# Transition Metal Complexes Bearing Hemilabile Pincer Ligands: Towards Enhanced Catalytic Activity

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# Preface

This thesis is a report of original research undertaken by the author and is submitted for the admission to the degree of Doctor of Philosophy at Macquarie University. This work was performed in the Department of Chemistry and Biomolecular Sciences at Macquarie University and the School of Chemistry at the University of New South Wales during the period of March 2013 to August 2016. The work and results presented in this thesis are those of the author, unless otherwise acknowledged.

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# List of Abbreviations

| | |
|---|---|
| Ar | aryl |
| acac | acetylacetonato |
| $BAr^F_4$ | *tetrakis*[3,5-*bis*(trifluoromethyl)phenyl]borate anion |
| bar | reaction pressure in bar |
| $BPh_4$ | *tetra*-phenylborate anion |
| bpm | *bis(pyrazolyl)methane* |
| br | broad (NMR) |
| $^tBu$ | tert-butyl |
| °C | degrees celcius |
| cat | catalyst |
| CO | carbon monoxide |
| COD | 1,5-cyclooctadiene |
| $C_2D_2Cl_4$ | deuterated 1,1,2,2-tetrachloroethane |
| conv. | conversion (%) |
| $\delta$ | chemical shift (ppm) |
| d | doublet (NMR) |
| DCM | dichloromethane |
| dppe | 1,2-bis(diphenylphosphino)ethane |
| dppp | 1,3-bis(diphenylphosphino)propane |
| equiv. | equivalent |
| ee | enantiomeric excess |

| | |
|---|---|
| ESI-MS | ElectroSpray Ionisation Mass Spectrometry |
| Et | ethyl |
| $Et_2O$ | diethyl ether |
| EtOAc | ethyl acetate |
| fwhm | full width at half maximum |
| GC-MS | Gas Chromatography-Mass Spectrometry |
| h | hour |
| Hz | hertz |
| HMBC | Heteronuclear Multiple Bond Coherence (NMR) |
| HSQC | Heteronuclear Single Quantum Coherence (NMR) |
| *i* | ipso |
| $^{i}Pr$ | isopropyl |
| IR | infrared |
| *J* | scalar coupling constant (NMR) |
| L | ligand |
| m | multiplet (NMR) |
| *m* | *meta* |
| Me | methyl |
| MeOH | methanol |
| min | minute(s) |
| mol | mole |
| mmol | millimoles |

| | |
|---|---|
| m/z | mass to charge ratio |
| nbd | norbornadiene |
| *NCN* | pincer ligands with nitrogen-carbon-nitrogen donor atoms |
| $NCN^{Et}$ | pyrazolyl-imidazolyl-pyrazolyl ligand (ethylene linker) |
| $NCN^{Me}$ | pyrazolyl-imidazolyl-pyrazolyl ligand (methylene linker) |
| $NEt_3$ | triethylamine |
| NHC | N-heterocyclic carbene |
| *NNN* | pincer ligands with Nitrogen-Nitrogen-Nitrogen donor atoms |
| NMR | Nuclear Magnetic Resonance |
| *o* | ortho |
| ORTEP | Oak Ridge Thermal Ellipsoid Plot (Program) |
| OTf | triflate |
| *p* | *para* |
| *PCP* | pincer ligands with Phosphorous-Carbon-Phosphorous donor atoms |
| PHOX | phosphinooxazolines |
| *PN* | bidentate ligands with Phosphorous-Nitrogen donor atoms |
| *PNP* | pincer ligands with Phosphorous-Nitrogen-Phosphorous donor atoms |
| *PNN* | pincer ligands with Phosphorous-Nitrogen-Nitrogen donor atoms |
| Ph | phenyl |
| ppm | parts per million |
| Py | pyridine |
| Pz | pyrazole |

| | |
|---|---|
| q | quartet (NMR) |
| RT | room temperature |
| s | singlet (NMR) |
| S/C | substrate to catalyst ratio |
| t | triplet (NMR) |
| THF | tetrahydrofuran |
| TOF | turnover frequency |
| Tol | toluene |
| Triphos | bis(2-diphenylphosphinoethyl)phenylphosphine |
| U.V. | Ultraviolet |
| VT | variable temperature |

# Table of Contents

Preface i

Acknowledgements iii

List of Abbreviations v

Table of Contents ix

List of Figures xvi

List of tables xix

List of Schemes xxi

Abstract xxv

Chapter 1. Introduction

1.1. Organometallic complexes in catalysis 1

1.2. Transition metal catalyst design 3

1.2.1. The metal centre 3

1.2.1.1. Ruthenium, nickel and gold as active and air/moisture stable catalysts 3

1.2.2. Ligand properties 4

1.2.2.1. N-Heterocyclic carbenes (NHCs) 4

1.2.2.2. Nitrogen donor ligands 6

1.2.2.3. Tridentate ligands 7

1.2.2.4. Hemilabile pincer ligands 8

1.2.3. Counterions 11

1.3. Transition metal complexes in homogeneous catalysis 12

1.3.1. Transition metal catalysed $H_2$ addition to a polar unsaturated bond 12

1.3.2. Transition metal catalysed C-C bond coupling reactions 14

1.3.3. Transition metal catalysed X-H bond addition reactions 16

1.4. Objectives 20

1.5. References 23

**Chapter 2. Ru(II) complexes of hemilabile pincer ligands for catalysed transfer hydrogenation reactions**

2.1. Introduction 27

2.1.1. Transition metal catalysed hydrogenation reaction 27

2.1.2. Ruthenium catalysed hydrogenation reactions 27

2.1.3. Transfer hydrogenation as an alternative to hydrogenation reactions 29

2.1.4. Transition metal complexes containing pincer ligands for the transfer hydrogenation of ketones 30

2.1.5. Ruthenium complexes containing pincer ligands for the transfer hydrogenation reaction 31

2.1.6. Ruthenium complexes containing hemilabile ligands 33

2.1.7. Ruthenium complexes containing hemilabile pincer ligands 35

2.1.8. Ruthenium complexes of pincer ligands with a central NHC donor 36

2.1.9. Rhodium and Iridium complexes with pincer ligands 37

2.2. Aims of this chapter 39

2.3. Synthesis of Ru(II) complexes containing a hemilabile *NCN*$^{Me}$ pincer ligand 40

2.3.1. Synthesis and characterisation of [Ag(I)(*NCN*$^{Me}$)$_2$]BPh$_4$ (**2**) 40

2.3.2. Synthesis and characterisation of [Ru(II)(η$^6$- C$_6$H$_6$)(*NCN*$^{Me}$)Cl]BPh$_4$ (**3**) 42

2.3.3. Synthesis and characterisation of Ru(II)(η$^6$- C$_{10}$H$_{14}$)(*NCN*$^{Me}$)Cl]BPh$_4$(**4**) 44

2.3.4. Synthesis and characterisation of [Ru(II)(H)CO(*NCN*$^{Me}$)(PPh$_3$)$_2$]BPh$_4$ (**5**) 47

2.3.4.1. Isomerisation reaction of [Ru(II)(H)CO(*NCN*$^{Me}$)(PPh$_3$)$_2$] (**5**) 49

2.3.4.2. Synthesis of an unexpected cubane structure [Ru(I)Cl(PPh$_3$)]$_4$ (**6**) 50

2.3.5. Synthesis and characterisation of [Ru(II)(*NCN*$^{Me}$)$_2$]BPh$_4$ (**7**) 52

2.3.6. Comparison of solid state structures 55

2.4. Catalysed transfer hydrogenation of ketones using complexes **3**, **4**, **4a**, **5**, **5a** and **7** 57

2.5. Conclusions 64

2.6. References 66

Chapter 3. Ni(II) complexes of hemilabile pincer ligands for catalysed Kumada cross coupling reactions

3.1. Introduction 70

3.1.1. Transition metal catalysed C-C bond formation reactions 70

3.1.2. Catalysts for the Kumada cross coupling reactions 71

3.1.3. The mechasims of Kumada cross coupling reactions 75

3.1.4. Nickel complexes containing pincer ligands as catalysts for the Kumada cross coupling reaction: ligand effects 76

3.1.4.1. Electron donating ability and its effects on catalytic activity 77

3.1.4.2. Pincer ligands with strongly coordinating side arm donors 78

3.1.4.3. Pincer ligands with weakly coordinating side arms: towards hemilability 80

3.2. Aims of this chapter 83

3.3. Synthesis of Ni(II) complexes containing an *NCN*$^{Me}$ hemilabile pincer ligand 84

3.3.1. Synthesis, characterisation and coordination study of [Ni(*NCN*$^{Me}$)Cl].$BPh_4$ (**8**) 84

3.3.2. Coordination chemistry of [Ni(*NCN*$^{Me}$)Cl]$BPh_4$ 90

3.3.3. Synthesis and characterisation of (*NCN*$^{Me}$)$PF_6$ (**1b**) 93

3.3.4. Synthesis and characterisation of [Ni(*NCN*$^{Me}$)Cl]$PF_6$ (**9**) 94

3.3.5. Synthesis and characterisation of [Ni(*NCN*$^{Et}$)$_2$]($BPh_4$)$_2$ (**10**) 96

3.3.6. Comparison of the inner coordination sphere of complexes **8**, **9** and **10**. 102

3.4. Catalytic activity of Ni(II) complexes for Kumada cross coupling of aryl halides 103

3.4.1. Catalytic activity of **8**, **9** and **10** for Kumada cross coupling reactions of chlorobenzene and bromobenzene 104

3.4.2. Substrate scope of complex **8** for the Kumada cross coupling reaction 106

3.5. Conclusions 109

3.6. References 111

Chapter 4. Gold(I) and Gold(III) complexes of hemilabile pincer ligands for catalysed activation of alkynes

4.1. Introduction 114

4.1.1. Transition metal catalysed addition of X-H bonds to alkynes 114

4.1.1.1. Transition metal catalysed hydroalkoxylation reactions 114

4.1.1.2. Transition metal catalysed hydroamination reactions 118

4.1.2. Transition metal complexes containing pincer ligands for catalysed addition of X-H bonds to alkynes 119

4.1.2.1. Transition metal complexes containing pincer ligands as catalysts for hydroalkoxylation reactions 120

4.1.2.2. Transition metal catalysts containing pincer ligands for hydroamination reactions 122

4.1.2.3. Metal complexes containing hemilabile pincer ligands for the addition of X-H bonds to the C-C multiple bond of alkenes or alkynes 124

4.2. Aims of this chapter 125

4.3. Synthesis of Gold(I) and Gold(III) complexes containing an $NCN^{Me}$ hemilabile pincer ligand 127

4.3.1. Synthesis and characterisation of [Au(I)($NCN^{Me}$)Cl]$BPh_4$ (**11**) 127

4.3.2. Synthesis and characterisation of [Au(III)($NCN^{Me}$)Cl]$BPh_4$ (**12**) 128

4.3.3. Comparison of the solid state structures of **11** and **12** 130

4.3.4. Attempted synthesis of Au(I)/Rh(I) bimetallic complexes 132

4.4. Catalysed hydroalkoxylation reactions using complexes **11** and **12**. 135

4.4.1. Catalysed dihydroalkoxylation of 2-(5-hydroxypent-1-ynyl)benzylalcohol (**14**). 135

4.4.2. Catalyst scope: investigating substrates with varying structure (**15**, **16**) 146

4.5. Catalysed hydroamination reactions using complexes **11** and **12**. 148

4.5.1. Intramolecular hydroamination reactions catalysed by complexes **11** and **12**. 149

4.5.2. Intermolecular hydroamination reactions catalysed by complexes **11** and **12** 153

4.6. Conclusions 156

4.7. References 157

Chapter 5. Conclusions and Future work

5.1. Conclusions 161

5.1.1. Chapter 2 161

5.1.2. Chapter 3 163

5.1.3. Chapter 4 164

5.2. Future work 166

Chapter 6. Experimental

General Procedures 169

6.1. Experimental for Chapter 2 171

6.1.1. Synthesis of Ru(II) complexes 171

6.1.2. Catalysed transfer hydrogenation reactions using Ru(II) complexes **3**-**6**. 177

General procedure for transfer hydrogenation reactions 177

6.1.3. Crystal data for chapter 2 183

6.2. Experimental for chapter 3 184

6.2.1. Synthesis of Ni(II) complexes 184

6.2.2. Catalysed Kumada cross coupling reactions using complexes **8**, **9** and **10**. 187

6.2.3. Crystal data for chapter 3 193

6.3. Experimental for chapter 4 197

6.3.1. Synthesis of Au(I) and Au(III) complexes 197

6.3.2. Catalysed dihydroalkoxylation reactions using complexes **11** and **12** 198

6.3.3. Catalysed hydroamination reactions using complexes **11** and **12** 209

6.3.4. Crystal data for chapter 4 215

6.4. References: 217

Appendices in CD

# List of Figures

Figure 1.1 General structures of imidazolylidenes and imidazolinylidenes ..... 5

Figure 1.2 Typical N-donor ligand systems..... 7

Figure 1.3 Common motifs of pincer ligands ..... 8

Figure 1.4 Varying coordination strengths of counterions..... 12

Figure 1.5 Pharmaceutical compounds containing nitrogen/oxygen heterocycles..... 17

Figure 2.1 Early examples of hydrogenation catalysts: a) Crabtrees catalyst, and b) (S)-iPr–PHOX. ..... 27

Figure 2.2 Ligand selective hydrogenation of ketones. ..... 28

Figure 2.3 Early Ru(II) catalysts for the transfer hydrogenation reaction, left: Schvo's catalyst, right: Ru(II)arene complex containing a *PN* bidentate ligand. ..... 30

Figure 2.4 Recent examples of catalysts for the transfer hydrogenation reaction a) [Co(II)(*PBP*)$N_2$], b) [Fe(II)(*PNP*)CO(H)Br], and c) [Ir(III)(*PNP*)$H_2$]. ..... 31

Figure 2.5 Ru(II) complexes containing pincer ligands by, a) van Koten and b) Milstein. ..... 32

Figure 2.6 Best catalyst for transfer hydrogenation of ketones. ..... 32

Figure 2.7 Transfer hydrogenation of ketones catalysed by Ru(II) complexes with hemilabile pincer ligands. ..... 36

Figure 2.8 Comparison of other carbene-based ligands with pendant N-heterocyclic donor groups.. ..... 38

Figure 2.9 X-ray crystal structure of the imidazolium bis-pyrazole ligand **1**. ..... 40

Figure 2.10 ORTEP depiction of the structure of complex **2** with ellipsoids at 50% probability. ..... 42

Figure 2.11 ORTEP depiction of the structure of complex **3** showing atom labeling scheme.. ..... 44

Figure 2.12 ORTEP depiction of the structure of complex **4a** showing atom labeling scheme. ..... 45

Figure 2.13 $^{1}$H NMR spectrum of Ru(II)($\eta^{6}$- $C_{10}H_{14}$)(*NCN*$^{Me}$)Cl]$BPh_4$[$B_5O_6(OH)_4$]. ..... 46

Figure 2.14 ORTEP depiction of the structure of complex **5** showing atom labeling scheme. ..... 49

Figure 2.15 Stacked $^{1}$H NMR spectra of the hydride resonance regions at 72 $^{o}$C for complexes **5** and **5a**. (H trans to pyrazole + H cis to pyrazole). ..... 50

Figure 2.16 Molecular structure of complex **6** showing atom labeling scheme.. ..... 51

Figure 2.17 Variable temperature $^{1}$H NMR spectra of [Ru(II)(*NCN*$^{Me}$)$_2$](BPh$_4$)$_2$(**7**) showing the isomerisation between the *fac* isomer (**7**) and *mer* isomer (**7a**). ..... 54

Figure 2.18 Facial and meridional coordination modes of [Ru(II)(*NCN*$^{Me}$)$_2$](BPh$_4$)$_2$..... 55

Figure 2.19 ORTEP depiction of the solid state structure of complex **7** at 50% probability thermal ellipsoids showing the *fac* coordination.. ..... 55

Figure 3.1 Ni(II) complexes containing pincer ligands with strongly coordinating NHC donors. ..... 79

Figure 3.2 ORTEP depiction of complex **8** with 50 % probability ellipsoids for all non-hydrogen atoms.. ..... 86

Figure 3.3 D-orbital energy level diagrams of the d-orbital electrons arising from different conformations possible for complexes of nickel(II). ..... 87

Figure 3.4 Variable temperature NMR (600 MHz, acetone-d$_6$) of complex **8**. ..... 89

Figure 3.5 Different conformations possible for complex **8**..... 90

Figure 3.6 $^{1}$H NMR (500 MHz, acetone-$d_6$, 25 °C) stacked plots of **8** reacting with hard donor ligands. (a) xylylisocyanide, (b) pyridine, (c) $PMe_3$, (d) CO, (e) complex **8**. ..... 91

Figure 3.7 ORTEP depiction of complex **9** with 50 % probability ellipsoids for all non-hydrogen atoms.. ..... 96

Figure 3.8 ORTEP depiction of ligand **1c** with 50% probability ellipsoids for all non-hydrogen atoms.. ..... 97

Figure 3.9 Variable temperature $^{1}$H NMR spectra (600 MHz, Acetone-d) of complex **10**... 100

Figure 3.10 ORTEP depiction of complex **10** with 50% probability ellipsoids for all non-hydrogen atoms.. ..... 101

Figure 4.1 ORTEP depiction of the solid state structure of complex **11** at 50% probability thermal ellipsoids.. ..... 128

Figure 4.2 ORTEP depiction of the solid state structure of complex **12** at 50% probability thermal ellipsoids.. ..... 130

Figure 4.3 ORTEP depiction of complex **11** showing the distance between pyrazole nitrogens. ..... 131

Figure 4.4 $^{1}$H NMR (600MHz, acetone-$d_6$) of complex **11**. ..... 133

Figure 4.5 Variable temperature $^{1}$H NMR (400MHz, acetone-$d_6$) of heterobimetallic complex **13**. ..... 134

Figure 4.6 Comparison in catalytic activity of **12** with complexes in literature. [32 34] ..... 142

Figure 5.1 Ru(II) complex bearing a ligand with a boronate pendant arm ..... 166

# List of tables

Table 2.1 Selected bond lengths (Å) and angles (°) for **3**, **4a**, **5**, and **7**. ..... 56

Table 2.2 Catalytic transfer hydrogenation of ketones using complexes **4a** and **4**. ..... 63

Table 3.1 Selected bond lengths (Å) and angles (°) for **8**, **9** and **10**. ..... 102

Table 3.2 Kumada cross coupling reactions of PhBr and PhCl with PhMgBr catalysed by **8**, **9** and **10**. ..... 104

Table 3.3 Catalysed Kumada cross coupling of PhCl and PhBr using **8** at different catalyst loadings. ..... 106

Table 3.4 Range of substrates catalysed by **8** for Kumada cross coupling reactions. ..... 107

Table 4.1 Selected bond lengths(Å) and angles(°) for **11** and **12**. ..... 131

Table 4.2 Comparison of Au(I) vs Au(III) catalysts and the effect of counterion. ..... 139

Table 4.3 Summary of intramolecular hydroamination reactions of 4-pentyne-1-amine (**17**) and 5-phenyl-4-pentynamine (**18**) using complexes **11** and **12**. ..... 152

Table 6.1 Quantities of acetophenone and catalyst used. ..... 178

Table 6.2 Quantities of catalyst **4** and substrates used at 82 °C. ..... 180

Table 6.3 Quantities of catalyst **4** and substrates used at RT. ..... 181

Table 6.4 Quantities of catalyst **4a** and substrates used at 82 °C. ..... 181

Table 6.5 Quantities of catalyst **4a** and substrates used at RT. ..... 182

Table 6.6 Quantities of catalyst 4a and substrates used for $^{i}$PrOH/THF solvent mix.. ..... 182

Table 6.7 Quantities of catalyst and chlorobenzene and PhMgBr used. ..... 189

Table 6.8 Quantities of catalyst, bromobenzene and PhMgBr used. ..... 189

Table 6.9 Quantities of catalyst and iodobenzene and PhMgBr used. ..... 190

Table 6.10 Quantities of catalyst and substrates used. ..... 190

Table 6.11 Quantities of catalyst **8** and substrates used. ..... 192

Table 6.12 Quantities of catalyst and substrate **14** used. ..... 199

Table 6.13 Quantities of catalyst **12**, $NaBAr^F_4$ and substrate **14** used. ..... 201

Table 6.14 Quantities of catalyst, $NaBAr^F_4$ and substrate **14** used. ..... 203

Table 6.15 Quantities of catalyst, $NaBAr^F_4$, $AgSbF_6$ and substrate **14** used..... 204

Table 6.16 Quantities of catalyst and substrate **15** used. ..... 206

Table 6.17 Quantities of catalyst and substrate **14**, **15** used.. ..... 207

Table 6.18 Quantities of catalyst and substrate **16** used. ..... 209

Table 6.19 Quantities of catalyst and substrate **17** used at RT.. ..... 210

Table 6.20 Quantities of catalyst and substrate **17** used at 70 °C. ..... 211

Table 6.21 Quantities of catalyst and substrate **17** used at 100 °C. ..... 211

Table 6.22 Quantities of catalyst and substrate **18** used.. ..... 212

Table 6.23 Quantities of catalyst and substrate **19**/**19a** used at 100 °C..... 213

Table 6.24 Quantities of catalyst and substrate **19**/**19a** used at 70 °C.. ..... 214

# List of Schemes

Scheme 1.1 Monsanto process.. ..... 1

Scheme 1.2 Homogeneous transition metal catalysts for the hydrogenation reaction of alkenes.. ..... 63

Scheme 1.3 Regioselective hydrogenation of quinaxoline.. ..... 102

Scheme 1.4 Pd and Rh complexes with an *SNS* hemilabile pincer ligand.. ..... 9

Scheme 1.5 Complexes containing hemilabile pincer ligands..... 10

Scheme 1.6 Ru(II) complex with a NNP hemilabile pincer ligand.. .....11

Scheme 1.7 Typical hydrogenation and dehydrogenative coupling reactions.. .....13

Scheme 1.8 Transition metal catlysed hydrogenation reactions... .....13

Scheme 1.9 Synthetic production of terpenes.. ..... 14

Scheme 1.10 Conversion of steroid ethers to 6-methyl steroids.....14

Scheme 1.11 Pd and Ni catalyzed coupling reactions.....16

Scheme 1.12 Dihydroalkoxylation of alkyne diols and hydroamination of alkynamines.....17

Scheme 1.13 X-H bond addition reactions catalyzed by simple metal complexes.....18

Scheme 1.14 X-H bond addition reactions catalyzed by copper complexes.....19

Scheme 2.1 First reported hemilabile ligand coordinated to Ru(II) and its reactivity to CO... .....34

Scheme 2.2 Ru(II) complexes containing hemilabile monophosphite ligands.....34

Scheme 2.3 Ru(II) complexes containing a pincer ligand with a central NHC donor.....37

