmen}).	282
Scheme 5.14: Synthesis of [Pd(H ₂ L _{dmen})(NH ₂ Lac[7])].	286
Scheme 5.15: Synthesis of H ₄ L _{amp} .	288
Scheme 5.16: Synthesis of [Pd(H ₃ L _{amp})]OAc.	289
Scheme 5.17: Synthesis of Hg(H ₂ L _{amp}).	289
Scheme 5.18: Synthesis of H ₄ L _{aep} .	290

Scheme 5.19: Synthesis of BPEDA·4HCl.	293
Scheme 5.20: Synthesis of H ₄ L _{msamp}	294
Scheme 5.21: Synthesis of [Pd ₂ (H ₂ L _{msamp})] [OAc] ₂	297

List of Tables

Table 2.1: Selected bond lengths (Å) and angles (°) for Pd(L _{Me})(DBU).	56
Table 2.2: Selected bond lengths (Å) and angles (°) for [PdI(L _{Me} {Me} ₂)]I.	72
Table 2.3: Selected bond lengths (Å) and angles (°) for Pd(L _{mtol})(CN- <i>p</i> -tolyl).	77
Table 2.4: Selected bond lengths (Å) and angles (°) for Pd(L _{mtol})(=C(NH- <i>p</i> -tolyl)(pyrl)).	82
Table 2.5: Selected bond lengths (Å) and angles (°) for Pd(L _{mtol})(=C(NH- <i>p</i> -tolyl) ₂). ...	87
Table 2.6: Selected bond lengths (Å) and angles (°) for Pd(L _{mtol})(DBU).	91
Table 2.7: Selected bond lengths (Å) and angles (°) for Pd(L _{ptol})(NCCH ₃).	97
Table 2.8: Selected bond lengths (Å) and angles (°) for Pd(L _{ptol})(DMSO- <i>d</i> ₆).	99
Table 2.9: Selected bond lengths (Å) and angles (°) for Pd(L _{ptol})(DBU).	103
Table 2.10: Selected bond lengths (Å) and angles (°) for Pd(L _{otol})(CN- <i>p</i> -tolyl).	110
Table 2.11: Δ <i>G</i> [‡] values for biphenyl derivatives.	117
Table 2.12: Selected bond lengths (Å) and angles (°) for Pd(L _{otol})(DBU).	118
Table 2.13: Results of DBU displacement experiments.	121
Table 3.1: Selected bond lengths (Å) and angles (°) for [H ₂ L _{Me} {Me} ₂][OTf].	129
Table 3.2: Selected bond lengths (Å) and angles (°) for [Pd(L _{Me} {Me} ₂)(NCCH ₃)] [OTf] ₂	136
Table 3.3: Selected bond lengths (Å) and angles (°) for [Pd(L _{Me} {Me} ₂)(OH ₂)] [OTf] ₂	139
Table 3.4: Selected bond lengths (Å) and angles (°) for [H ₂ L _{opy} {Me} ₂][OTf] ₂	153
Table 3.5: Selected bond lengths (Å) and angles (°) for [Pd(L _{opy} {Me} ₂)(OH ₂)] [OTf] ₂	156
Table 3.6: Selected bond lengths (Å) and angles (°) for H ₂ L _{mpy}	160
Table 3.7: Selected bond lengths (Å) and angles (°) for [H ₂ L _{mpy} {Me} ₂][OTf] ₂	163
Table 3.8: Selected bond lengths (Å) and angles (°) for [H ₂ L _{ppy} {Me} ₂][OTf] ₂	169
Table 3.9: -CH ₃ ...O=C distances in <i>N</i> -methylnicotinamide derivatives.	170
Table 3.10: Selected bond lengths (Å) and angles (°) for [Pd(OAc)(L _{ppy} {Me} ₂)]OTf.	174
Table 3.11: Selected bond lengths (Å) and angles (°) for L _{opy} {Me} ₂	183

Table 3.12: Half-times for <i>p</i> -tolyl carbene formation.	190
Table 3.13: $\nu(\text{C}\equiv\text{N})$ for isocyanide complexes.	192
Table 4.1: Chemical shifts (ppm) and coupling constants (Hz) for $[\text{Pd}(\text{H}_2\text{L}_{\text{acrA}})]_2$ vinyl groups used in simulation of ^1H NMR spectrum.	201
Table 4.2: Selected bond lengths (\AA) and angles ($^\circ$) for $\text{Pd}(\text{OAc})_2(\text{H}_4\text{L}_{\text{pdnA}})$	215
Table 4.3: Selected bond lengths (\AA) and angles ($^\circ$) for $[\text{Hg}(\text{H}_2\text{L}_{\text{pdnA}})]_2$	228
Table 5.1: Selected bond lengths (\AA) and angles ($^\circ$) for $\text{PdCl}(\text{H}_3\text{L}_{\text{nBu}})$	250
Table 5.2: Selected bond lengths (\AA) and angles ($^\circ$) for $\text{Pd}(\text{H}_2\text{L}_{\text{nBu}})(\text{NH}_2\text{Lac}[7])$	255
Table 5.3: Selected bond lengths (\AA) and angles ($^\circ$) for $\text{Pd}(\text{H}_2\text{L}_{\text{nBu}})(\text{OH}_2)$	264
Table 5.4: Selected bond lengths (\AA) and angles ($^\circ$) for $\text{Hg}(\text{H}_2\text{L}_{\text{dmen}})$	284