Scheme 2.4 Synthesis of imidazolium bis-pyrazole ligand **1** from chloromethylpyrazole and trimethylsilyl imidazole.. .....40

Scheme 2.5 Synthesis of $[Ag(I)(NCNMe)_2]BPh_4$ (**2**).....41

Scheme 2.6 Synthesis of $[Ru(II)(\eta^6\text{-}C_6H_6)(NCN^{Me})Cl]BPh_4$ (**3**) from **2**.....43

Scheme 2.7 Synthesis of $[Ru(\eta^6\text{–}C_{10}H_{14})(NCN^{Me})Cl]BPh4[B_5O_6(OH)_4]$ (**4a**).....45

Scheme 2.8 Synthesis of $[Ru(II)(\eta^6\text{-}p\text{-cym})(NCN^{Me})Cl]BPh_4$ (**4**).....47

Scheme 2.9 Synthesis of $[Ru(H)CO(NCN^{Me})(PPh_3)_2]BPh_4$ (**5**) from **1**.....48

Scheme 2.10 Synthesis of $[Ru(II)(NCN^{Me})_2](BPh_4)_2$ (**7**).....52

Scheme 3.1 Kumada cross coupling as a key synthetic step in the production of (a) Aliskiren and (b) polythiophenes.....71

Scheme 3.2 Kumada cross coupling reactions catlysed by: (a) an in situ generated bis-oxazoline Ni(II) complex, (b) a pre-prepared Ni(II) catalyst and (c) an iron(III) catalyst... .....73

Scheme 3.3 Recent Pd(II) and Ni(II) catalysed Kumada cross coupling reactions.....74

Scheme 3.4 Selective Kumada cross coupling reactions.....75

Scheme 3.5 Kumada coupling mechanisms: a) conventional mechanism and b) mechanism with Ni(IV) intermediate.. .....76

Scheme 3.6 Effect of varying electron donating abilities of ligands used in Ni(II) catalysed Kumada cross coupling reactions: (a) coupling of alkyl Gringard reagents; (b) coupling of aryl Grignard reagents.. .....78

Scheme 3.7 Ni(II) complexes containing pincer ligands with tunable catalytic properties....80

Scheme 3.8 Ni(II) hemilabile complexes of pincer ligands containing a single NHC donor...82

Scheme 3.9 Ni(II) complex of a pincer ligand with a central NHC donor... .....82

Scheme 3.10 Synthesis of $[Ni(NCN^{Me})Cl]BPh_4$ (**8**).....84

Scheme 3.11 Proposed equilibrium between the square planar and tetrahedral conformations of complex **8**.....87

Scheme 3.12 Equilibrium between the square planar and tetrahedral conformations of $Ni(PPh_3)_2Cl_2$.....88

Scheme 3.13 Synthesis of NCN pincer ligand ($NCN^{Me}$)$PF_6$ (**1b**)... .....94

Scheme 3.14 Synthesis of [Ni($NCN^{Me}$)Cl]$PF_6$ (**9**).....94

Scheme 3.15 Synthesis of ($NCN^{Et}$) $BPh_4$ (**1c**).....97

Scheme 3.16 Synthesis of [Ni($NCN^{Et}$)$_2$]($BPh_4$)$_2$ (**10**).....98

Scheme 3.17 Kumada cross coupling reactions of PhBr and PhCl with PhMgBr catalysed by **8**, **9** and **10**.....104

Scheme 4.1 Examples of Pd(II) catalysed hydroalkoxylation reactions.(a) aromatic alkynes,[6] (b) aromatic and alkyl substituted alkynes,[7] (c) disubstituted aromatic alcohols.[8].....115

Scheme 4.2 Cu(I) catalysed intramolecular hydroamination of alkynyl alcohols.....115

Scheme 4.3 Rh(I) and (Ir) catalysts synthesised in the Messerle group for the dihydroalkoxylation reaction... .....116

Scheme 4.4 Catalysed dihydroalkoxylation of alkyne diols.....116

Scheme 4.5 (a) Intermolecular hydroalkoxylation catalysed by $Au(PPh_3)Me$. (b) Intramolecular hydroalkoxylation catalysed by LAuNCMe... .....117

Scheme 4.6 Au(I) catalysed intramolecular dihydroalkoxylation of alkyne diols.....118

Scheme 4.7 Samarium catalyst for the intramolecular hydroamination of aminoalkynes... .....118

Scheme 4.8 Rh(I) and Ir(I) catalysts for the hydroamination reaction of 4-pentyn-1-amine... .....119

Scheme 4.9 Highly active Au(I) catalyst for the intermolecular hydroamination reaction... .....119

Scheme 4.10 (a) First example of a Ru(II) catalysed intermolecular addition of allyl alcohols to acetylenes. (b) An iridium complex bearing a PCP pincer ligand for the hydroaryloxylation reaction of olefins .....121

Scheme 4.11 Key Pd(II) intermediate stabilised by the tridentate coordination of PON or POP pincer ligands.....122

Scheme 4.12 (a) Ir(III) catalyst with a pincer ligand for the hydroamination of 2-alkynylanilines. (b) Ti catalyst with a pincer ligand for the hydroamination of alkenes.. .....123

Scheme 4.13 Ti catalyst used for three component intermolecular hydroamination reactions... .....123

Scheme 4.14 Hemilabile magnesium pincer catalyst for the hydroamination of aminoalkenes.....124

Scheme 4.15 Rh(I) catalyst containing the hemilabile pincer ligand 1 for the hydroalkoxylation of 4-pentynoic acid.....125

Scheme 4.16 Synthesis of [Au(I)(NCN$^{Me}$)Cl] (**11**).. .....127

Scheme 4.17 Synthesis of [Au(III)(NCN$^{Me}$)Cl] (**12**)... .....129

Scheme 4.18 Synthesis of a heterobimetallic Au(I)/Rh(I) complex (**13**).....132

# Abstract

This thesis describes the synthesis of new Ag(I), Ru(II), Ni(II), Au(I) and Au(III) complexes containing an imidazolyl-pyrazolyl ligand motif (*NCN*$^{Me}$- methylene linker, and NCN$^{Et}$- ethylene linker). The synthesised complexes were tested as catalysts for a number of organic transformations.

Complexes [Ag(*NCN*$^{Me}$)$_2$]BPh$_4$ (**2**), [Ru(*NCN*$^{Me}$)$_2$](BPh$_4$)$_2$ (**7**), [Ru(H)CO(*NCN*$^{Me}$)(PPh$_3$)$_2$]BPh$_4$ (**5a**), [Ru(H)CO(*NCN*$^{Me}$)(PPh$_3$)$_2$]BPh$_4$ (**5**), [Ru(η$^6$-C$_6$H$_6$)(*NCN*$^{Me}$)Cl]BPh$_4$ (**3**), [Ru(η$^6$-C$_{10}$H$_{14}$)(*NCN*$^{Me}$)Cl]BPh$_4$[B$_5$O$_6$(OH)$_4$] (**4a**), [Ru(η$^6$-C$_{10}$H$_{14}$)(*NCN*$^{Me}$)Cl]BPh$_4$ (**4**), [Ni(*NCN*$^{Me}$)Cl]BPh$_4$ **(8),** [Ni(*NCN*$^{Me}$)Cl]PF$_6$**(9)** and [Ni(*NCN*$^{Et}$)$_2$](BPh$_4$)$_2$ **(10),** [Au(I)(*NCN*$^{Me}$)Cl] (**11**) and [Au(III)(*NCN*$^{Me}$)Cl$_3$] (**12**) were synthesised and fully characterised. Solid state structures of **1a**, **1c**, **2**, **3**, **4a**, **5a**, **6**, **7**, **8**, **9**, **10**, **11** and **12** were analysed using X-ray crystallography. The presence of an unusual boronate counterion [B$_5$O$_6$(OH)$_4$] and a new Ru(I) compound [RuCl(PPh$_3$)]$_4$ were also revealed using X-ray crystallography.

Ruthenium complexes **3**, **4**, **4a**, **5**, **5a** and **7** were tested as catalysts for the transfer hydrogenation reaction of ketones. Complexes containing arene co-ligands [Ru(η$^6$-C$_6$H$_6$)(*NCN*$^{Me}$)Cl]BPh$_4$ (**3**), [Ru(η$^6$-C$_{10}$H$_{14}$)(*NCN*$^{Me}$)Cl]BPh$_4$[B$_5$O$_6$(OH)$_4$] (**4a**), [Ru(η$^6$-C$_{10}$H$_{14}$)(*NCN*$^{Me}$)Cl]BPh$_4$ (**4**) were found to be more active catalysts for the organic transformation with [Ru(η$^6$-C$_{10}$H$_{14}$)(*NCN*$^{Me}$)Cl]BPh$_4$[B$_5$O$_6$(OH)$_4$] (**4a**) exhibiting the best activity showing that the boronate counterion [B$_5$O$_6$(OH)$_4$]$^-$ enhances catalytic activity. The complexes achieved complete conversions for all substrates within short reaction times (< 1 hr). [Ru(η$^6$-C$_{10}$H$_{14}$)(*NCN*$^{Me}$)Cl]BPh$_4$[B$_5$O$_6$(OH)$_4$] (**4a**) was catalytically active for the organic transformation at room temperature.

Nickel complexes **8**, **9** and **10** were found to exhibit broad resonances in NMR spectroscopy. Analysis using UV vis spectroscopy and variable temperature NMR spectroscopy revealed that the Ni(II) complexes were diamagnetic in nature and that the broad spectra at room temperature resulted from conformational changes due to the flexible nature of the ligands. All three complexes were tested as catalysts for the Kumada cross coupling reaction of aryl halides with phenylmagnesium bromide. Complexes **8** and **9** containing a tridentate coordination of the pincer ligand were found to be more active for the organic transformation in comparison to the bidentate complex **10**. The choice of counterion was found to alter the activity for the conversion of selected chlorinated and brominated substrates. A reduction in catalyst loading resulted in reduced activity of complex **8** for the conversion of chlorobenzene, whereas a negligible effect was observed for the catalytic conversion of bromobenzene using reduced catalyst loading.

The oxidation states and structure of gold complexes **11** and **12** were determined using X-ray crystallography and UV vis spectroscopy. Both complexes were tested as catalysts for intramolecular dihydroalkoxylation reactions. Both complexes were highly active for the organic transformation, with complex (**12**) showing excellent activity, exceeding TOF values of 18,000 and maintaining high catalytic activity even at room temperature. Direct comparison of Au(I) complex **11** and Au(III) complex **12** showed that **12** was significantly more active for the organic transformation showing that catalytic activity can be altered by changing the oxidation state of the gold catalysts.

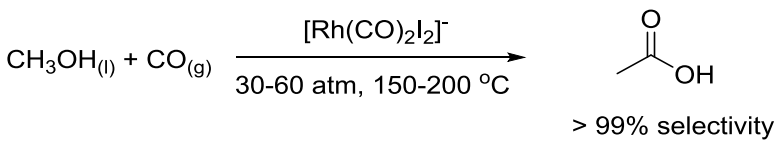
Complexes **11** and **12** proved to be highly active for the intramolecular hydroamination reactions of pentyn-4-amine and phenylpentynamine achieving complete conversions

within thirty minutes and moderate conversions for the intermolecuar hydroamination reactions of aniline with phenylacetylene.

# Chapter 1. Introduction

## 1.1. Organometallic complexes in catalysis

Organometallic complexes are defined as a chemical species containing at least one bond between a metal and the carbon atom in an organic molecule, ion or substituent group.[1] These complexes have been studied over many years and used as catalysts to modify the routes of organic transformations. The ability of organometallic complexes to influence synthetic reactions has resulted in their use in a wide range of industrial processes. A well-known and important reaction in industry that relies on organometallic catalysts is the Monsanto process. Developed in 1966, the Rh(I) catalysed transformation is used to produce acetic acid from methanol and carbon monoxide (Scheme 1.1).[2]

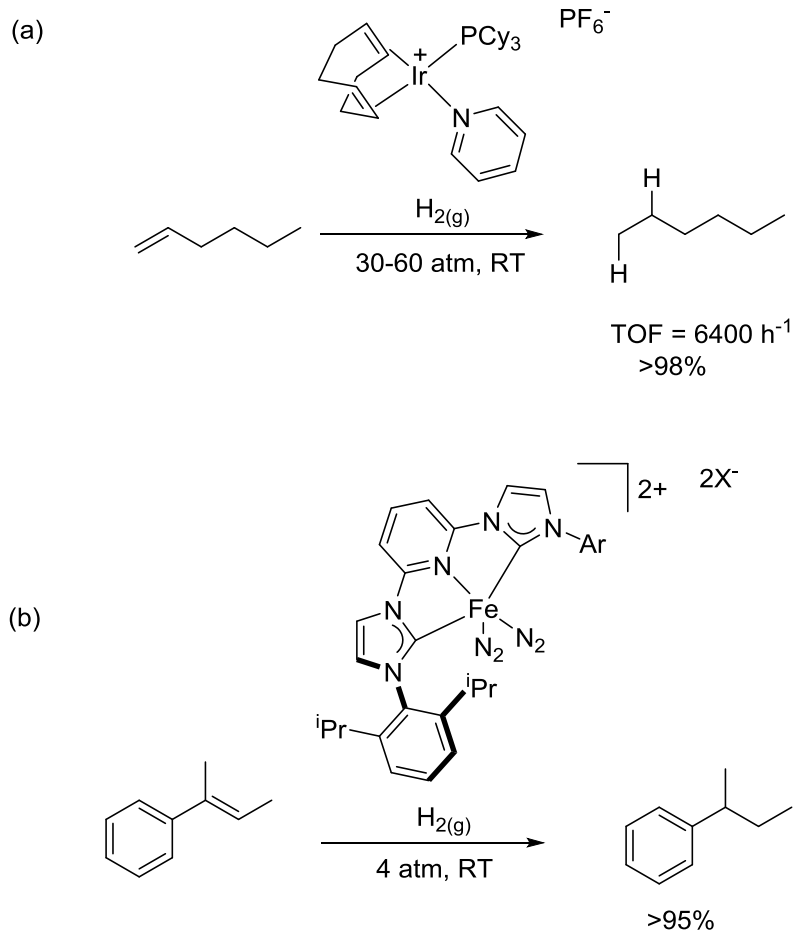



**Scheme 1.1** Monsanto process.

A catalyst is a substance that increases the rate of a reaction by lowering the activation energy without itself being consumed in the reaction.[3] The overall Gibbs free energy of the reaction is not altered by the catalyst, the catalyst merely accelerates the thermodynamically favoured reactions. As the catalyst remains unchanged upon completing the transformation, it can be recycled to complete more organic transformations. Catalysts can also achieve high selectivity in reactions by favouring certain reaction pathways over others.[4]

The production of pharmaceutical products and other high value chemicals often rely on the use of homogeneous catalysts to reduce production costs, minimise use of resources, improve reaction rates and provide milder/safer reaction conditions.[5] Reactions that were

inaccessible through traditional synthetic methods can also be carried out by the use of homogeneous catalysts.[6] For example, the hydrogenation of alkenes requires catalysts to initiate and complete the reaction. Non-catalytic approaches to hydrogenating alkenes require extremely high temperatures and pressures. Homogeneous transition metal catalysts, achieve high turnover frequency (TOF)[7] values (Scheme 1.2a) for the hydrogenation reactions of alkenes, and high conversions at room temperature conditions (Scheme 1.2).[8]




**Scheme 1.2** Homogeneous transition metal catalysts for the hydrogenation reaction of alkenes.

## 1.2. Transition metal catalyst design

Homogeneous transition metal catalysts are particularly useful for modifying the level of reactivity of an organic transformation. This is achieved by modifying different components in the structure of the catalyst, such as the coordination environment of the metal centre, the metal centre itself and the counterion used.

### 1.2.1. The metal centre

The catalytic properties of an organometallic complex are largely defined by the characteristics of the metal centre. Transition metals can exist in various oxidation states, some of which have unfilled d-orbitals which allow them to readily exchange electrons. This allows the metals to easily access substrates and makes them ideal candidates as catalysts for a wide array of organic transformations. Late transition metals are more electronegative in nature and this allows them to withdraw electrons from coordinated bonds. Therefore, unsaturated ligands bound to late transition metals are more likely to undergo nucleophilic attack.[9, 10]

#### 1.2.1.1. Ruthenium, nickel and gold as active and air/moisture stable catalysts

Ruthenium and nickel complexes are highly utilised in industry and since the synthesis of Grubbs' catalyst and Ni(*bis*-phosphino) dichloride complexes,[11] have been extensively investigated as catalysts for a number of organic transformations including hydrogenations and C-C coupling reactions. Complexes of Ru and Ni tend to be highly air and moisture stable in the +II oxidation state.[12] Ni(II) complexes can also be both four, five and six coordinate allowing for a wide range of coordination geometries. Different oxidation states of either ruthenium or nickel can adopt different geometries such as four coordinate

tetrahedral, square planar and six coordinate octahedral geometries. Both ruthenium and nickel are late transition metals that can access multiple oxidation states, which makes them useful as catalysts for organic transformations that involve redox changes at the metal centre during the catalytic cycle, e.g. oxidative addition and reductive elimination.

Similar to ruthenium and nickel complexes, gold complexes are highly air and moisture stable.[13] Gold complexes have received significant attention in catalysis due to their high levels of reactivity and wide applicability for different synthetic reactions.[13] Gold complexes often occur in the +I and +III oxidation states, and can hence access linear or square planar geometries. Gold(I) and gold(III) complexes have the added advantage that the complexes are diamagnetic which allows for easy characterisation of the complexes using NMR spectroscopy.

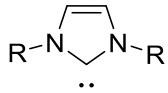
### 1.2.2. Ligand properties

The catalytic activity of a transition metal catalyst can be greatly affected by the associated ligand. The properties of ligands depend on different factors such as the coordinating strength/lability of donor atoms, type of coordination modes and steric and electronic environments. A number of ligand types are described below.

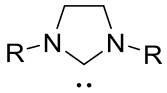
#### 1.2.2.1. N-Heterocyclic carbenes (NHCs)

N-Heterocyclic carbenes (NHCs) consist of an $sp^2$ hybridised six-electron carbene group embedded in an N-heterocyclic ring.[14] NHCs are stronger σ donors than phosphines, which leads to a reduced lability of the ligand and therefore results in complexes of higher thermal stability and robustness than complexes containing phosphine ligands.[15] Due to their potential as strongly coordinating ligands to the metal, NHC bearing transition metal

complexes have been used widely as catalysts for homogeneous and heterogeneous organic transformations.[16] Altering the steric and electronic properties of NHCs has proven to be significantly easier than altering the same properties of phosphines.[17] The most commonly employed NHCs in transition metal catalysts are imidazolylidenes and imidazolinylidenes (Figure 1.1). The coordination chemistry of NHCs bearing the imidazolylidene motif has been studied using a wide array of transition metals.[17] This versatility in coordination allowed transition metal complexes bearing NHC ligands to be used as catalysts in a large number of synthetic reactions, such as C-C bond formation and X-H (X = O, N) bond activation reactions.



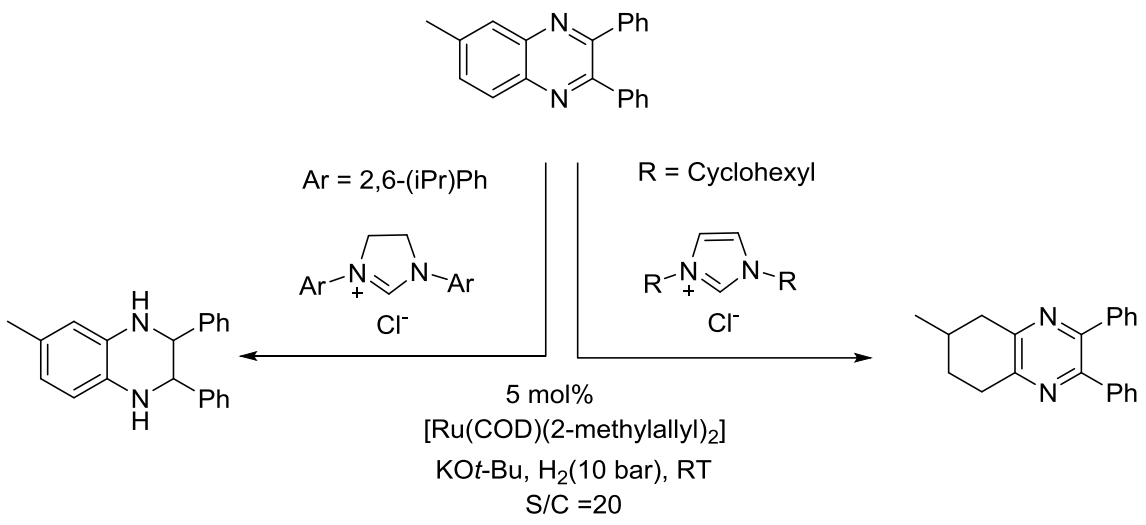

Imidazolylidenes




Imidazolinylidenes

**Figure 1.1** General structures of imidazolylidenes and imidazolinylidenes.

Variation of the electronic properties of NHCs used in transition metal complexes as shown in Figure 1.1 (imidazolylidenes compared to imidazolinylidenes) can significantly effect the selectivity of transition metal catalysed reactions. For example, the regioselective hydrogenation of quinoxaline[18] as shown in Scheme 1.3.




**Scheme 1.3** Regioselective hydrogenation of quinaxoline.

### 1.2.2.2. Nitrogen donor ligands

Coordination of nitrogen donor atoms to transition metals is widely known in naturally occurring processes. For example, the haem b group in haemoglobin consists of an iron ion bound to four nitrogens in the centre of a protoporphyrin ring.[19] A number of transition metal complexes containing nitrogen donor ligands have been synthesised with aims to mimic and even improve upon the effective catalytic activity of these biological processes and achieve higher catalytic activity for different organic transformations.[20] The relatively labile character of ligands containing nitrogen donor atoms compared to stronger donors such as phosphines allow the resulting transition metal catalyst to produce vacant coordination sites more readily, which is desirable for enhancing the catalytic reactivity. Typical N-donor ligand systems in transition metal complexes often include pyrazole, pyridine, pyrrole and imine groups (Figure 1.2).[20] These $sp^2$ N-donors, in particular the heterocyclic systems, are less likely to undergo oxidation processes themselves which are common in phosphine donor systems.[21] The increased robustness of ligands containing N-

donor atoms relative to other donors have resulted in the popular use of the resulting metal complexes as catalysts for a number of different organic transformations.

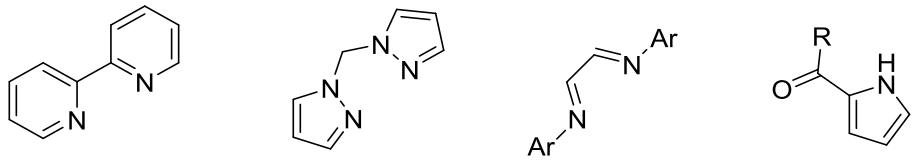



**Figure 1.2** Typical N-donor ligand systems.

### 1.2.2.3. Tridentate ligands

Tridentate pincer ligands provide an excellent platform for modifying the steric and electronic properties of a complex. Tridentate ligands are advantageous over bidentate ligands due to an increased chelate effect, which enhances the chemical stability of the resulting metal complex.[12] A popular class of tridentate ligands are pincers, which are commonly denoted in the form *DYD*', where Y denotes the central donor atom and *D/D*' the two sidearm donor atoms (Figure 1.3).[22, 14] The central donor (Y) is most commonly a phenyl or pyridyl ring, although amide, silyl and NHC donors have also been reported.[23] A diverse array of side arm donor groups (D/D') have been used in pincer complexes, such as phosphines, phosphites, amines, amides, thioethers and NHC donors.[23] A short and rigid linker between the central donor and the side arm donor groups typically promotes a meridional coordination of the ligand to a metal centre, such that all three donor groups lie in the same plane, however facial coordination modes are also possible.

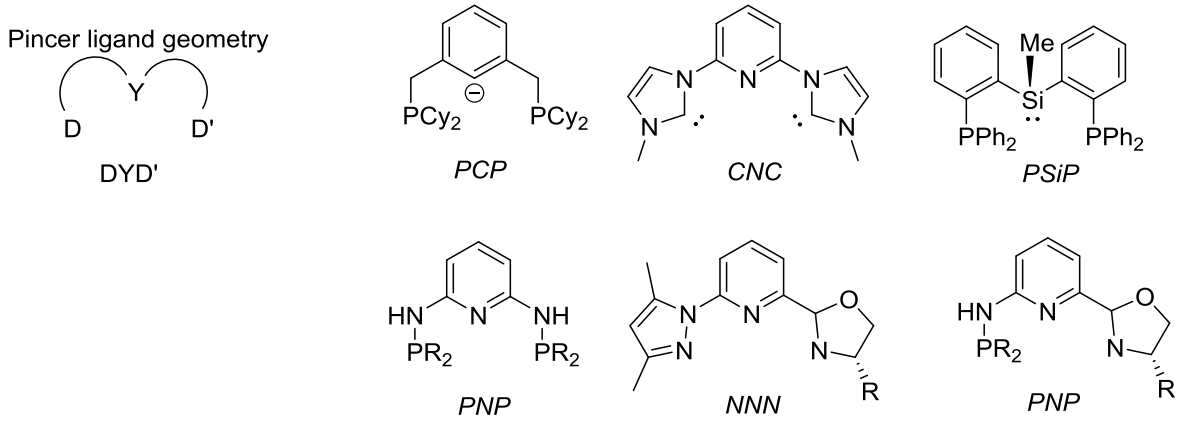
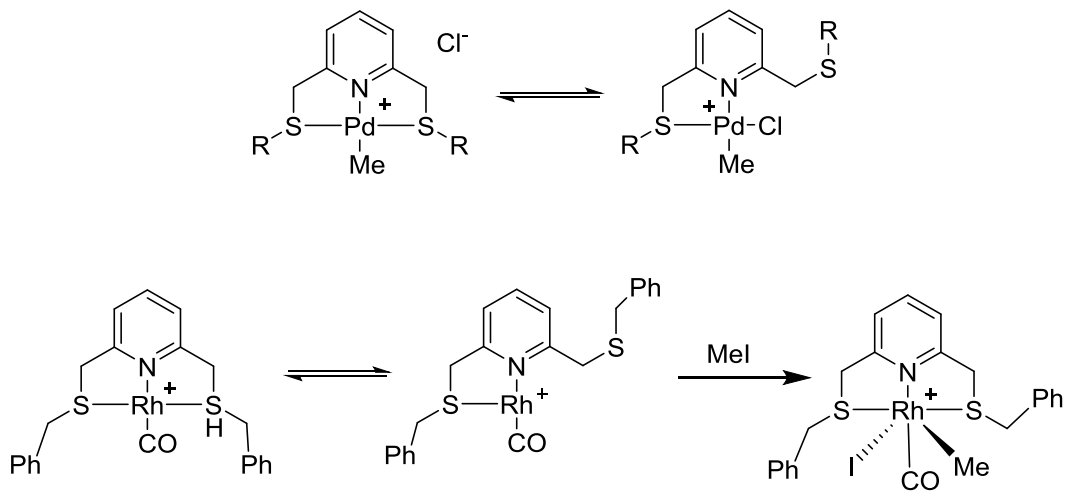



**Figure 1.3** Common motifs of pincer ligands.

A strong meridional coordination of the pincer ligand to a metal centre can result in complexes of high thermal stability. This is due to a restricted arrangement of the remaining coordination sites which can inhibit potential decomposition pathways. For example, Shaw *et al.* reported that a Ni(II) complex containing the *PCP* ligand in Figure 1.3 was stable up to 240 $^{o}$C.[12]

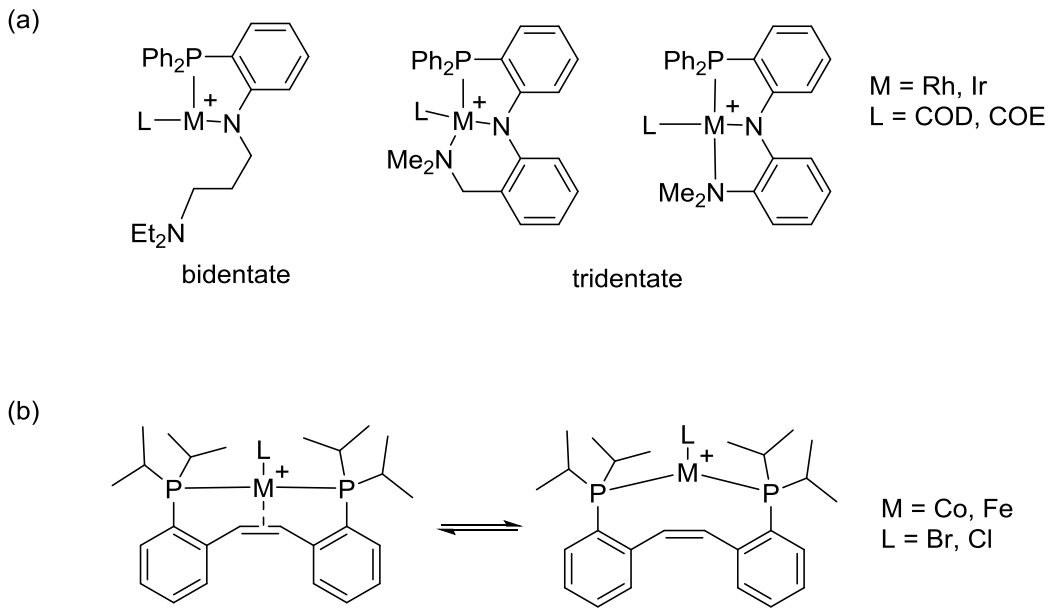
### 1.2.2.4. Hemilabile pincer ligands

The use of weakly coordinating side arms in pincer ligands can lead to tridentate ($\kappa^3$), bidentate ($\kappa^2$) and even monodentate ($\kappa^1$) coordination modes. For example, Canovese *et al.* observed an equilibrium between $\kappa^2$ and $\kappa^3$ coordination modes in a Pd complex containing an *SNS* pincer ligand with labile thioether side arms (Scheme 1.4).[24] The ligand system has since been investigated using different metals, for example, a Rh(I) complex containing the *SNS* ligand exhibited hemilabile character and was shown to facilitate the oxidative addition reaction of methyl iodide. [24, 25a]




**Scheme 1.4** Pd and Rh complexes with an *SNS* hemilabile pincer ligand.

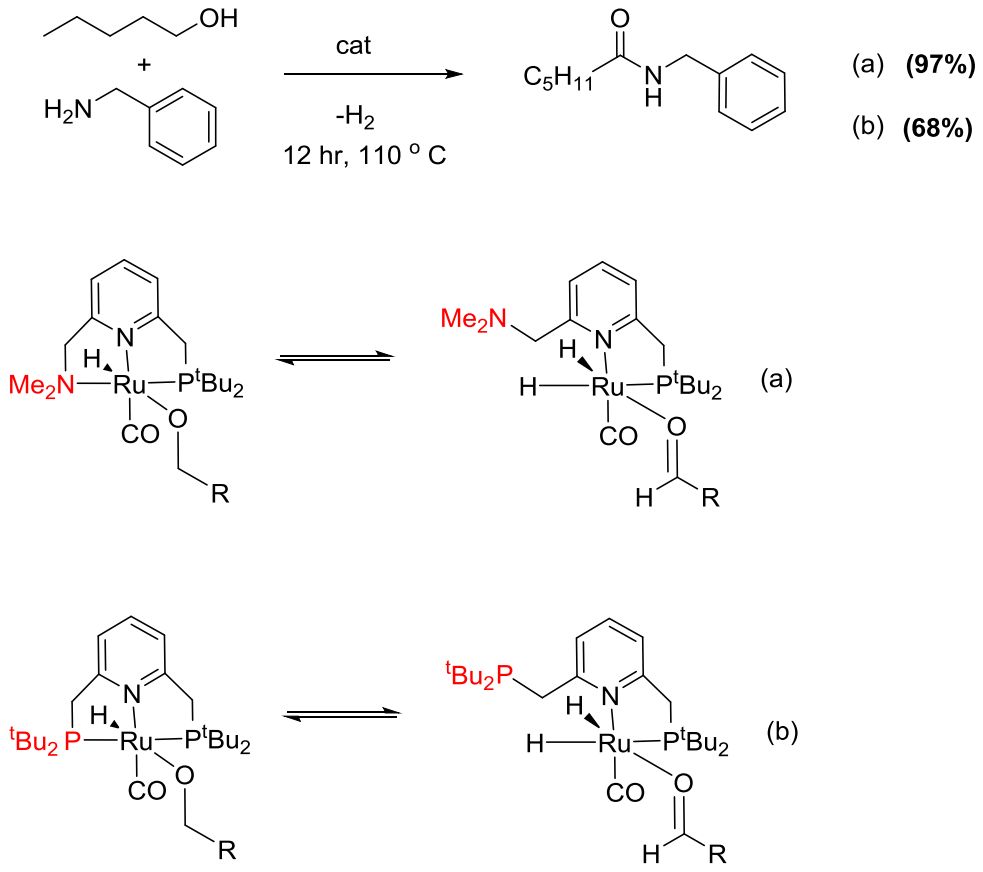
Recent work has demonstrated that the hemilability of pincer ligands is tunable through variable donor strength and spacer length/rigidity. Lindner *et al.* demonstrated this by testing the coordination chemistry of *PNN* pincer ligands with varying R substituents on the labile N donor arm and the spacer linker between the side arms donors and the central donor (Scheme 1.5a).[25b] Hemilability of complexes are also not limited to use of weakly coordinating heteroatom donors such as nitrogen, oxygen and sulphur. A pincer ligand containing a central alkene was reported to exhibit hemilabile character as shown in Scheme 1.5b.[25c]




**Scheme 1.5** Complexes containing hemilabile pincer ligands.

Transition metal complexes bearing ligands that exhibit hemilabile character have been shown to enhance catalytic activities for a number of organic transformations. Nitrogen moieties are commonly used as side arm donors in hemi-labile pincer complexes, and show increased lability compared to phosphorus donors.

A Ru(II) complex containing an *NNP* pincer ligand was reported to produce enhanced catalytic activity for the intermolecular dehydrogenative hydroamination reaction (Scheme 1.6) of alcohols and amines. In comparison, the analogous *PNP* pincer complex exhibits significantly reduced conversions of substrates to amide product.[26, 27]




**Scheme 1.6** Ru(II) complex with a *NNP* hemilabile pincer ligand.

### 1.2.3. Counterions

In transition metal complexes, counter anions are typically used to balance the positive charge associated with the cationic metallic species. The counterions tend to exist within the coordination sphere of the metal ion.[28] Varying the counterion of a transition metal catalyst has been shown to alter its ability to perform organic transformations.[29] This can be associated with the varying coordination strengths and steric bulk of the counterion, which has the potential to alter the electrophilicity and steric effects of the resulting metal complex.

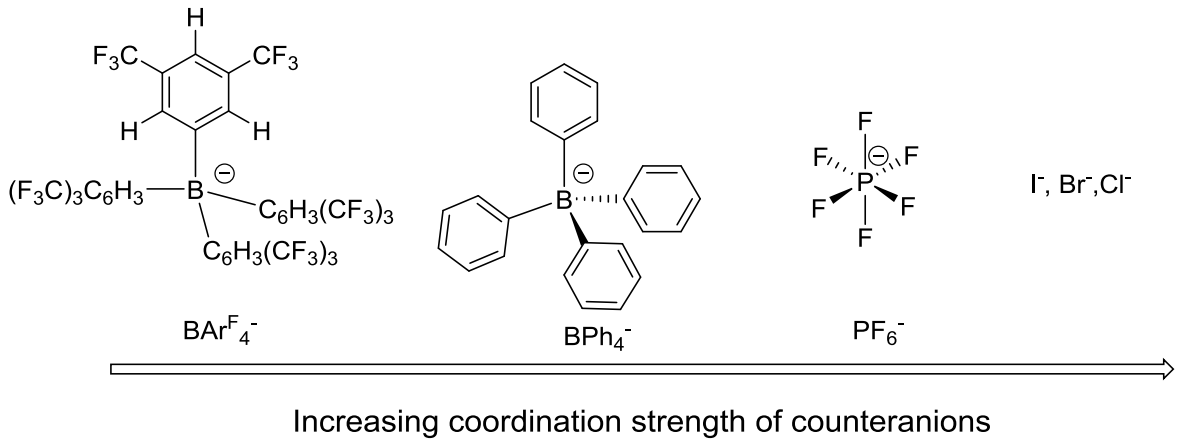


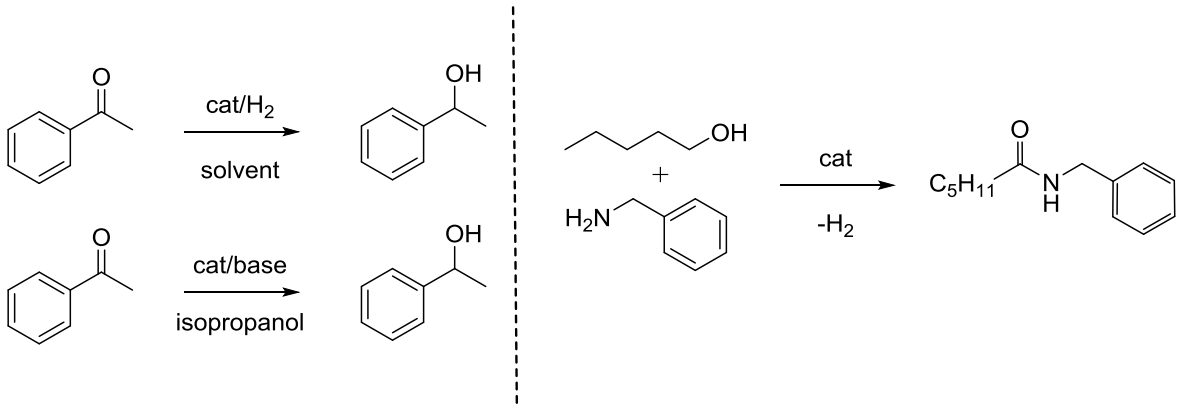

**Figure 1.4** Varying coordination strengths of counterions

Weakly coordinating counterions are commonly used in transition metal catalysts with the aim to optimise interaction between catalyst and substrates during catalysis.[30] Most of the weakly coordinating counterions include borates such as $BPh_4^-$(tetraphenylborate), $B(C_6F_5)_4^-$ and $BAr^F{}_4^-$ (tetrakis(-3, 5-bis(trifluoromethyl)phenyl) borate).[30, 31]

## 1.3. Transition metal complexes in homogeneous catalysis

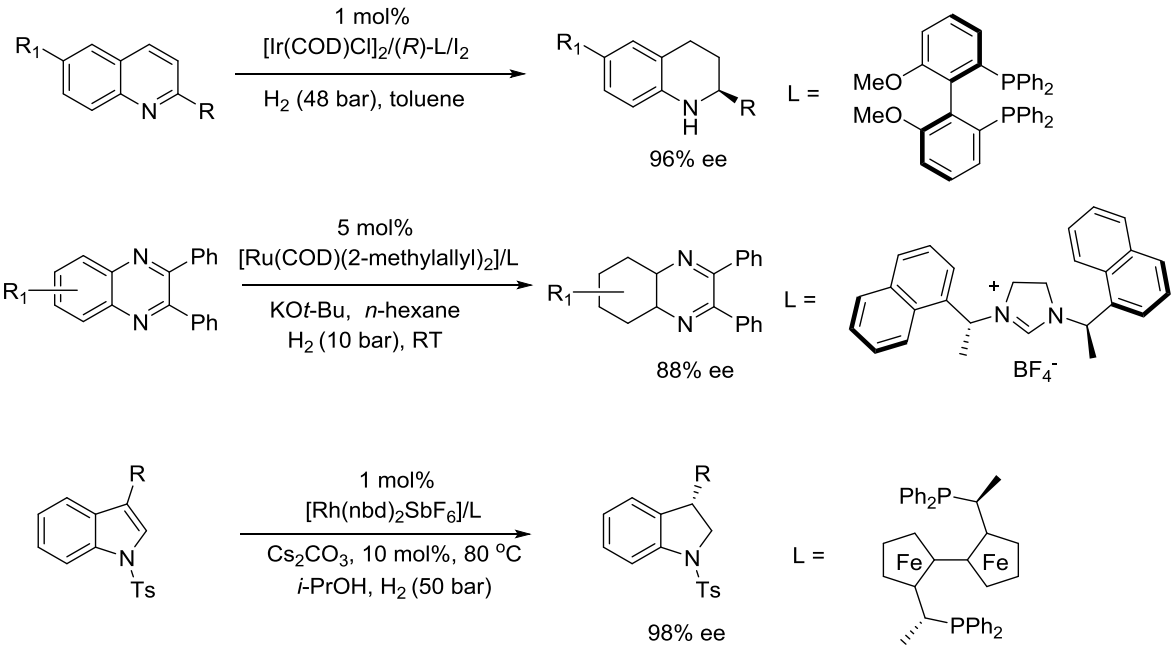
### 1.3.1. Transition metal catalysed $H_2$ addition or removal to a polar unsaturated bond

The metal mediated addition of $H_2$ to or removal of $H_2$ from a polar unsaturated bond has been studied using various transition metals.[32] These types of reactions typically involve the hydrogenation of ketones and imines, the reductive cleavage of esters and the dehydrogenative coupling of alcohols and amines (Scheme 1.7).[33, 34]



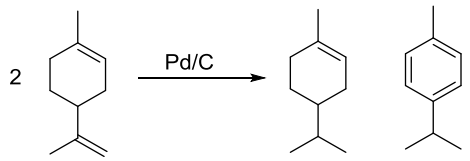

**Scheme 1.7** Typical hydrogenation and dehydrogenative coupling reactions.

Among the $H_2$ transfer reactions, catalysed hydrogenation and transfer hydrogenation reactions have received significant attention due to the wide number of applications in industrial scale synthesis, green chemistry and medicinal chemistry.[35] These catalytic hydrogenation reactions are accessible using a number of transition metals including rhodium, iridium, iron and ruthenium (Scheme 1.8).[36]

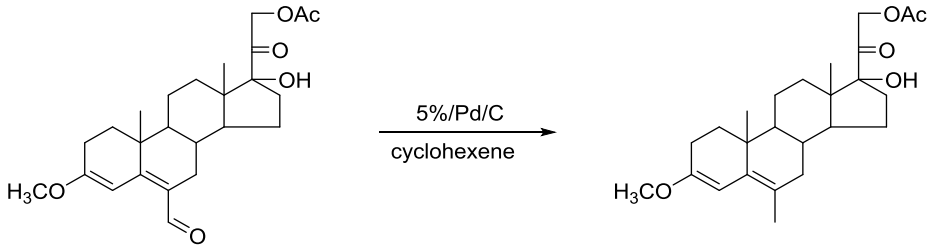



**Scheme 1.8** Transition metal catlysed hydrogenation reactions.

Transfer hydrogenation can provide a milder route to the formation of alcohols and alkanes from ketones and alkenes respectively compared to conventional hydrogenation reactions where the use of high temperatures, pressures and potentially dangerous gases such as hydrogen[32] can be avoided. The transfer hydrogenation process can also offer different selectivities to hydrogenation reactions,[37] which can be useful for the selective production of stereoisomers. Well known uses of transfer hydrogenation in industry include the synthetic production of terpenes and functionalisation of steroids (Scheme 1.9).[35] For example, the conversion of steroid ethers to 6-methyl steroids was achieved with high selectivity where other functional groups on the steroid remained unaffected (Scheme 1.10).[38]