List of Charts

Chart 3.1: Histogram comparing selected bond lengths of BTDP, $\text{L}_{\text{opy}}\{\text{Me}\}_2$, $\text{H}_2\text{L}_{\text{opy}}\{\text{Me}\}_2$, and $[\text{H}_2\text{L}_{\text{Me}}\{\text{Me}\}_2][\text{OTf}]_2$	187
Chart 3.2: Histogram comparing selected bond lengths of $\text{L}_{\text{opy}}\{\text{Me}\}_2$, $[\text{H}_2\text{L}_{\text{Me}}\{\text{Me}\}_2][\text{OTf}]_2$, $[\text{Pd}(\text{L}_{\text{Me}}\{\text{Me}\}_2)(\text{NCCH}_3)][\text{OTf}]_2$, $[\text{Pd}(\text{L}_{\text{Me}}\{\text{Me}\}_2)(\text{OH}_2)][\text{OTf}]_2$ and $[\text{PdI}(\text{L}_{\text{Me}}\{\text{Me}\}_2)]\text{I}$	188
Chart 3.3: Histogram comparing selected bond lengths of $[\text{H}_2\text{L}_{\text{ppy}}\{\text{Me}\}_2][\text{OTf}]_2$ and $[\text{Pd}(\text{OAc})(\text{L}_{\text{ppy}}\{\text{Me}\}_2)]\text{OTf}$	189

List of Equations

Equation 2.1	116
Equation 2.2	116
Equation 2.3	116
Equation 3.1	187

List of Abbreviations

1D = One dimensional

2D = Two dimensional

AR = Analytical reagent

bipy = 2,2'-Bipyridyl

BPEDA = *N,N'*-Bis(2-pyridylmethyl)ethylenediamine

BTDP = (2-Benzoylimino)-1,4,6-trimethyl-1,2-dihydropyridine

br = Broad

Calc = Calculated

CCDB = Cambridge Crystallographic Database

CCDC = Cambridge Crystallographic Data Centre

COD = 1,5-Cyclooctadiene

COSY = Homonuclear correlation spectroscopy

Cp = Cyclopentadiene

d = Doublet

DBN = 1,5-Diazabicyclo[4.3.0]non-5-ene

DBU = 1,8-Diazabicyclo[5.4.0]undec-7-ene

DEPT 135 = Distortionless Enhancement by Polarization Transfer, 135° pulse angle

DIPA = Diisopropanolamine

DMSO = Dimethylsulfoxide

DPPM = bis(diphenylphosphino)methane

DPPP = 1,3-bis(diphenylphosphino)propane

Edited-HSQC = Heteronuclear Single Quantum Coherence, CH₂ peaks inverted

EI = Electron Impact

FAB = Fast Atom Bombardment

gem = Geminal

H₂EDTA²⁻ = Ethylenediaminetetraacetic acid, disodium salt

HMBC = Heteronuclear Multiple Bond Correlation

HSQC = Heteronuclear Single Quantum Coherence

LUMO = Lowest Unoccupied Molecular Orbital

m = Multiplet (NMR) / Medium (infrared)

NDB = Norbornadiene

NH₂Lac[5] = *N*-(3-Aminopropyl)- γ -butyrolactam

NH₂Lac[7] = *N*-(3-Aminopropyl)- ϵ -caprolactam

NHC = *N*-heterocyclic carbene

NMR = Nuclear Magnetic Resonance

N_{obs} = Number of observations

ORTEP = Oak Ridge Thermal Ellipsoid Plot

q = Quaternary

RCM = Ring Closing Metathesis

s = Singlet

SCE = Saturated calomel electrode

SD = Standard deviation

t = Triplet

TFA = Trifluoroacetate anion

THF = Tetrahydrofuran

TLC = Thin-layer chromatography

TMS = Tetramethylsilane

TOCSY = Total Correlation Spectroscopy

VT NMR = Variable Temperature Nuclear Magnetic Resonance