**Scheme 1.9** Synthetic production of terpenes.

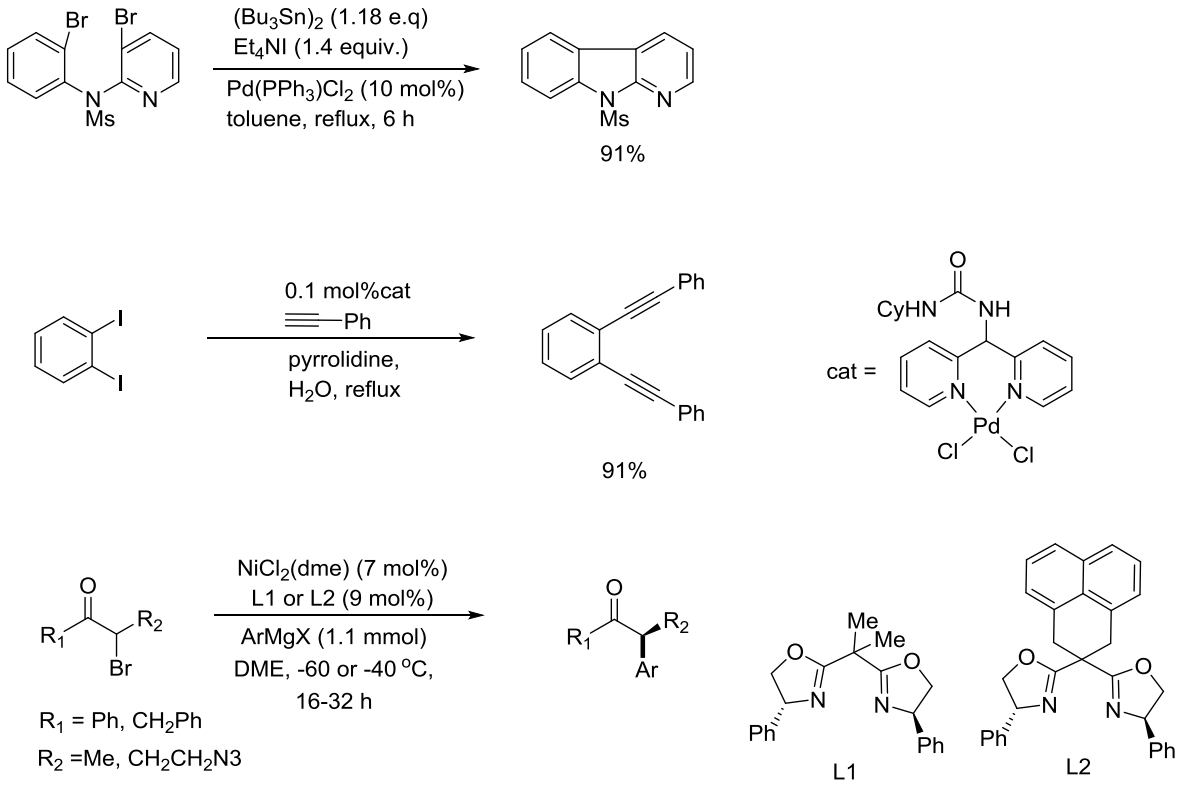



**Scheme 1.10** Conversion of steroid ethers to 6-methyl steroids.

### 1.3.2. Transition metal catalysed C-C bond coupling reactions

The formation of C-C bonds remains amongst the most vital reactions in organic synthesis and has been used for industrial processes such as crude oil refining and production of pharmaceutical drugs.[39] Since the introduction of transition metal catalysts to these

processes, the volume and number of different catalysed C-C coupling reactions has significantly increased over time. Typical C-C bond formation reactions include Suzuki, Negishi, Stille, Sonogashira and Kumada cross coupling reactions. Early accounts of C-C bond formation reactions involved the coupling of Grignard reagents with organic halides. Karasch and Fields first reported the enhanced coupling reaction of Grignard reagents with organic halides by utilising a cobalt catalyst.[40] However, the early reports of these catalysed coupling reactions resulted in the formation of significant homo-coupled products and poor yields for the desired products. Introduction of nickel and palladium based catalysts alleviated this problem; Corriu and Kumada reported nickel and palladium catalysed coupling reactions of Grignard reagents with organic halides achieving high yields.[41] A number of palladium and nickel catalysts have since been synthesised to catalyse different coupling reactions under a wide range of conditions of solvent, temperature and co-reagents with supporting ligands being used to control both reactivity and selectivity (Scheme 1.11).[39]



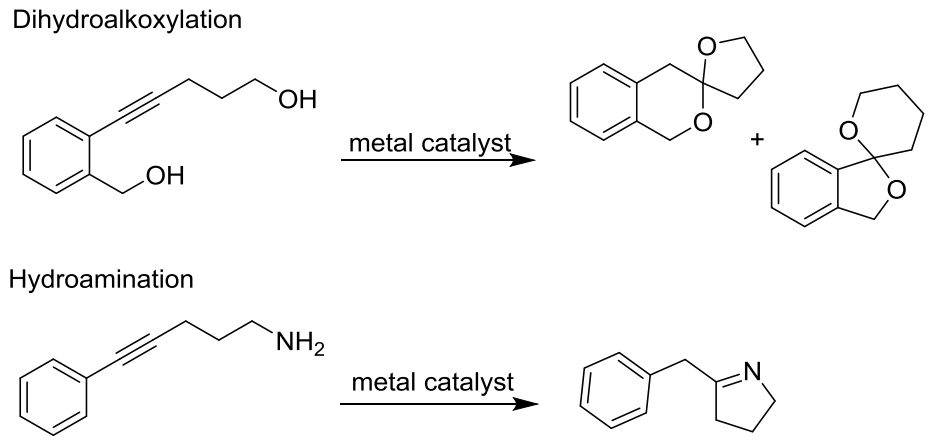

**Scheme 1.11** Pd and Ni catalyzed coupling reactions.

The advantages provided by transition metal complexes such as high stereoselectivity and reduction of unwanted by-products allows for the advent of efficient methods to forge C-C bonds.

### 1.3.3. Transition metal catalysed X-H bond addition reactions

The addition of X-H (X = N, O, S, Se or P) across an alkyne functionality, known as hydroelementation reactions, using transition metal complexes as catalysts has received significant attention in organometallic chemistry.[42] The great potential for hydroelementation processes to achieve 100% atom economy makes them an attractive approach to organic syntheses and green chemistry. Intramolecular reactions involving X-H bond addition are also highly efficient methods for the production of heterocycles containing nitrogen and oxygen groups.[42, 43] Formation of such heterocycles is critical in the

pharmaceutical industry for the production of valuable medicinal compounds. The dihydroalkoxylation reaction (Scheme 1.12) of alkyne diols produces spiroketals which are moieties commonly found in natural products such as (-)Berkelic acid (Figure 1.5).[44] Similarly, the intramolecular hydroamination reaction of alkynamines (Scheme 1.12) results in the formation of nitrogen containing heterocycles which are moieties commonly found in pharmaceutical compounds such as pyrrolysine (Figure 1.5).[45]




**Scheme 1.12** Dihydroalkoxylation of alkyne diols and hydroamination of alkynamines.

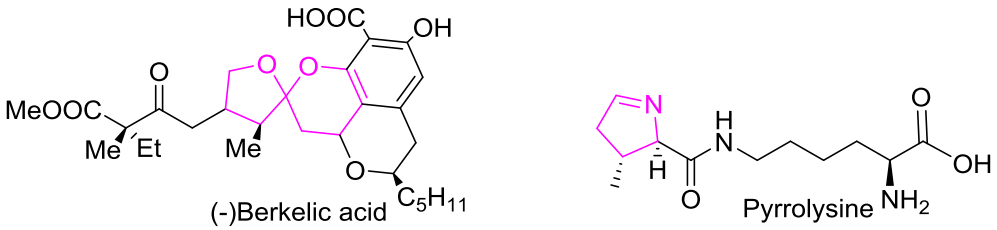
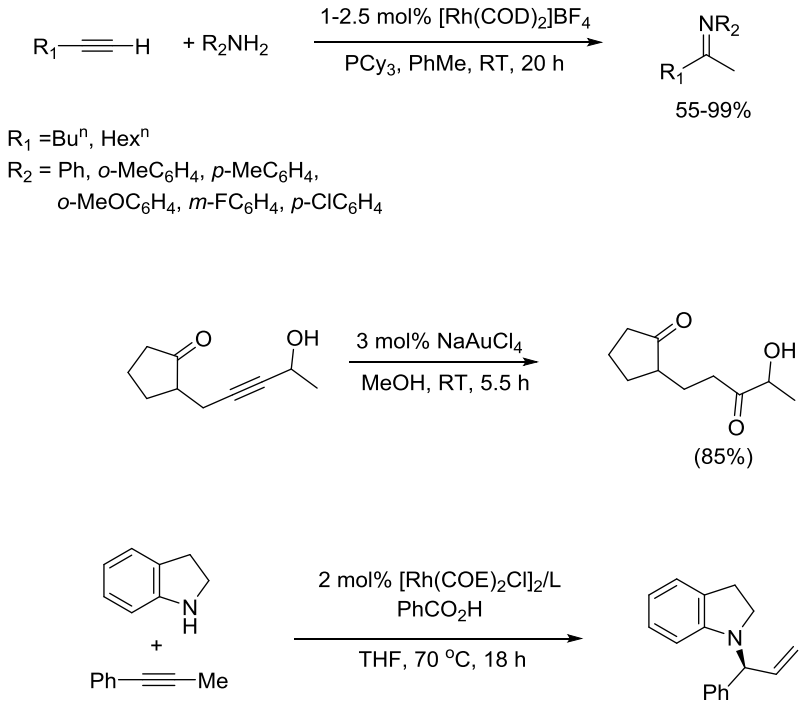


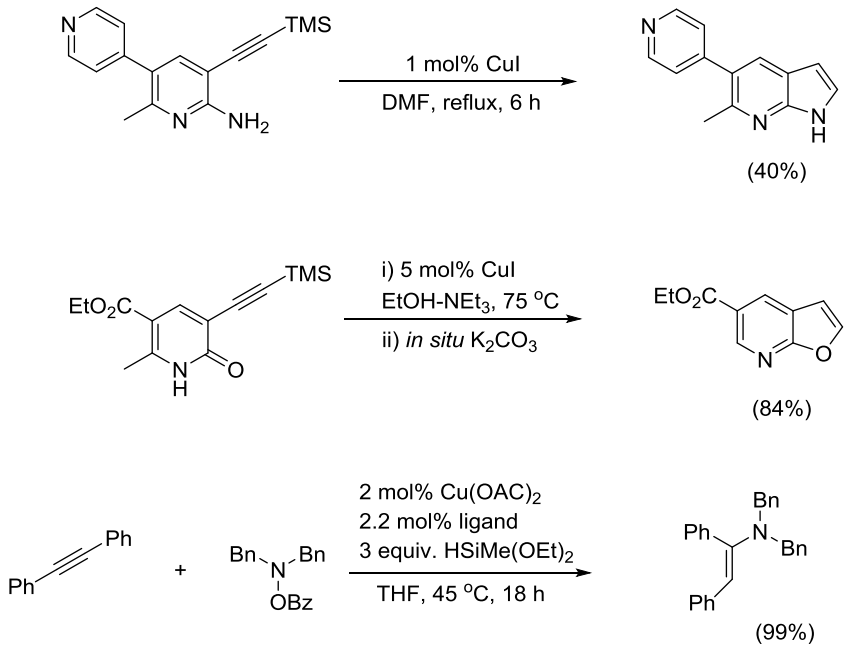

**Figure 1.5** Pharmaceutical compounds containing nitrogen/oxygen heterocycles.

The X-H bond addition reactions are able to proceed under mild conditions and are versatile as a result of the number of different transition metals that are able to catalyse the organic transformations.[43, 46, 47] As shown in Scheme 1.13, both the intermolecular hydroamination and intramolecular hydroalkoxylation reactions achieve high conversions at room temperature and utilise simple metal complexes to catalyse the transformations.




**Scheme 1.13** X-H bond addition reactions catalyzed by simple metal complexes.

High regioselectivity is also usually achieved with metal catalysed X-H bond addition reactions of alkynes. The broad applicability of a range of transition metals also allows the use of inexpensive transition metals such as copper (Scheme 1.14).[48, 49]




**Scheme 1.14** X-H bond addition reactions catalyzed by copper complexes.

## 1.4. Objectives

Current catalytic systems which are highly active tend to have reduced stability and a combination of high stability and reactivity is rarely present. Improvements to such systems can be made by utilising tridentate systems containing both strong and weakly coordinating donors. The goals of this research project were to synthesise novel complexes using Ru, Ni, and Au, which contain a pincer ligand with a central NHC donor and labile pyrazole pendant donors, and to investigate the efficiency of these complexes as homogeneous catalysts for a variety of organic transformations. The aim was to determine whether the hemilability of the ligands can lead to higher activity of the complexes as catalysts without compromising stability, for the selected transformations. The formation of complexes containing bidentate or tridentate coordination modes was therefore targeted such that the weakly coordinated pendant arms can readily dissociate during catalysis, providing vacant coordination sites. The goals of the project were:

- To synthesise novel transition metal complexes (Ru(II), Ag(I), Ni(II), Au(I) and Au(III)) containing pincer ligands with a central imidazolium group flanked by labile pyrazole pendant arms.
- To analyse the structural properties and coordination chemistry of these novel complexes, which were carried out using a range of analytical techniques including NMR and U.V. spectroscopy.
- To investigate the catalytic activity of novel Ru(II) complexes for transfer hydrogenation reactions, Ni(II) complexes for Kumada cross coupling reactions and Au(I)/Au(III) complexes for X-H bond addition reactions.

General structure of this thesis:

**Chapter 1 : Introduction**

This chapter describes the use of transition metal complexes as catalysts for different organic transformations and the different compositional aspects of a homogeneous catalyst that affects its reactivity. The importance of ligand design in a metal complex is presented highlighting aspects of donor types and hemilability.

**Chapter 2: Ru(II) complexes containing hemilabile pincer ligands for catalysing transfer hydrogenation reactions:**

This chapter describes the synthesis of Ag(I) and Ru(II) complexes containing hemilabile pincer ligands. Structural analyses of the complexes were conducted using different characterisation techniques including X-ray crystallography and NMR spectroscopy. The resulting Ru(II) complexes were tested as catalysts for the transfer hydrogenation reaction of acetophenone. Optimised catalytic conditions were established and the transfer hydrogenation reaction was investigated using a range of ketone substrates.

**Chapter 3: Ni(II) complexes containing hemilabile pincer ligands for catalysing Kumada cross coupling reactions.**

This chapter describes the synthesis of Ni(II) complexes containing hemilabile pincer ligands. The structural and electronic properties of the complexes were analysed using different coordinating donor ligands and counteranions, and their coordination chemistry investigated using different characterisation techniques. These Ni(II) complexes were tested as catalysts for the Kumada cross coupling reaction and the effect of counterions on catalytic activity was examined.

**Chapter 4: Au(I) and Au(II) complexes containing hemilabile pincer ligands for alkyne activation reactions.**

This chapter investigates the coordination chemistry of hemilabile pincer complexes contianing Au(I) or Au(II) metal centres. The properties of the synthesised gold complexes including oxidation state and geometry were analysed using X-ray crystallography and U.V spectroscopy. Gold complexes of both (I) and (III) oxidation states were tested as catalysts for X-H bond addition reactions, specifically dihydroalkoxylation and hydroamination reactions. The effect of oxidation states on catalytic activity between the Au(I) and Au(III) catalysed hydroelementation reactions were analysed.

**Chapter 5: Conclusions and future work.**

Provides a summary of the work presented in the project and promising possibilities in future work as a follow up on the findings of this work.

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# Chapter 2. Ru(II) complexes of hemilabile pincer ligands for catalysed transfer hydrogenation reactions

## 2.1. Introduction

### 2.1.1. Transition metal catalysed hydrogenation reaction

Hydrogenation of polar, unsaturated bonds is a widely researched area in organometallic chemistry. The process is important in food, petrochemical and pharmaceutical industries. Applications of hydrogenation include the production of daily commodity items such as margarine, and commonly used chemicals such as aniline.[1] Some of the early, well known active catalysts for the hydrogenation reaction include Crabtree's catalyst and complexes containing the (S)-iPr-PHOX ligand developed by Braunstein (Figure 2.1).[2, 3]

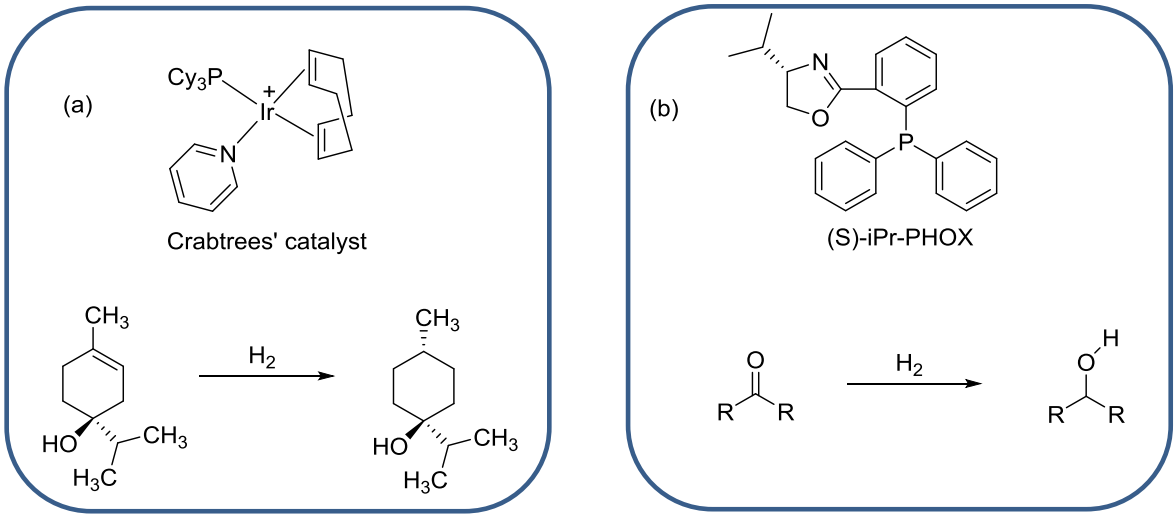



**Figure 2.1** Early examples of hydrogenation catalysts: a) Crabtree's catalyst,[2] and b) (S)-*i*Pr–PHOX.[3]

### 2.1.2. Ruthenium catalysed hydrogenation reactions

Ruthenium(II) complexes containing pincer ligands proved to be efficient catalysts for transformations that involve the metal mediated addition (or removal) of $H_2$ to a polar unsaturated bond. This includes the reductive cleavage of esters using $H_2$, and the dehydrogenative coupling of alcohols and amines to form amides.[4] Recently Ru(II) catalysts

have been used for the hydrogenation reaction of ketones where excellent yields and selectivity were achieved.[5] Noyori, *et al.* used a Ru(II) catalyst bearing a BINAP (2,2'-bis(diphenylphosphino)-1,1'-binaphthyl) ligand (Figure 2.2a). The structure of the ligand was shown to be essential for achieving high enantioselectivity for the alcoholic product shown in Figure 2.2a.[5a] Using the (*R*)-isomer instead of the (*S*)-isomer of the BINAP ligand resulted in poor enantioselectivity which was attributed to the altered sterics about metal centre. Beller *et al.* also showed similar results for the hydrogenation of secondary and tertiary amides to amines (Figure 2.2b) using a simple [Ru(acac)$_3$]/Triphos catalyst system.[5b]

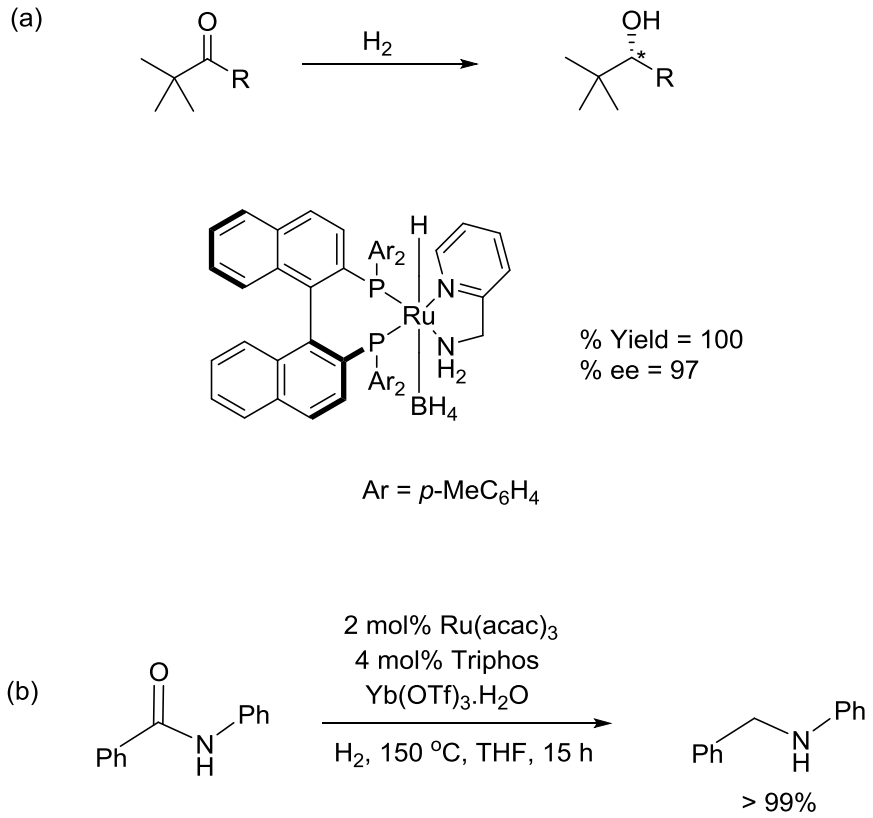



**Figure 2.2** Ligand selective hydrogenation of ketones.

### 2.1.3. Transfer hydrogenation as an alternative to hydrogenation reactions

Typical hydrogenation reactions utilise hydrogen gas as the source of hydrogen and are carried out under harsh reaction conditions, requiring the use of high temperatures and/or pressures.[6] This results in dangerous conditions involving potentially explosive $H_2$ gas, and as such, these reactions also require expensive apparatus to safely contain the harsh reaction conditions. An alternative to direct hydrogenations of substrates with $H_2$ is the transfer hydrogenation reaction. This reaction typically involves a proton donor (usually an alcohol) as the hydrogen source, which avoids the harsh reaction conditions involved in hydrogenation reactions, and provides a milder alternative route. The product selectivities of transfer hydrogenation reactions differ from those of the traditional hydrogenation reactions as the degree of enantioselectivity varies even under altered pressure conditions.[7] These reactions have been extensively studied using transition metal complexes as catalysts and Ru(II) systems have proved to be the most common and effective for the organic transformations.[8] Early work on Ru(II) catalysed transfer hydrogenation reactions focused on complexes containing bidentate ligands and arene co-ligands (Figure 2.3).[10] The earliest examples include the well-known Schvo's catalyst, which was found to operate *via* an "outer sphere mechanism" for the hydrogenation reaction.[9] Ru(II) complexes containing arene co-ligands were targeted in early work as catalysts for the transfer hydrogenation reaction of carbonyl bonds as shown in (Figure 2.3) as they proved to be efficient catalysts for the organic transformation.[10]

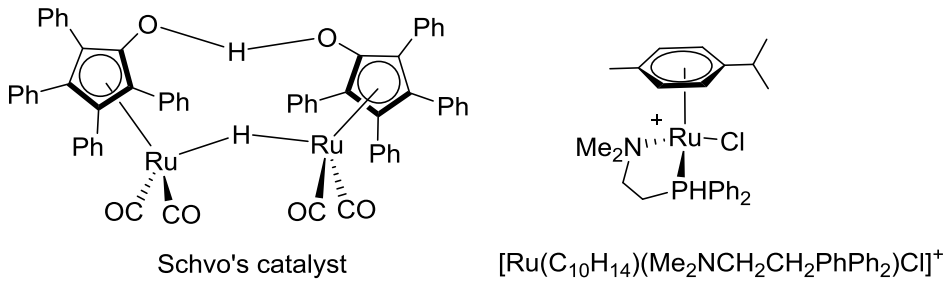



**Figure 2.3** Early Ru(II) catalysts for the transfer hydrogenation reaction, left: Schvo's catalyst,[9] right: Ru(II)arene complex containing a *PN* bidentate ligand.[10]

### 2.1.4. Transition metal complexes containing pincer ligands for the transfer hydrogenation of ketones

Transition metal complexes containing pincer ligands have been used successfully as catalysts for promoting a wide range of transformations and evidence showed that selected coordination motifs may significantly improve catalysis rates and/or selectivities.[11] Much of the attention on transfer hydrogenation reactions have been focused on transition metal complexes containing pincer ligands as catalysts partly due to the increased thermal and catalytic stability of pincer complexes.[12b]

Pincer complexes containing different transition metals have been utilised for the transfer hydrogenation reaction, including Rh(III), Ir(III) and Ru(II) and more recently Fe(II) and Co(II) have also been investigated (Figure 2.4).[12, 13, 14, 15]

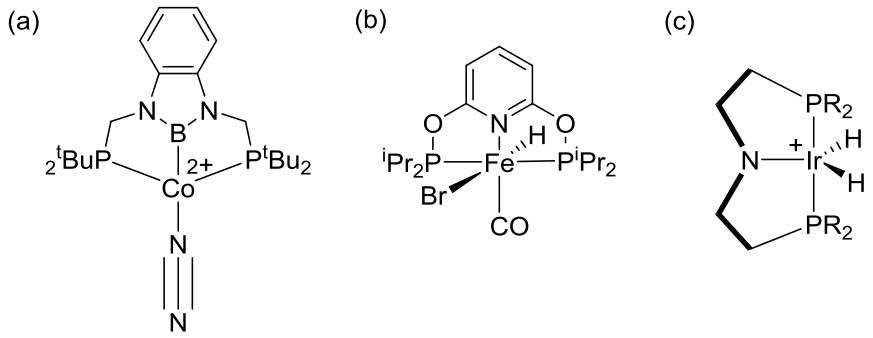



**Figure 2.4** Recent examples of catalysts for the transfer hydrogenation reaction a) [Co(II)(*PBP*)$N_2$][12], b) [Fe(II)(*PNP*)CO(H)Br][13], and c) [Ir(III)(*PNP*)$H_2$].[14]

### 2.1.5. Ruthenium complexes containing pincer ligands for the transfer hydrogenation reaction

Different transition metals provide varied degree of stereoselectivity for the transfer hydrogenation of functional groups containing polar unsaturated bonds, such as ketones and imines. Among these catalysts, Ru(II) complexes containing pincer ligands proved to be the most effective catalysts for the transfer hydrogenation reaction involving carbonyl groups. The majority of such catalysts contain pincer ligands with a central aryl or pyridyl donor group with phosphine and amido side arms.[4, 15] For example, van Koten and co-workers have shown that Ru(II) complexes containing *NNN* and *PCP* pincer ligands are efficient transfer hydrogenation catalysts,[4b] while more recently Milstein and co-workers used a Ru(II)complex containing a *PNN* pincer ligand as an efficient catalyst for the coupling of alcohols and amines (Figure 2.5).[15]

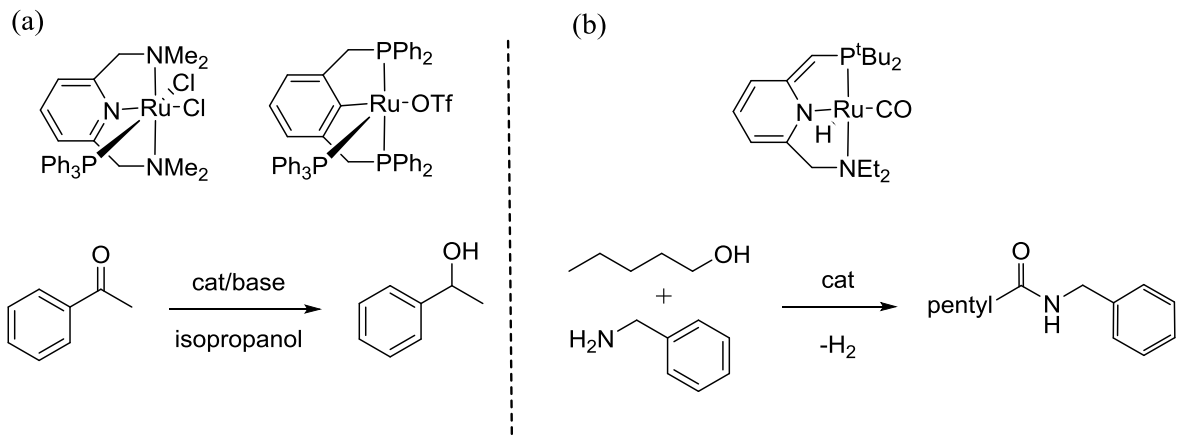



**Figure 2.5** Ru(II) complexes containing pincer ligands by, a) van Koten and b) Milstein.

Among the best catalysts for the transfer hydrogenation of ketones were reported recently by Zhenkun Yu[16] with turnover frequencies (TOFs) exceeding 345600 $h^{-1}$ (Figure 2.6).[16b] As the asymmetric Ru(II) complex contained a combination of relatively strong (pyridine) and weak (benzimidazole and pyrazole) *N*-donor ligands, and the presence of the weakly coordinating donor atoms are likely key for effective transfer hydrogenation catalysis.

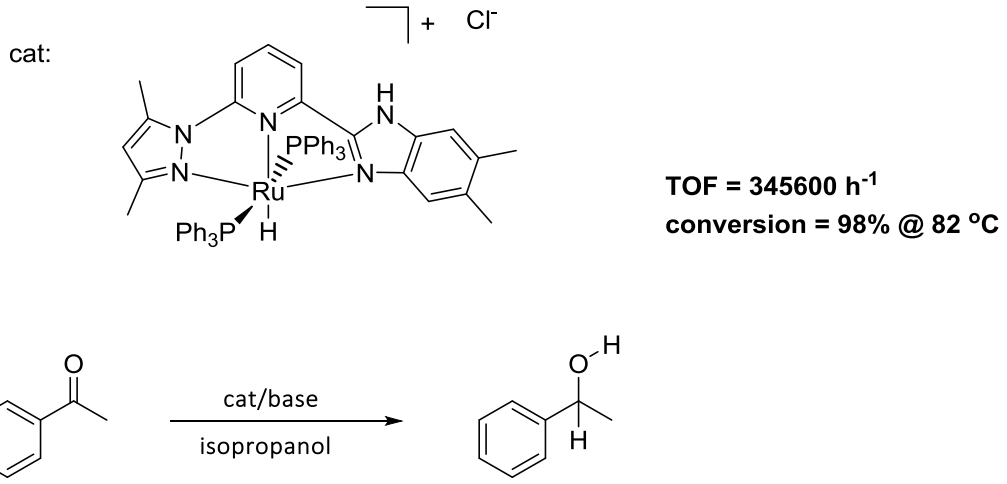


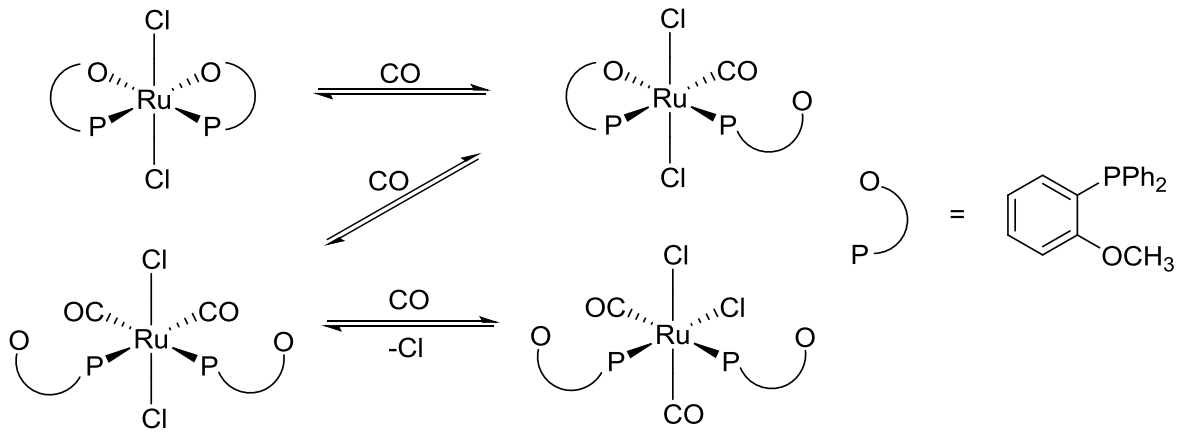

**Figure 2.6** Best catalysts for transfer hydrogenation of ketones.

The complex achieves near complete conversions within 20-30 seconds and maintains high catalytic activity under ambient conditions. However, such complexes are known to be unstable during catalysis due to the weak coordination of the ligand to the metal centre

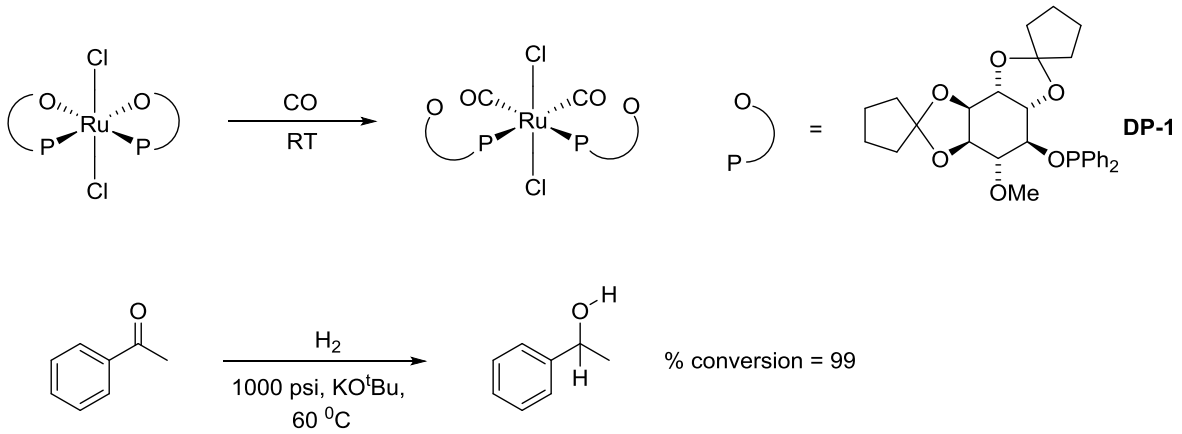
and conversion of larger quantities of substrate could be difficult.[17] Therefore, the utilisation of ligand motifs containing a strong central donor, such as N-heterocyclic carbenes (NHC), in combination with weakly coordinating pendent donor arms could prove to be useful for the transfer hydrogenation reaction. A central NHC donor would increase the stability of the catalyst while labile pendent donors would allow for high catalytic activity by rapid coordination/decoordination opening up vacant co-ordination sites on the metal centre to allow substrate interaction.

### 2.1.6. Ruthenium complexes containing hemilabile ligands

In an effort to create organometallic complexes with diverse coordination modes, pincer ligands which utilise hemilability with a mix of strongly donating donors and weakly donating pendant arms that may or may not coordinate to a metal ion have received significant attention. However, few Ru(II) complexes have been reported in literature with such hemilabile character. Jeffrey and Rauchfuss, *et al.* reported the first ligand to be classified as hemilabile which was an ether-phosphine ligand, *o*-(diphenylphosphino)anisole.[18] The hemilabile character of the ligand was determined by monitoring the co-ordination of the ligand to a Ru(II) metal centre using IR spectroscopy (Scheme 2.1). This was achieved by recording multiple C≡O stretches which correspond to the presence of complexes bearing different numbers of metal bound CO. The data demonstrated that the oxygen donor atoms of the ligand were labile and opened up vacant sites for CO to bind to the Ru centre.




**Scheme 2.1** First reported hemilabile ligand coordinated to Ru(II) and its reactivity to CO.[18]




**Scheme 2.2** Ru(II) complexes containing hemilabile monophosphite ligands.

The ligand system has since been modified to produce effective catalytic systems (Scheme 2.2).[19] In an analogous reaction to that of the Ru(II) *o*-(diphenylphosphino)anisole complex,[18] addition of CO gas to the $RuCl_2(DP\text{-}1)_2$ complexes (Scheme 2.2) resulted in the displacement of the oxygen donors by the CO co-ligands. The $Ru(II)Cl_2(DP\text{-}1)_2$ complexes containing the hemilabile phosphinite motif proved to be superior catalysts for the asymmetric hydrogenation reaction in comparison to the analogous complexes containing strong phosphine donor atoms. This exemplified that the hemilabile character of weakly donating *O*-donor ligands (easily displaced by CO) on the complexes is a crucial character of effective catalysts for the asymmetric hydrogenation reaction of aromatic ketones.

### 2.1.7. Ruthenium complexes containing hemilabile pincer ligands

Xu *et al.* has also recently reported Ru(II) complexes with pincer ligands containing a strong phosphine side arm donor in combination with weakly coordinating N, S and O donor atoms.[20] The work demonstrated that the coordination site of the labile group/co-ligand can affect the catalytic activity of the complex bearing the pincer ligand. The Ru(II) complexes with hemilabile pincer ligands containing *PNX* (X = N, O or S) donors produced catalytic activity that varied significantly with different modes of coordination (Figure 2.7). Ru(II) complexes containing the ligand coordinated to the metal centre in a meridional (*mer*-) configuration produced greatly enhanced activity compared to complexes bearing ligands in a *fac* configuration for the hydrogenation of aromatic ketones. For example, the Ru(II) complex containing a pyridine co-ligand *trans* to the pendant phosphine donor achieves near complete conversion for the hydrogenation of acetophenone. In comparison, the analogous complex with the ligand bound to the metal centre in a (*fac*-) geometry (Figure 2.7) only achieves 10 % conversion of substrate.

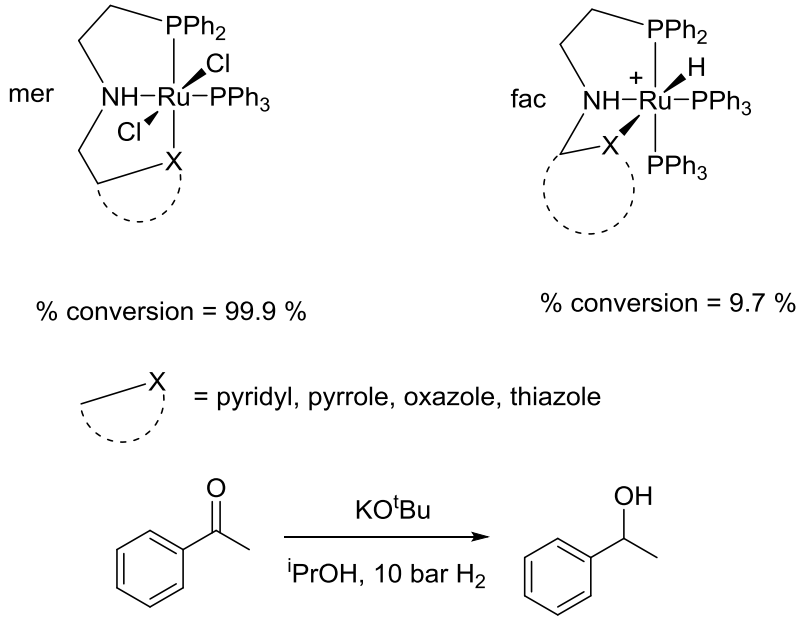
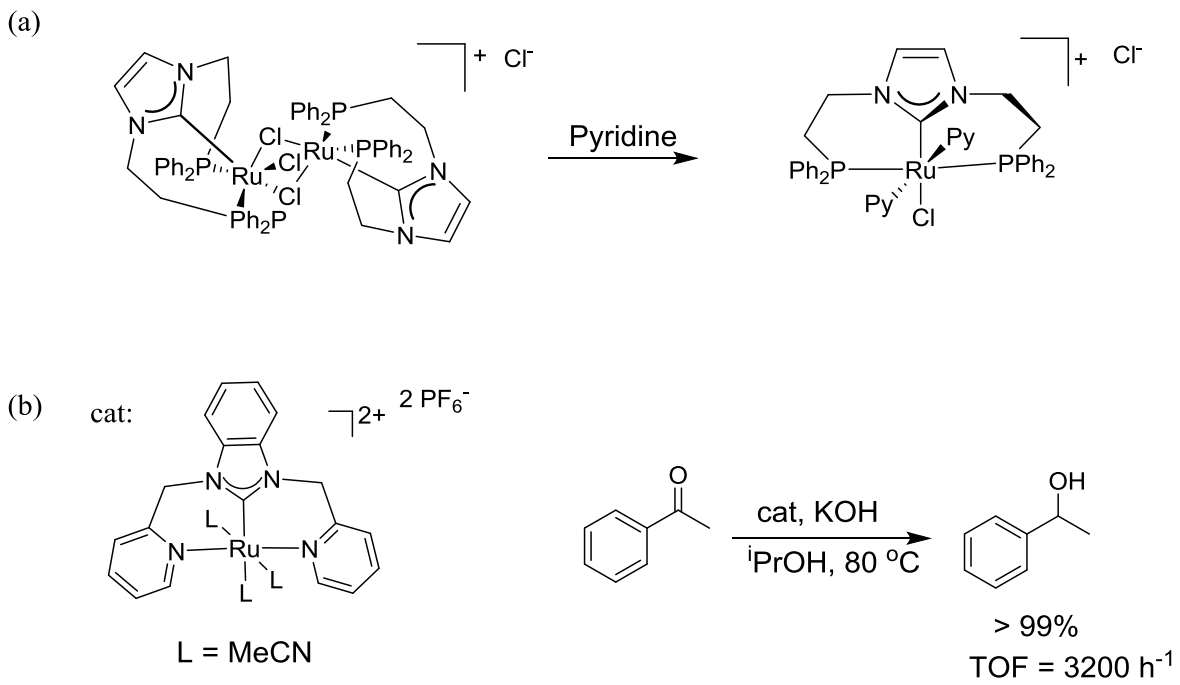



**Figure 2.7** Transfer hydrogenation of ketones catalysed by Ru(II) complexes with hemilabile pincer ligands.

### 2.1.8. Ruthenium complexes of pincer ligands with a central NHC donor

Very little work has been reported on Ru(II) complexes bearing pincer ligands where the ligand contains a central NHC donor group. There are only three previous reports of such complexes, and in two cases, relatively strong phosphine donor side arms were present.[21a] A range of coordination modes were observed for these ligands depending on the co-ligands present. For example, a facial configuration of a *PCP* pincer ligand was observed in the bimetallic $[Ru(II)_2(PCP)_2Cl_3]$ complex (Scheme 2.3a). However, upon addition of pyridine the dimer is cleaved in two resulting in a $[Ru(II)(PCP)Py_2Cl]^+$ complex where a meridional coordination of the PCP ligand is observed (Scheme 2.3a). Recently a Ru complex bearing an *NCN* pincer ligand with a central imidazolium donor and pyridyl side arms was synthesized. A meridional coordination of the ligand to the ruthenium metal centre was observed for the complex (Sceme 2.3b)[21b]. The $[Ru(II)(NCN)(CH_3CN)](PF_6)_2$ complex

(Scheme 2.3b) proved to be highly active for the transfer hydrogenation of aromatic ketones.




Scheme 2.3 Ru(II) complexes containing a pincer ligand with a central NHC donor.

### 2.1.9. Rhodium and Iridium complexes with pincer ligands

Other complexes with different metals in have been reported in the literature including Pd(II), Rh(I) and Ir(I) complexes containing a central NHC donor and weakly coordinating side donor arms.[22, 23] A number of these complexes show superior catalytic activity in comparison to analogous complexes with strongly coordinating side arm donors. For example, an Ir(I) complex with a carbene ligand and two pendant pyridyl donor groups, hence potentially a $\kappa^2$ or $\kappa^3$ complex, demonstrated enhanced catalytic turnovers for transfer hydrogenation (Figure 2.8) relative to the efficiency of other Ir(I) NHC complexes.[22] Similar to the ligand system under investigation here, Shreeve and co-workers reported Pd(II) complexes with bidentate ligands containing the strongly donating carbene donor as

well as the weakly coordinating pyrazole donors as catalysts for the Heck and Suzuki reactions in ionic liquids, (Figure 2.8).[23] The hemilability of this ligand facilitated the weakly coordinating pyrazole to dissociate from the metal centre, allowing the catalyst to pass through the key Pd(0) intermediate for enhancing catalysis.

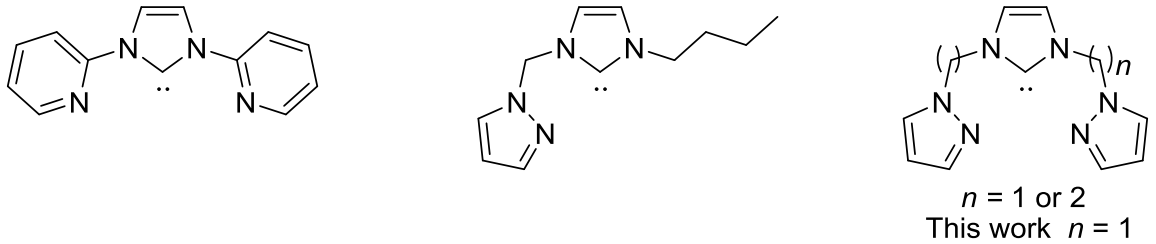



**Figure 2.8** Comparison of other carbene-based ligands with pendant N-heterocyclic donor groups. In this work, n = 1.

We have recently reported the coordination chemistry and catalytic activity of Rh(I) and Ir(I) complexes containing a pincer ligand with a central NHC and a pair of weakly coordinating pyrazole pendant donors (Figure 2.8).[24] As with many other hemilabile carbene containing ligands, these Rh(I) and Ir(I) complexes exhibited a diverse coordination chemistry, including the less flexible ligands (n = 1). The Ir(I) and Rh(I) complexes with the ligand featuring a methylene bridge (n = 1) were shown to be good catalysts for both hydroamination and hydroacyloxylation but not hydrosilylation reactions. It was found that an increase in hemilability of the pendant donors, achieved using a longer linker between the pendant donor and the central NHC donor (ethylene vs methylene bridge), resulted in much poorer catalytic activity for hydrocarboxylation reactions. A similar reactivity was observed in hydroamination reactions.

## 2.2. Aims of this chapter

The work presented in this chapter focuses on pincer ligands containing a central *N*-heterocyclic carbene donor together with labile pendant pyrazole donors. The carbene donor should provide a strong σ-bond to the metal centre,[11a] thereby stabilising metal complexes which use this particular ligand giving access to a range of different coordination modes. Complexes of such hemilabile pincer ligands are known to display enhanced catalytic activity over analogous complexes where the pendant arms are strongly binding.

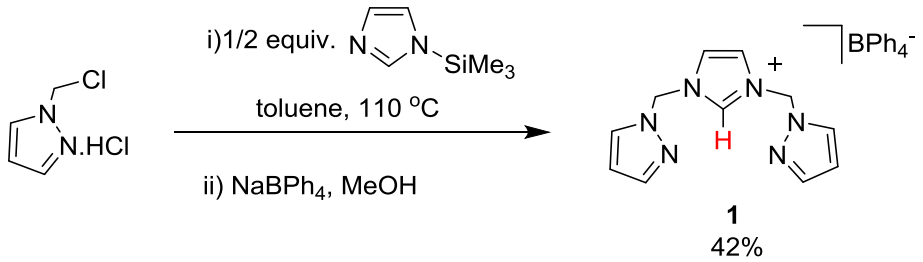
The specific aim of this chapter is to investigate the synthesis and co-ordination chemistry of a number of novel Ru(II) complexes containing a hemilabile $NCN^{Me}$ pincer ligand and subsequently test the novel complexes as catalysts for the transfer hydrogenation reaction of ketones. The specific aims were:

- To synthesise a range of Ru(II) complexes of the $NCN^{Me}$ pincer ligand containing different co-ordination modes with the aim of controlling the coordination mode via careful reagent selection.
- To characterise the new complexes and analyse the co-ordination chemistry using NMR spectroscopy, mass spectrometry, elemental and X-ray crystallography.
- To test the catalytic activity of all synthesised Ru(II) complexes for the transfer hydrogenation of acetophenone. To explore the scope of the catalysis for a range of ketone substrates.

## 2.3. Synthesis of Ru(II) complexes containing a hemilabile *NCN*$^{Me}$ pincer ligand

### 2.3.1. Synthesis and characterisation of [Ag(I)(*NCN*$^{Me}$)$_2$]BPh$_4$ (2)

The *NCN*$^{Me}$ ligand **1** was synthesised according to a procedure previously published from our group. This was achieved by treating chloromethylpyrazole with half a molar equivalent of trimethylsilyl imidazole in refluxing toluene (Scheme 2.4).[24] After 16 hours, a viscous brown oil formed; upon anion exchange with NaBPh$_4$, (*NCN*$^{Me}$)BPh$_4$ (**1**) was isolated as colourless crystals in 42% yield.




**Scheme 2.4** Synthesis of imidazolium bis-pyrazole ligand **1** from chloromethylpyrazole and trimethylsilyl imidazole.

Crystals suitable for X-ray analysis were grown by slow evaporation of a saturated acetone solution of **1**. As expected, the solid state structures confirmed the chemical structure of the ligand essentially in a linear conformation (Figure 2.9).

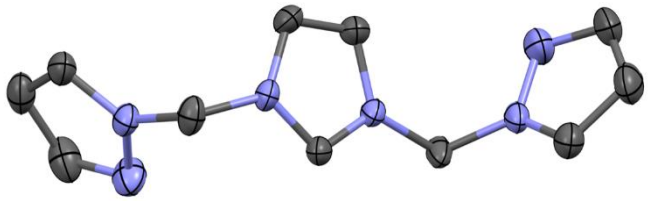


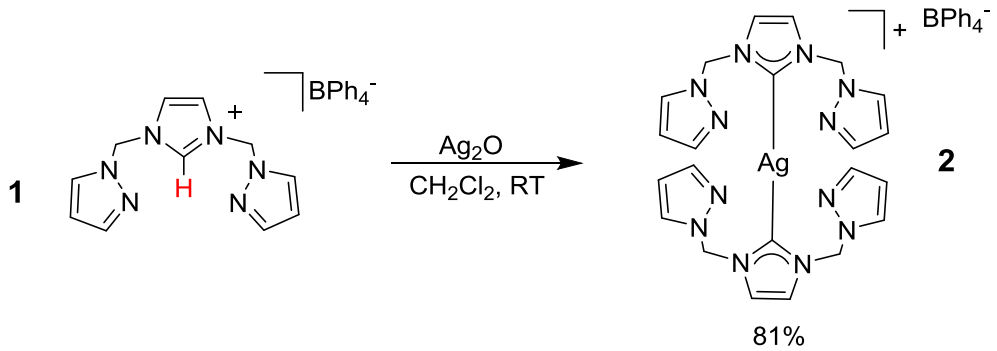
**Figure 2.9** X-ray crystal structure of the imidazolium bis-pyrazole ligand **1**. Ellipsoids shown with 50% probability, hydrogen atoms and BPh$_4$ anion have been omitted for clarity.

Initial attempts to produce a Ru(II) complex directly using the ligand **1** were undertaken by reacting the metal precursor [Ru(II)($\eta^6$-C$_6$H$_6$)Cl$_2$]$_2$ with the *NCN*$^{Me}$ ligand **1** in the presence of NEt$_3$ as an external base in refluxing methanol or ethanol. The resulting mixture

contained multiple species and subsequent isolation of the desired complex was attempted by recrystallising the product from the crude mixture using dichloromethane and *n*-pentane. However, any single Ru(II) complex proved to be inseparable from the unwanted components in the crude mixture. Multiple attempts at recrystallisation reduced the number of unwanted by-products in the crude mixture, however, separation of any major product proved to be unsuccessful.

Silver transmetallation has proven to be a mild and efficient method for the synthesis of Ru(II) complexes containing carbene ligands.[25] Due to the versatility of Ag(I) complexes for transmetallating with many transition metals, the silver complex of ligand **1** was first targeted and isolated. This approach also avoids any problem arising from simple deprotonation of imidazolium salts that generate free carbene ligands in solution which can be extremely unstable and are prone to react/decompose.

The silver complex containing the *NCN*$^{Me}$ ligand **1** was synthesised by treating **1** with excess $Ag_2O$ in dichloromethane to produce [Ag(I)(*NCN*$^{Me}$)$_2$]$BPh_4$ (**2**) as a white solid in 81% yield (Scheme 2.5).




**Scheme 2.5** Synthesis of [Ag(I)(*NCN*$^{Me}$)$_2$]$BPh_4$ (**2**).

The $^1$H NMR spectrum of complex **2** exhibits eight proton resonances, five of which are attributed to the ligand protons, while the other three are due to the $BPh_4^-$ protons. The

absence of imidazolium proton resonances indicated successful complexation of Ag(I) metal to the ligand. The 2D $^{1}H$-$^{13}C$ HMBC spectrum revealed the resonance value for the imidazolium (ImC2) carbon to be 183.9 ppm, which is characteristic of silver metal bound carbonic carbons. Only one set of proton resonances was present which suggested a symmetric structure of the silver intermediate. The ratio of integration of ligand proton resonances to $BPh_4^-$ proton resonances was 2:1, indicating a bis-carbenic-$\kappa^1$-*NCN* geometry. X-ray crystallography confirmed both the $\kappa^1$-*NCN* coordination to Ag(I) in a linear geometry as well as the symmetric structure of the *bis*-ligand monometallic complex (Figure 2.10).

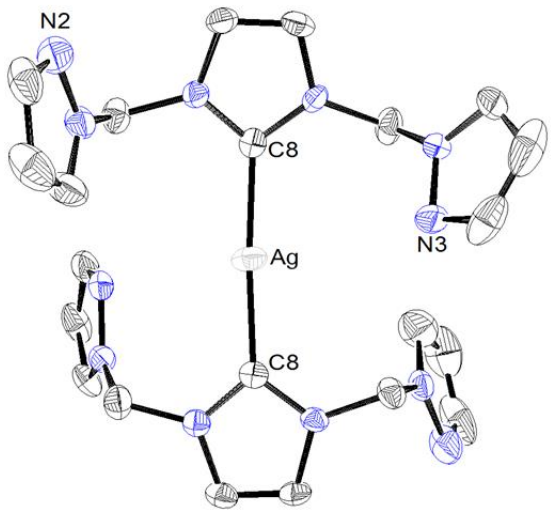
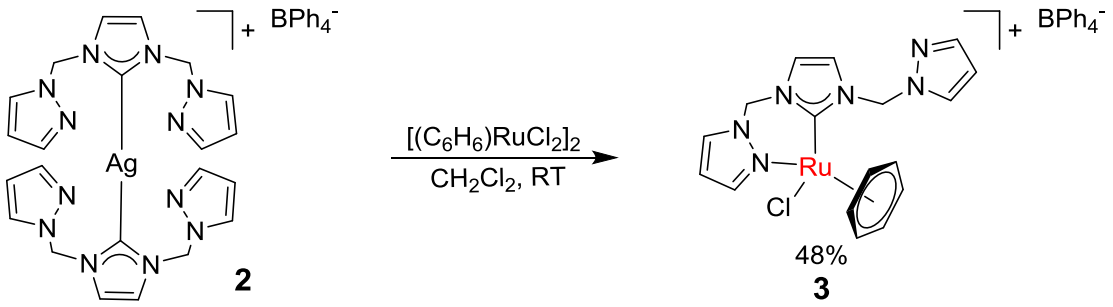



**Figure 2.10** ORTEP depiction of the structure of complex **2** with ellipsoids at 50% probability. Hydrogen atoms and $BPh_4$ have been omitted for clarity.

### 2.3.2. Synthesis and characterisation of [Ru(II)(η$^6$- $C_6H_6$)(*NCN*$^{Me}$)Cl]$BPh_4$ (3)

The precursor [Ru(II)(η$^6$ -$C_6H_6$)$Cl_2$]$_2$ with was reacted with one molar equivalent of **2** to afford the complex [Ru(II)(η$^6$ -$C_6H_6$)(*NCN*$^{Me}$)Cl]$BPh_4$ (**3**) as a bright yellow solid in 48% yield (Scheme 2.6).




**Scheme 2.6** Synthesis of [Ru(II)($\eta^6$-$C_6H_6$)(*NCN*$^{Me}$)Cl]$BPh_4$ (**3**) from **2**.

The $^1$H NMR spectrum of complex **3** contains sixteen resonances. Twelve of the $^1$H resonances were attributed to the *NCN* ligand protons, one to the benzene co-ligand and three to the $BPh_4^-$ counterion. The presence of twelve $^1$H resonances for the *NCN*$^{Me}$ ligand **1** suggests there is asymmetry in the three dimensional structure of the complexes. Although only two resonances were expected for the methylene protons, the presence of four resonances indicated the diastereotopic nature of the methylene protons. The integration ratio of the proton resonances due to ortho Ar-H of the $BPh_4^-$ counterion and a ligand proton resonance is 8:1 which indicates a 1:1 Ru(II) complex to $BPh_4^-$ counterion ratio. A Cl co-ligand is likely to be co-ordinated to the Ru(II) metal centre to balance the remaining 1+ charge of the Ru(II) species. As the benzene co-ligand appears as a singlet, it indicates that it is still bound to Ru(II) in an $\eta^6$ co-ordination, and occupies three co-ordination sites of the Ru(II) metal. Only two co-ordination sites remain on the Ru(II) metal centre which infers a bidentate co-ordination of *NCN*$^{Me}$ ligand **1** to Ru(II). The expected structure containing the bidentate co-ordination geometry was confirmed using X-Ray crystal structure analysis (Figure 2.11). Mass spectrometry of the isolated yellow solid shows a single dominant signal at 443.03 m/z which is attributed to the loss of the $BPh_4^-$ counterion. The isotope pattern of the signal matches the expected isotope pattern typical of Ru(II) complexes.

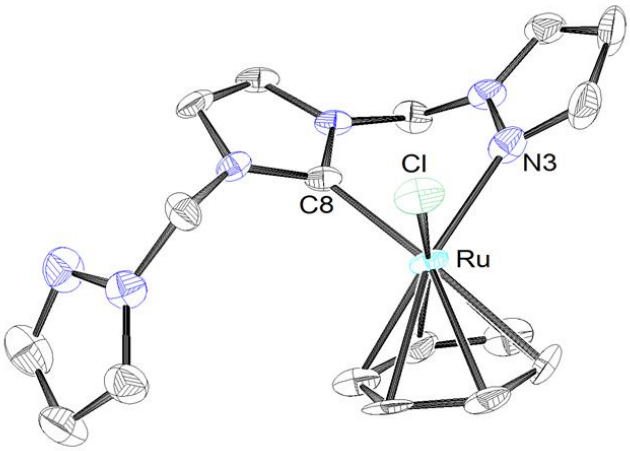
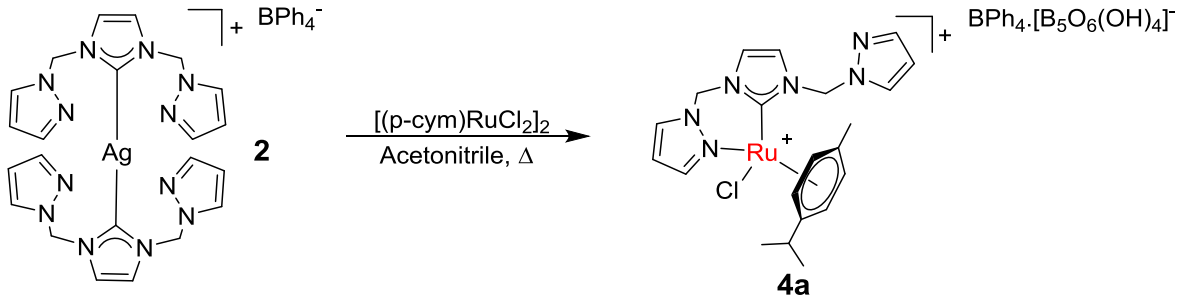



**Figure 2.11** ORTEP depiction of the structure of complex **3** showing atom labelling scheme. Hydrogen atoms and $BPh_4^-$ have been omitted for clarity.

### 2.3.3. Synthesis and characterisation of Ru(II)($\eta^6$- $C_{10}H_{14}$)(*NCN*$^{Me}$)Cl]$BPh_4$ (4)

Due to the successful synthesis of complex **3** using the isolated silver intermediate **2**, the silver transmetallation route was utilised in attempts to produce the analogous complex containing the *p*-cymene co-ligand. Reaction of the precursor [Ru(II)($\eta^6$-*p*-cym)$Cl_2$]$_2$ with one molar equivalent of [Ag(*NCN*$^{Me}$)$_2$]$BPh_4$ (**2**) (Scheme 2.7) was expected to produce the complex [Ru(II)($\eta^6$-*p*-cym)(*NCN*$^{Me}$)Cl]$BPh_4$ (**4**). However, the elemental analysis of the mixture had a carbon composition 20% below the expected value (C: 65.97, H: 5.78, N: 10.26). Elucidation of the solid state structure of the mixture using X-ray crystallography revealed the presence of **4a** with only an unusual $[B_5O_6(OH)_4]^-$ counterion (Figure 2.12). The $^1$H NMR spectrum of the mixture showed the expected proton resonances consistent with the structure of complex **4**; similar to complex **3**, twelve proton resonances are attributed to the ligand. However, the integration ratio of *o*-$BPh_4$ proton resonances to a ligand proton resonance was approximately 0.7:1, this is approximately 14% of the expected ratio of 8:1.




**Scheme 2.7** Synthesis of $[Ru(\eta^6-C_{10}H_{14})(NCN^{Me})Cl]BPh_4[B_5O_6(OH)_4]$ (**4a**).

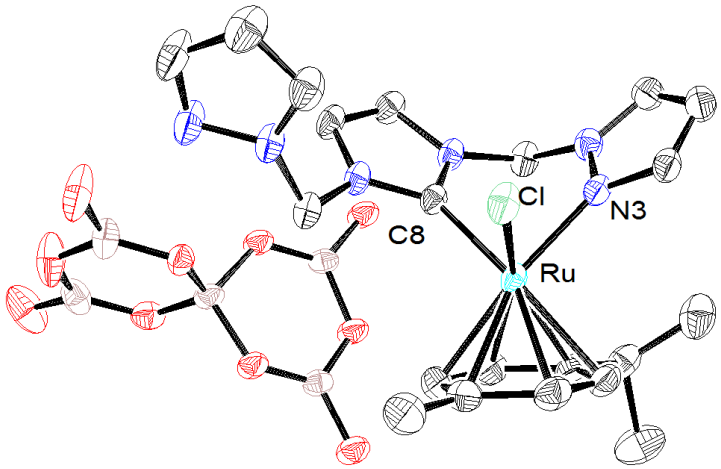



**Figure 2.12** ORTEP depiction of the structure of complex **4a** showing atom labelling scheme (red: oxygen, purple: boron). Hydrogen atoms have been omitted for clarity.

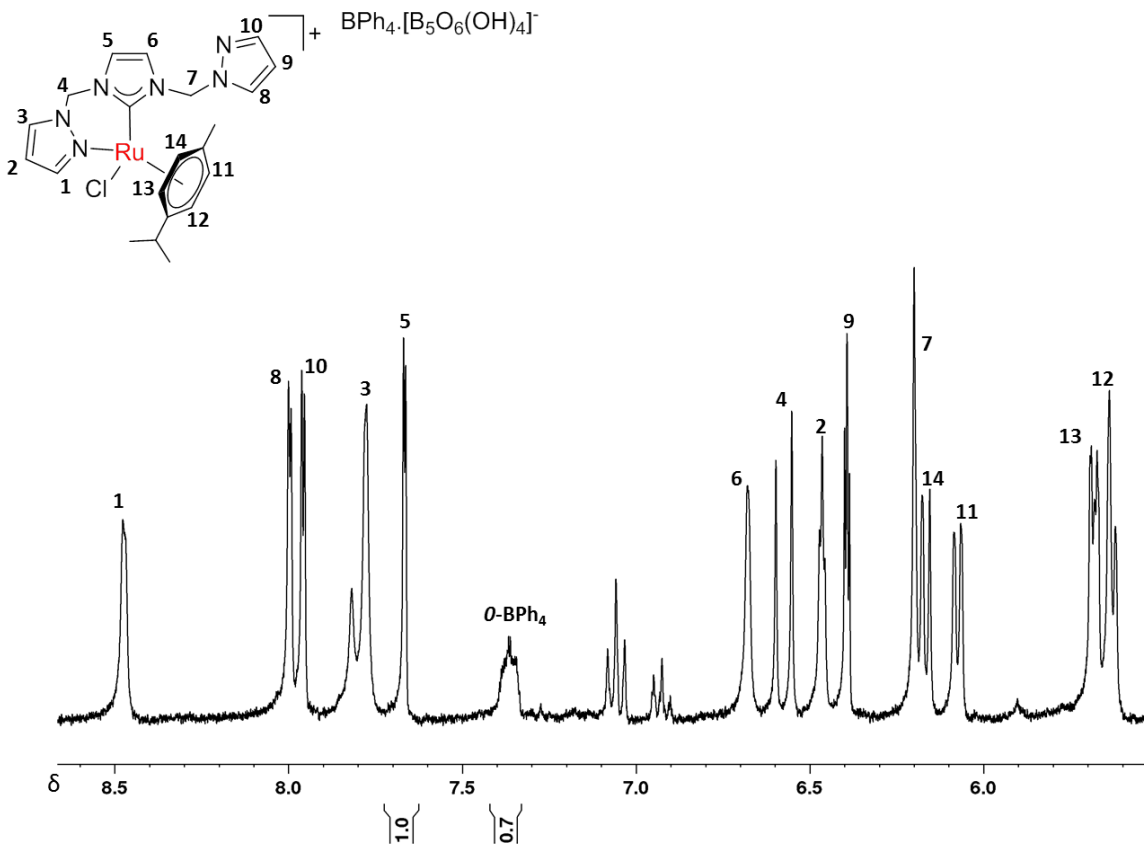
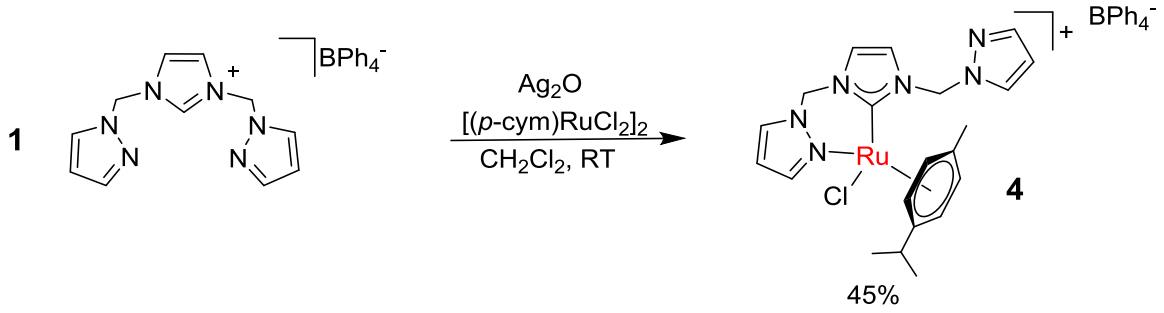



**Figure 2.13** $^1$H NMR spectrum of Ru(II)(η$^6$- $C_{10}H_{14}$)(*NCN$^{Me}$*)Cl]$BPh_4$[$B_5O_6(OH)_4$] (**4a**).

The integration ratio of ligand protons in the mixture: *o*-protons of the $BPh_4^-$ counterion is 1: 0.7 as shown in Figure 2.13, which is equivalent to a ligand: $BPh_4^-$ ratio of 1: 0.175. This ratio shows 14% of the counterion is $BPh_4^-$ and that the ratio of [$B_5O_6(OH)_4$]:$BPh_4$ is 86:14. This counterion ratio is in close agreement with the elemental analysis. However, slightly different ratio of counterions were produced upon attempts to repeat the reaction.

An *in situ* silver transmetallation reaction was carried out in an attempt to avoid the $BPh_4$/[$B_5O_6(OH)_4$]$^-$ mixture where the *NCN$^{Me}$* ligand (**1**) was reacted with half a molar equivalent of [Ru(II)(η$^6$ -*p*-cym)$Cl_2$]$_2$ in the presence of $Ag_2O$ in dichloromethane (Scheme

2.8). The reaction was successful and afforded complex **4** as an orange-yellow solid in 45% yield which does not contain the $[B_5O_6(OH)_4]^-$ anion, only $BPh_4^-$.



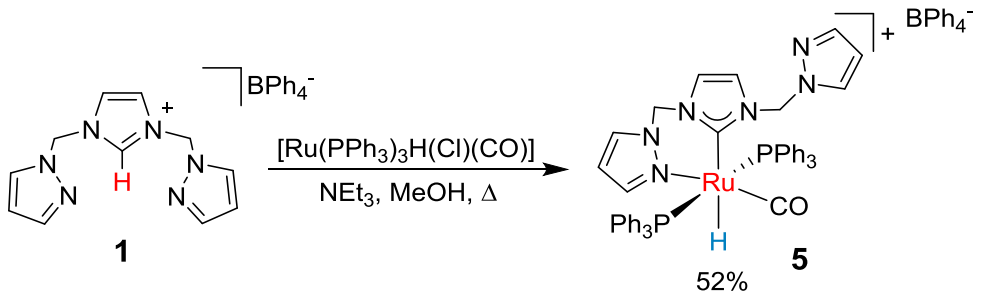

**Scheme 2.8** Synthesis of [Ru(II)($\eta^6$-*p*-cym)(*NCN*$^{Me}$)Cl]$BPh_4$ (**4**).

The $^1$H NMR spectrum of **4** showed a similar set of proton resonances to the complex **4a** which contained the unusual counterion $[B_5O_6(OH)_4]^-$. However, the integration ratio of *o*-$BPh_4^-$ proton resonances to a ligand proton resonance for complex **4** is 8:1. Elemental analysis of the complex (C: 65.86; H: 5.77; N: 9.83) confirmed the calculated values and suggested that only $BPh_4^-$ is present as the counterion.

### 2.3.4. Synthesis and characterisation of [Ru(II)(H)CO(*NCN*$^{Me}$)($PPh_3$)$_2$]$BPh_4$ (5)

Deprotonation of imidazolium salts using an external base such as triethylamine is a common method for the synthesis of Ru(II) NHC complexes.[26] If the metal precursor is also added into the reaction mixture along with the base the accumulation of the free carbene can be avoided.

Reaction of the imidazolium ligand **1** with one molar equivalent of the precursor [Ru(II)(H)Cl(CO)($PPh_3$)$_3$] in the presence of excess $NEt_3$ in refluxing methanol resulted in the formation of complex **5** as a white powder in 52% yield (Scheme 2.9).




**Scheme 2.9** Synthesis of [Ru(H)CO($NCN^{Me}$)$(PPh_3)_2$]$BPh_4$ (**5**) from **1**.

The $^1$H NMR spectrum of complex **5** shows ten ligand proton resonances and is indicative of the asymmetric structure of complex **5**. The resonances of the protons of one of the pyrazole rings are at significantly different chemical shifts to those of the other pyrazole ring suggesting a $\kappa^2$-coordination (NC) of ligand **1** to the Ru(II) metal centre. Additionally, a triplet resonance due to a Ru(II) bound hydride was observed at -6 ppm ($^2J_{H\text{-}P}$= 21.9 Hz) indicative of a hydride that is situated *cis* to two chemically equivalent phosphorous atoms which are *trans* to one another ($^{31}$P NMR, $\delta$ = -48 ppm, $^2J_{H\text{-}P}$ = 21.9 Hz).[27] Unlike complex **4**, only two resonances were assigned to the methylene protons as singlets which indicated the absence of diasteretopic coupling. The structure of complex **5** was confirmed by single crystal X-ray structure analysis (Figure 2.14), with the hydride in a *trans* configuration relative to the carbonic carbon (Im C2) and *cis* to the two $PPh_3$ groups. The IR spectrum contained two distinct, strong signals for the Ru-H (1606 cm$^{-1}$) and Ru-CO (1938 cm$^{-1}$) stretches.

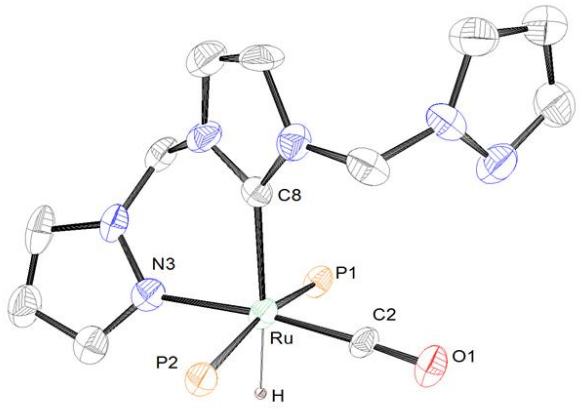



**Figure 2.14** ORTEP depiction of the structure of complex **5** showing atom labelling scheme. Hydrogen atoms have been omitted for clarity. Phenyl groups of the $PPh_3$ ligands were omitted for clarity.

#### 2.3.4.1. Isomerisation reaction of [Ru(II)(H)CO(*NCN*$^{Me}$)($PPh_3$)$_2$] (5):

Upon analyzing the $^1$H NMR data of **5** a second hydride resonance and a second set of ligand peaks in the base line were observed. Variable temperature $^1$H NMR experiments were undertaken to determine if this second set of resonances was due to the free pyrazole arm binding to the metal centre to produce a $\kappa^3$-coordination geometry of the pincer ligand. When the complex was heated to 70 $^\circ$C in $CH_3CN$ for 24 h the second set of resonances increased in intensity. 2D NMR (NOESY, COSY) did not reveal any cross peaks between the two sets of proton resonances which would have indicated some exchange process. It was determined that the second set of proton resonances represented an isomerisation of the CO and H co-ligands (Figure 2.15). As the isomer which contains the hydride co-ligand in a *trans* position to the pyrazole nitrogen produces a distinct triplet resonance at -13 ppm; the ratio of **5** and **5a** was monitored overtime by calculating the integration ratio of the two resonances at -6 and -13 ppm. The irreversible reaction to **5a** achieves over 95% conversion after 36 hours in refluxing acetonitrile.

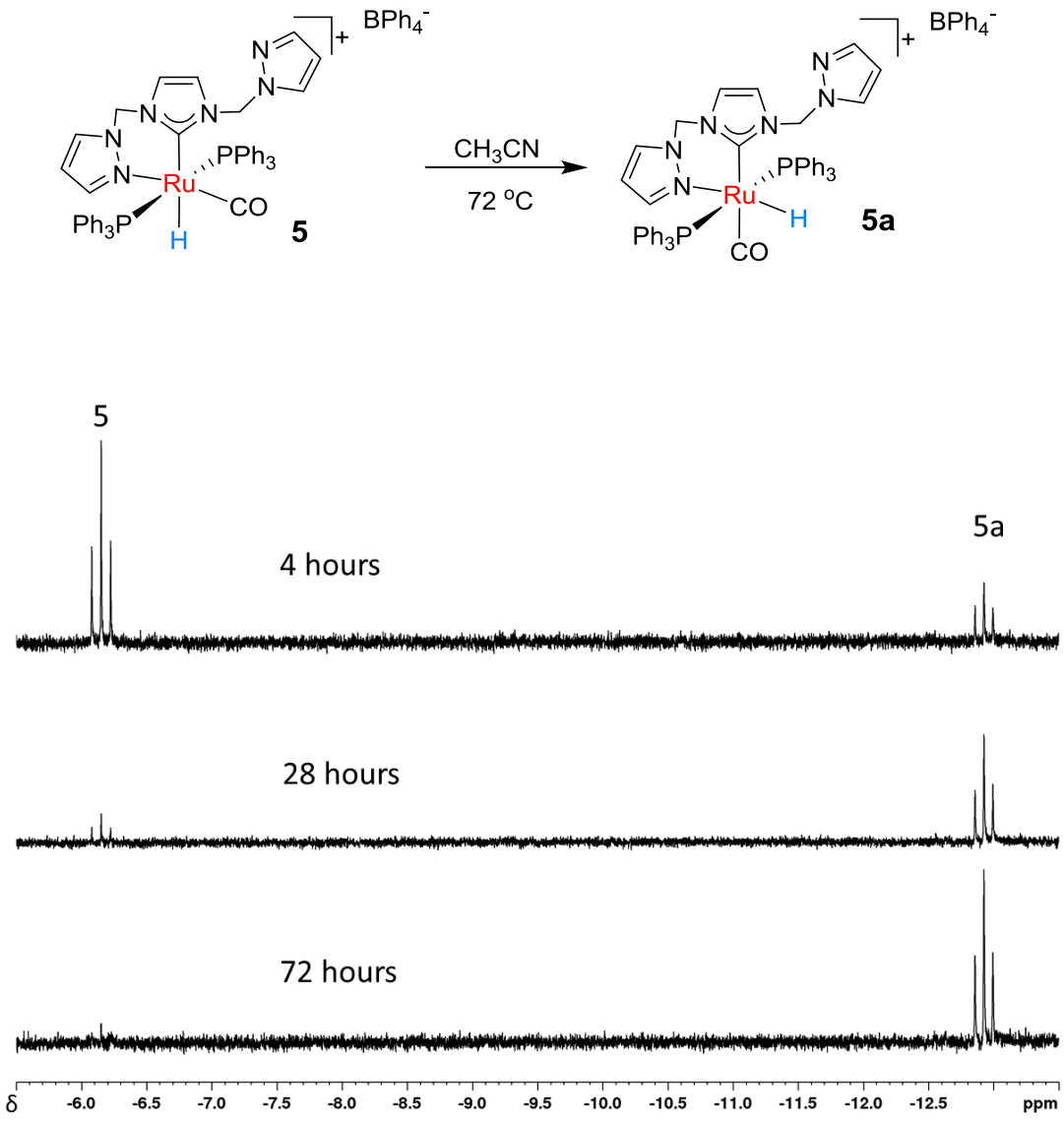



**Figure 2.15** Stacked $^{1}$H NMR spectra of the hydride resonance regions at 72 $^{o}$C for complexes **5** and **5a.** (H *trans* to pyrazole + H *cis* to pyrazole).

### 2.3.4.2. Synthesis of an unexpected cubane structure [Ru(I)Cl(PPh$_3$)]$_4$ (6)

Initial attempts to produce the complex [Ru(II)(H)CO(*NCN*$^{Me}$)(PPh$_3$)$_2$]BPh$_4$ (**5**) by reacting the silver intermediate [Ag(I)(*NCN*$^{Me}$)$_2$]BPh$_4$ with one molar equivalent of [Ru(II)(H)ClCO(PPh$_3$)$_3$] resulted in isolation of a grey powder which was found to be a mixture of a complex with different counterions, [Ru(II)(H)CO(*NCN*$^{Me}$)(PPh$_3$)$_2$]X (where X = BPh$_4$ or Cl). The $^{1}$H NMR spectrum of the mixture showed an ortho BPh$_4^{-}$: *NCN*$^{Me}$ ligand proton resonance ratio

significantly lower than the expected value of 8:1 indicating that the remaining amount of counterion is likely Cl. Multiple attempts to purify complex **5** from the crude mixture by recrystallisation proved to be unsuccessful. However, single crystals suitable for X-ray crystallography were grown from the crude mixture. Elucidation of the resulting green crystals by X-ray analysis revealed an unusual distorted Ru(I) cubane structure (Figure 2.16).

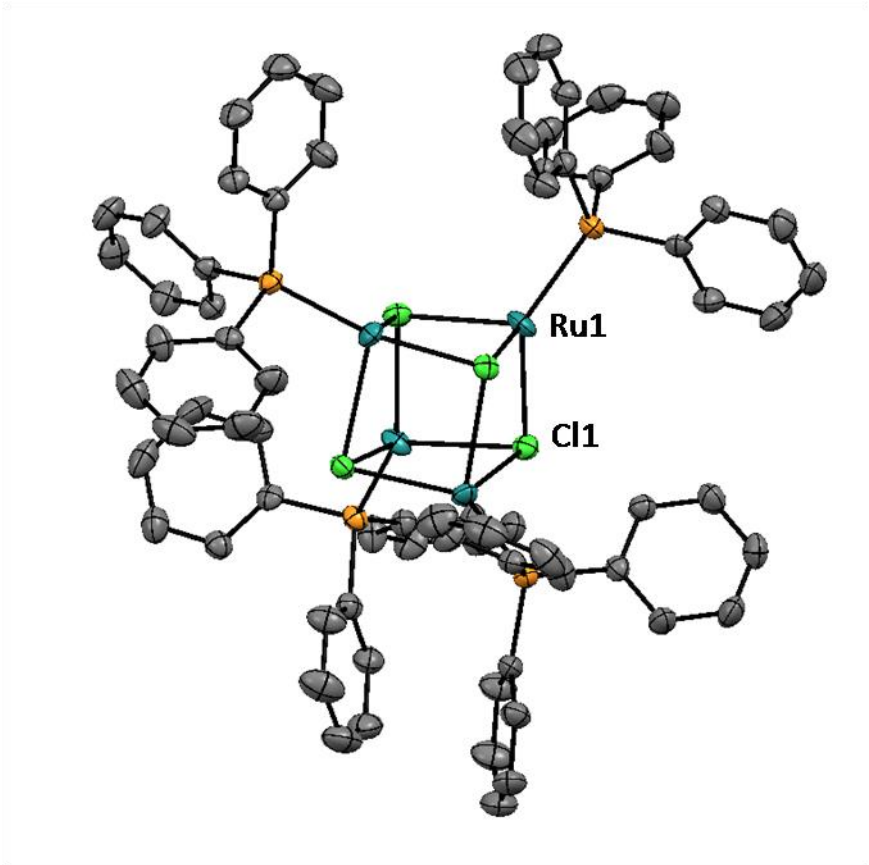


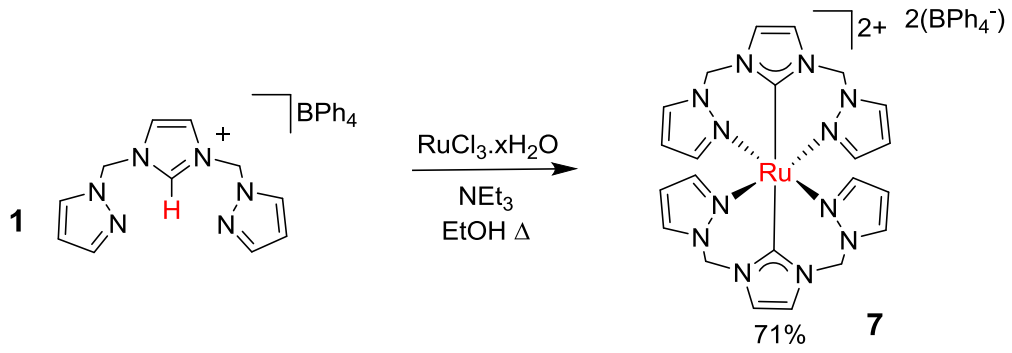

**Figure 2.16** Molecular structure of complex **6** showing atom labelling scheme. Hydrogen atoms have been omitted for clarity.

Interestingly, complex **6** has not been reported in literature and only a few Ru complexes are reported to contain an analogous cuboid structure.[28] The analogous$[Ru(II)Cl(Cp)]_4$ complex is a useful precursor for the production of a number of Ru(II) complexes.[28a] Isolation of $[Ru(I)Cl(PPh_3)]_4$ in higher yields could prove to be important as the complex can

be utilised as a new class of ruthenium(I) precursor. As shown in Figure 2.16, the cubane structure consists of two distorted tetrahedral units of ruthenium(I) and chlorine atoms, each ruthenium ion is also coordinated to a single $PPh_3$ ligand. The Ru(I)-Cl bond distances range from 2.523 Å to 2.761 Å. These distances are closely comparable to the isostructural $Ag_4Cl_4(PPh_3)_4$ reported in literature.[28] The Ru(I)-P bond distances are smaller (2.369 Å-2.377 Å) in comparison to the Ru(I)-Cl bond distances. Interestingly, all Ru(I)-P-C angles which range from 112.75- 116.55° are larger than typical tetrahedral angles likely due to the strained cubic structure. This trend is also evident for the P-Ru(I)-Cl bond angles which range from 112.07- 139.78°.

### 2.3.5. Synthesis and characterisation of $[Ru(II)(NCN^{Me})_2](BPh_4)_2$ (7)

Deprotonation of the pro ligand **1** using $NEt_3$ as an external base followed by complexation with one molar equivalent of $Ru(III)Cl_3.xH_2O$ in refluxing ethanol afforded complex **7** in 71% yield as a dull green solid (Scheme 2.10).




**Scheme 2.10** Synthesis of $[Ru(II)(NCN^{Me})_2](BPh_4)_2$ (**7**)

The $^1H$ NMR spectrum of complex **7** contained two sets of ligand proton resonances. Careful analysis of the prepared complex showed that these two sets of resonances could be attributed to the formation of two products or a pair of isomers (Figure 2.17). In

attempts to separate the two different species, single crystals were isolated from the green solid. Dissolution of the green solid in acetone followed by slow evaporation at room temperature in a crystallisation tube afforded multiple yellow single crystals suitable for X-ray crystallography. Upon dissolution of the isolated single crystals, the identical two sets of resonances remained. Mass spectrometry showed one strong signal at 279.08 m/z which indicated the presence of a single species and is assigned to the loss of two $BPh_4^-$ counterions. Elemental analysis of the isolated crystals was in complete agreement with the calculated value of complex **7**, confirming that only one species was present. Variable temperature NMR studies showed the intensity of one set of proton resonances reduced upon reduction of temperature (Figure 2.17). Lowering the temperature also resulted in the reduction of fluctionality of the equivalent methylene ($CH_2$) protons; which is evident from the conversion of the broad resonance between 6.0 to 6.1 ppm to a sharp (fwmh 13.7 Hz) signal. This indicates that one type of isomer is favoured at lower temperatures.

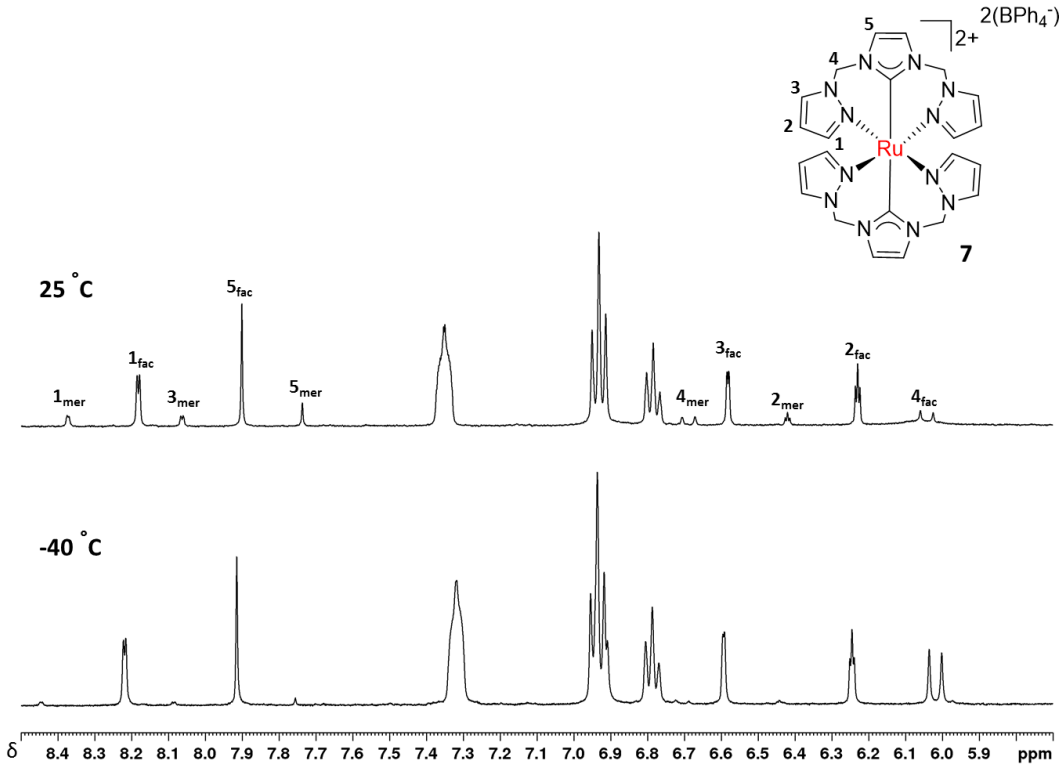



**Figure 2.17** Variable temperature $^{1}$H NMR spectra of [Ru(II)($NCN^{Me}$)$_2$](BPh$_4$)$_2$(**7**) showing the isomerisation between the *fac* isomer (**7**) and *mer* isomer (**7a**).

A Ru(II) bis-carbene structure was confirmed by analysis of the solid state structure using X-ray crystallography (Figure 2.19). Complex **1** can coordinate to the Ru(II) metal centre either in a facial or meridional coordination mode although only the *fac* coordination was observed by X-ray crystallography (Figure 2.18). It may be coincidental that the crystals of each isomer were indistinguishable and therefore the *mer*-isomer was not resolved by X-ray crystallography. Alternatively, the *fac* isomer could selectively crystallise but isomerises in solution.

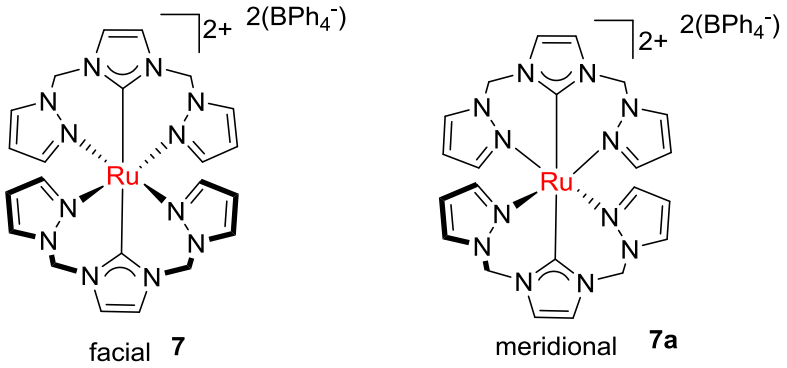



**Figure 2.18** Facial and meridional coordination modes of [Ru(II)($NCN^{Me}$)$_2$](BPh$_4$)$_2$.

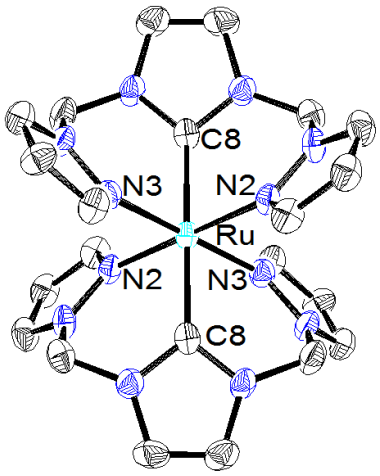



**Figure 2.19** ORTEP depiction of the solid state structure of complex **7** at 50% probability thermal ellipsoids showing the *fac* coordination. Hydrogen atoms and BPh$_4$counterions have been omitted for clarity.

### 2.3.6. Comparison of solid state structures

Ru(II) complexes **5** and **7** adopt an octahedral geometry, with the main difference being that the $NCN^{Me}$ ligand is bound to Ru(II) in a bidentate co-ordination mode in complex **5**, while in complex **7**, the ligand adopts a tridentate co-ordination mode to the metal centre (Figure 2.18). Complex **7** is also the only species in the series that consists of a bis- NHC structure where all co-ordination sites are occupied by two ligands. The Ru-C(1) and Ru-N(3) bond lengths are slightly longer in complex **5** in comparison to the analogous bond lengths in **7**, indicating stronger bonding

interaction between Ru(II) and pyrazole in **7** as strong π back-donation from Ru(II) to CO in **5** weakens the Ru-pyrazole bond located in the *trans* position, see Table 2.1. The carbene carbons and pyrazole nitrogens (N2, N3) in complex **7** show no distortion from linearity as the Ru(II) ion lies on an inversion centre (C-Ru-C/N-Ru-N: 180.00(2)°). However, similar alignments in complex **5** (X-Ru-Y, where X=N, Y=C, or X=Y=P) exhibit heavy distortion from linearity (P-Ru-P: 168.77(2)°) likely due to the steric bulk of the two $PPh_3$ groups.

| Atoms | **7**(Figure 2.19) | **5**(Figure 2.14) | **3**(Figure 2.11) | **4a**(Figure 2.12) |
|---|---|---|---|---|
| Ru(1)-C(1) | 2.049(5) | 2.117(6) | 2.04(1) | 2.046(2) |
| Ru(1)-C(2) | ---- | 1.810(5) | ---- | ---- |
| Ru(1)-N(2) | 2.076(4) | ----- | ----- | ----- |
| Ru(1)-N(3) | 2.088(4) | 2.122(5) | 2.096(7) | 2.085(2) |
| Ru(1)-Cl | ----- | ----- | 2.399(2) | 2.408(1) |
| Ru(1)-P(1) | ----- | 2.368(1) | ----- | ----- |
| Ru(1)-P(2) | ----- | 2.369(1) | ----- | ----- |
| C(1)-Ru(1)-N(3) | 84.2(2) | 86.6(2) | 83.3(3) | 83.58(9) |
| C(1)-Ru(1)-N(2) | 82.1(2) | ----- | ----- | ----- |

**Table 2.1** Selected bond lengths (Å) and angles (°) for **3**, **4a**, **5**, and **7**.

Complexes **3** and **4a** each adopt a psuedo-octahedral geometry and are similar in structure, for example, the Ru-C(1) bond lengths are the same within 1 esd. Structural similarity of complexes **3** and **4a** was further confirmed by comparison of the Ru-N(3) or Ru-Cl bond lengths, which fall within 0.01 Å of each other, as well as the C(1)-Ru-N(3) angle which differs by only 0.2° between complexes **3** and **4a**. The Ru-C1 bond lengths of complexes **3**, **4**, **4a**, **5**, **5a** and **7** are comparable to similar

Ru(II) complexes reported in the literature.[29] The boron counterion $[B_5O_6(OH)_4]^-$ in **4a** was identified using X-ray crystallography. The counterion is composed of a central tetrahedral boron as the apex of two six-membered rings composed of alternating boron and oxygen atoms, the counterion is terminated by four hydroxy units. The two six-membered rings in the complex are perpendicular to one another relative to the central boron atom.

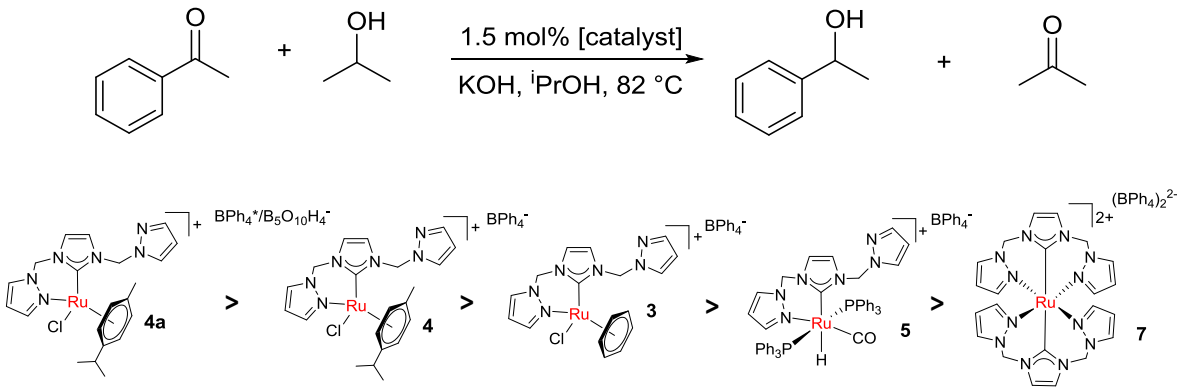
As expected the crystal structure of Ag(I) complex **2** showed two *NCN*$^{Me}$ ligands coordinated to the Ag(I) ion through the carbene unit. In the solid state the pendant pyrazole arms are directed toward the same face such that the complex has a centre of inversion through the silver centre. The Ag-C1 and Ag-C2 each have a bond length of 2.08 Å typical of similar silver *bis*-NHC complexes and the angle between C1-Ag-C2 is 4$^o$ off linearity (180°).[30] There is also slight rotation of one of the NHC ligands out of the plane relative to the other in complex **2** giving a torsion angle of 17°.

## 2.4. Catalysed transfer hydrogenation of ketones using complexes 3, 4, 4a, 5, 5a and 7

Ru(II) complexes have proven to be effective catalysts for the activation of polar unsaturated bonds including transfer hydrogenation of ketones.[4b] The transfer hydrogenation upon use of metal catalysts such as Ru(II) does not require harsh reaction conditions. Therefore, complexes $[Ru(II)(\eta^6\text{-}C_6H_6)(NCN^{Me})Cl]BPh_4$ (**3**),$Ru(II)(\eta^6\text{-}C_{10}H_{14})(NCN^{Me})Cl]BPh_4$ (**4**), $Ru(II)(\eta^6\text{-}C_{10}H_{14})(NCN^{Me})Cl]BPh_4[B_5H_{10}O_4]^-$ (**4a**), $[Ru(II)(H)CO(NCN^{Me})(PPh_3)_2]BPh_4$ (**5**) and $[Ru(II)(NCN^{Me})_2]BPh_4$ (**6**) were tested as catalysts for the catalysed transfer hydrogenation of ketones. A selecton of substrates including aromatic and aliphatic ketones were used to test the scope of catalytic activity for the Ru(II) complexes. The reactions were carried out in refluxing $^i$PrOH using KOH as a base and a

catalyst loading of 1.5 mol% unless otherwise stated. For complete experimental details, refer to chapter 6.

Interestingly, the complexes with the pseudo-octahedral coordination geometry (**4**, **4a** and **3**) proved to be the most active for the transfer hydrogenation reaction and also gave the highest yield of hydrogenated products, see Chart 2.1. The mixed catalyst [Ru(II)($\eta^6$-$C_{10}H_{14}$)(*NCN*$^{Me}$)Cl]$BPh_4[B_5H_{10}O_4]^-$ **4a** containing the unusual boron counterion achieves over 90% conversion of acetophenone to 1-phenylethan-1-ol in less than 30 minutes at 83 °C, and complete conversion within four hours. The efficacy of **4a** as a catalyst for transfer hydrogenation is comparable to some of the best Ru(II) catalysts reported for this reaction, such as [Ru(II)(OTf)(*PCP*)$PPh_3$].[31]



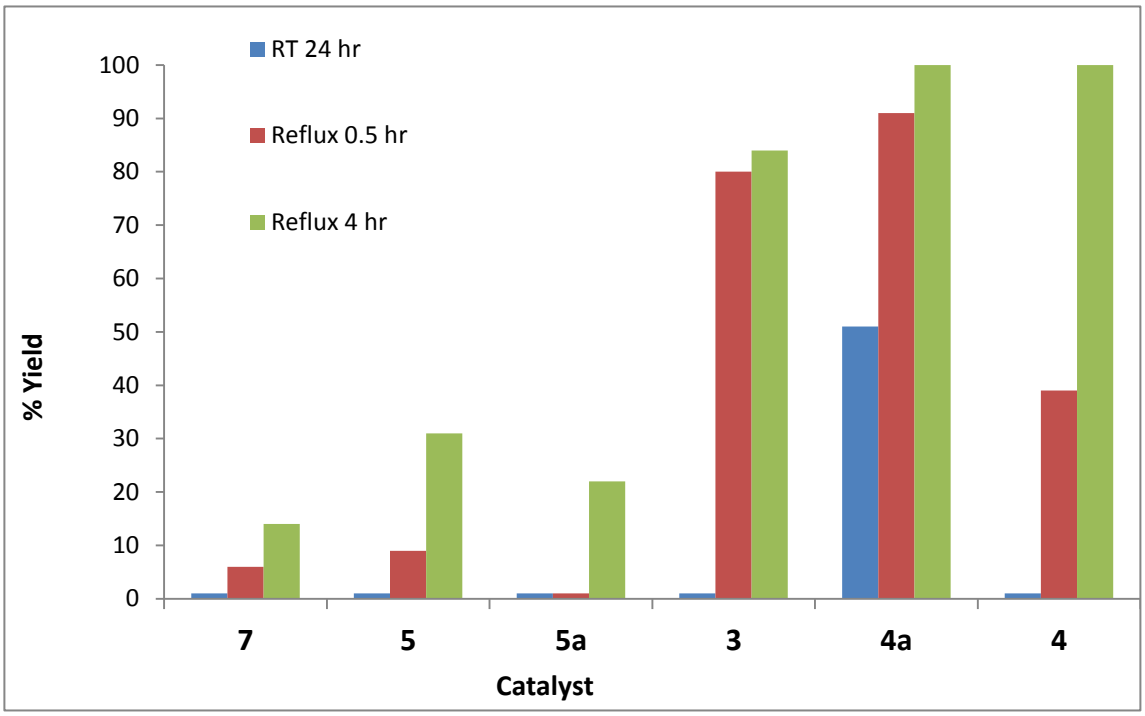




**Chart 2.1** Catalytic transfer hydrogenation of ketones. % Conversion refers to conversion of acetophenone to 1-phenylethan-1-ol. Values in graph represent results from individual experiments.

Comparing the efficacy of complex **4a** containing the mixed borate anion with complex **4** containing pure $BPh_4$ anion, it was found that the catalyst **4a** is more active, achieving 91% conversion in 0.5 hours vs. 39% conversion for **4** (Chart 2.1). This indicates that the presence of $[B_5O_6(OH)_4]^-$ does enhance the catalytic activity for the transfer hydrogenation reaction and is therefore non-innocent, potentially acting as a catalyst in its own right. Oxygenated four-coordinate boron compounds

have been reported previously in literature as catalysts with a moderate efficiency for the transfer hydrogenation reaction of ketones. In these reports, the boron atom is covalently linked to an organic scaffold unlike the counterion used here.[32] This suggests that reasonable increase in catalytic activity is a result of the pentaborate anion.

Catalysts **3** and **4a** exhibit different catalytic rates for the transfer hydrogenation of acetophenone despite the similarity in structure of the two complexes, with the only difference being the arene co-ligand (benzene, **3**, vs. *p*-cym, **4a**). Whilst complex **4** achieves complete conversion within four hours, complex **3** only reached a maximum conversion of 80% over the same period of time. The stronger electron donating properties of the *p*-cym co-ligand of complex **4** may stabilise **4** more effectively than the benzene co-ligand of complex **3**, resulting in the catalyst remaining stable for a longer period of time under the reaction condition and hence a higher conversion of the substrate.

Complex **5** catalysed the formation of the 1-phenylethan-1-ol product yielding 24% of the product after four hours at reflux, and >99% conversion after 24 hours at reflux. This slow reactivity was unexpected as the complex contains a pre-existing hydrido group which should enable a more efficient transfer hydrogenation reaction, as one of the key steps in the catalytic cycle is the transfer of a hydride from the catalyst to the substrate. It is possible that the catalytic activity is affected by the relative position of the hydride and carbonyl co-ligands on the complex, which were found to interconvert upon heating the complex in solution (*vida supra*). To test this hypothesis, complex **5** was heated to 73 °C for 24 hours to produce the isomer **5a**

with the hydrido group trans to the pyrazole. However, on testing **5a** as a catalyst for the transfer hydrogenation reaction, it achieved only 22% conversion of the substrate within four hours at 83 °C. This conversion was nearly identical to that of the *trans* isomer (**5**). Complex **5** could follow an "inner sphere mechanism" for the transfer hydrogenation reaction where an initial chloride exchange with alkoxide occurs followed by β-hydride elimination to give a ruthenium hydride species. However, the reaction likely proceeds at a slower rate as there is no chloride that can be lost to allow binding of the alkoxide.[9]

The complex with two NHC ligands **7** was expected to perform poorly for the transfer hydrogenation reaction due to the metal centre being enclosed by two pincer ligands which occupy all six available co-ordination sites. Indeed, complex **7** only promoted the transfer hydrogenation reaction to a conversion of 14% after four hours at 83 °C, and after 24 hours reached a maximum conversion of 30% (see Chart 2.1). As complex **7** is coordinatively saturated, any activity must result from the hemilability of the pyrazole side arms or decomposition to an active species.

The catalytic activity for the transfer hydrogenation of acetophenone was assessed for all Ru(II) complexes (**3**, **4**, **4a**, **5**, **5a**, and **7**) at room temperature (25 °C). Intriguingly, it was found that mixed anion complex **4a** was the only active catalyst at room temperature, resulting in a 51% conversion within 24 hours (Chart 2.1). Complexes **3**, **4**, **5**, **5a**, and **7** did not catalyse the reaction at room temperature even after 24 hours. This would suggest that the pentaborate anion does indeed play a non-innocent role in the catalysed transfer hydrogenation reaction and likely has an entirely separate mechanism from the carbene pincer based catalyst. All efforts to

isolate the pentaborate anion via salt metathesis reactions and chromatography failed, otherwise a potassium or sodium pentaborate salt would have provided an interesting set of control experiments. While most Ru(II) complexes that have been reported as catalysts for the transfer hydrogenation reaction of ketones to alcohols are effective at elevated temperatures (> 50 $^{o}$C), there are relatively few reports of Ru(II) complexes capable of catalysing the reaction at room temperature.[16] The catalyst containing the pentaborate anion (**4a**) is indeed a unique system which requires further mechanistic investigation.

Whilst using complex **4** for the transfer hydrogenations it transpired that this complex was only partially soluble in the solvent/substrate propan-2-ol, and this could have led to reduced catalytic activity of the complex. Addition of THF as a co-solvent in a propan-2-ol: THF ratio of 9:1 aided solubility of the catalyst. The catalytic activity of complex **4** in either neat propan-2-ol or in the propanol-2-ol/THF mixture for the transfer hydrogenation reaction of acetophenone proved to be nearly identical (THF/iPrOH:45% at 0.5 h, >99% at 4 h. iPrOH: 39% at 0.5 h, > 99% at 4h). To ensure that THF was not affecting the reactivity of the complex, complex **3** was also tested for the transfer hydrogenation reaction of acetophenone using the 9:1 propan-2-ol: THF solvent ratio. The addition of THF to the reaction mixture resulted in complete conversion of the substrate (87% after 0.5 h, >99% at 4 h), the catalytic rate remains relatively constant in comparison to using neat propan-2-ol as solvent. It is likely that the complete conversion achieved by catalyst **3**, was a result of co-ordination of THF to the Ru(II) metal centre, stabilising the catalyst resting state and prolonging the lifetime of the catalyst.

The most active catalysts, **4a** and **4**, were further screened for the transfer hydrogenation reaction with a number of different ketone substrates (both aromatic and aliphatic, see Table 2.2). Both catalysts successfully catalysed the reactions at reflux and were able to achieve complete conversion of substrate for each case with the exception of the *p*-nitro-acetophenone (Table 2.2, entry 3). As was observed for the transfer hydrogenation reaction of acetophenone, catalyst **4a** was more efficient for the conversion of all substrates in comparison to **4**. Catalyst **4a** was tested for the transfer hydrogenation reaction of acetophenone, benzophenone and cyclohexanone at room temperature and reasonable yields of 51%, 41% and 59% were achieved respectively after 24 hours. (Table 2.2, entries 1, 2 and 4).

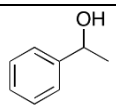
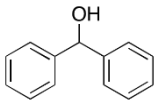
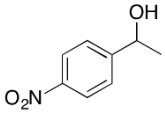
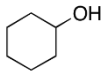
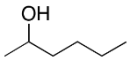
| entry | product | catalyst | % conv. at time (h) | | | |
|---|---|---|---|---|---|---|
| | | | 0.5h[a] | 2h[a] | 4h[a] | 24h[b] |
| 1 |  | **4a** | 91 | 96 | >99 | 51 |
| | | **4** | 39 | 82 | >99 | - |
| 2 |  | **4a** | 91 | 91 | >99 | 41 |
| | | **4** | 69 | 97 | >99 | - |
| 3 |  | **4a** | 0 | 0 | 0 | - |
| | | **4** | 0 | 0 | 0 | - |
| 4 |  | **4a** | 92 | >99 | >99 | 59 |
| | | **4** | 72 | >99 | >99 | - |
| 5 |  | **4a** | 51 | 94 | >99 | - |
| | | **4** | 44 | 78 | >99 | - |

**Table 2.2** Catalytic transfer hydrogenation of ketones using complexes **4a** and **4** [a] refluxing propan-2-ol, 1.5 mol% catalyst. [b] 25 °C, 1.5 mol% catalyst.

This mixed anion catalyst (**4a**) was found be the most active catalyst for the transfer hydrogenation reaction, promoting the conversion of a range of aromatic and aliphatic ketone substrates to alcohols with high yields in reasonable times at elevated temperature. The catalysed transfer hydrogenation reaction could also be conducted at room temperature, with catalyst **4a** found to be moderately active, whereas complexes **3**, **4**, **5**, **5a** and **6** were catalytically inactive. Comparison of the catalytic activities of **4a** and **4** revealed that the presence of the $[B_5O_6(OH)_4]^-$ counterion enhanced the rate of reaction by catalysing transfer hydrogenation reactions *via* a separate mechanism from the organometallic catalyst. Few boron compounds have been reported to perform the transfer hydrogenation reaction. Kilic *et al.* has recently shown that boron compounds containing a bidentate N, O donor system can achieve high conversions for the transfer hydrogenation reaction of acetophenone.[32] However, the reaction requires over eight hours in refluxing isopropanol to achieve near complete conversions and the boron compounds are inactive as catalysts for transfer hydrogenation at room temperature. In comparison, complex **4a** achieves moderate conversions even at room temperature.

## 2.5. Conclusions

This chapter describes the coordination chemistry of the $NCN^{Me}$ pincer ligand precursor **1** with Ru(II) and Ag(I) salts and investigates the activity of the resulting Ru(II) complexes as catalysts for transfer hydrogenation reactions. A series of coordination motifs were observed for the complexes in the solid state, ranging from a fully saturated tridentate Ru(II) dimer to a mono-dentate Ag(I) dimer, all of which could be preferentially synthesised by careful reagent choice. Crystallographic

analysis unexpectedly revealed a rare pentaborate anion for complex **4a**. Indeed, this mixed anion complex was found to be the most active catalyst for the transfer hydrogenation reaction, promoting the conversion of a range of aromatic and aliphatic ketone substrates to alcohols with high yields in reasonable times at elevated temperature. The catalysed transfer hydrogenation reaction could also be conducted at room temperature using catalyst **4a**. Complexes **2**, **3**, **4**, **5**, **5a** and **7** were catalytically inactive at room temperature. Comparison of the catalytic activities of the mixture **4a** and complex **4** revealed that the presence of the $[B_5O_6(OH)_4]^-$counterion enhanced the rate of reaction, most probably by catalysing transfer hydrogenations *via* a separate mechanism from the organometallic catalyst. Despite not being amongst the most active hemilabile Ru(II) in the literature, the discovery and catalytic activity of the pentaborate anion warrants further investigation.

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# Chapter 3. Ni(II) complexes of hemilabile pincer ligands for catalysed Kumada cross coupling reactions

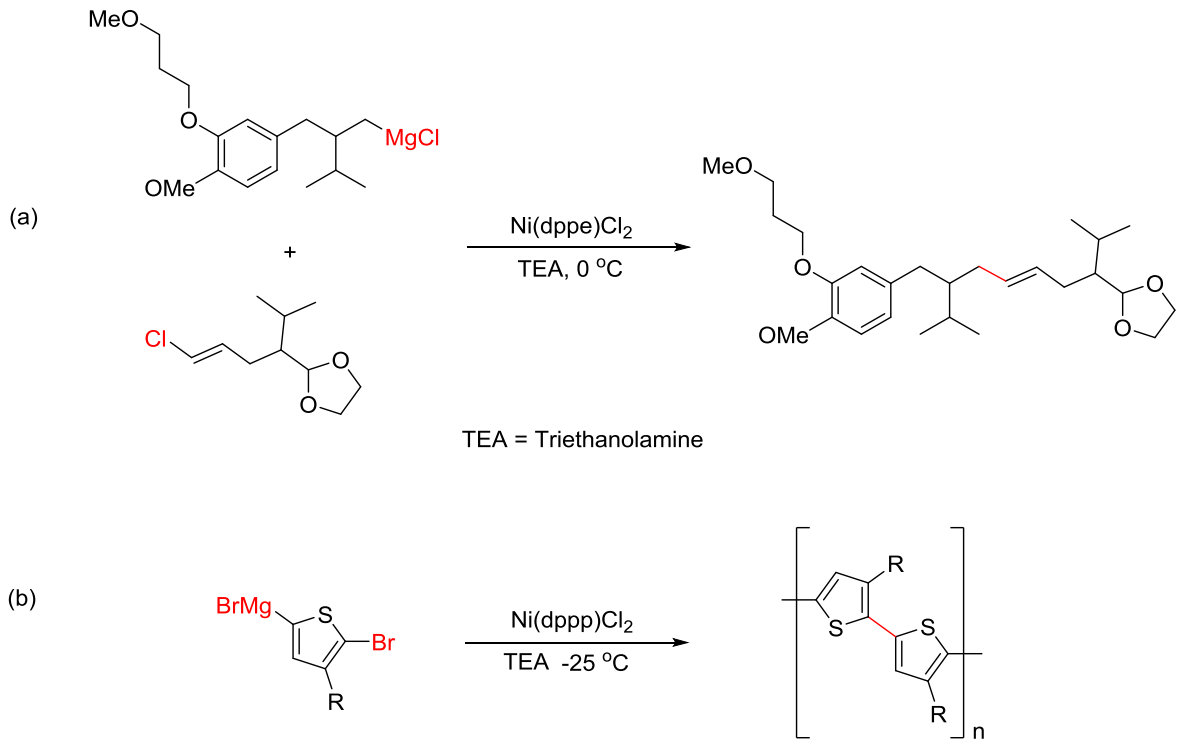
## 3.1. Introduction

### 3.1.1. Transition metal catalysed C-C bond formation reactions

Carbon-carbon bond cross coupling reactions have been studied extensively in the field of organometallic chemistry.[1] Among the first reported catalytic C-C coupling reactions is the Kumada cross coupling reaction.[2] The reaction involves the catalysed cross coupling between a Grignard reagent and an organic halide, which results in the formation of a new C-C bond. Despite the advent of alternative reactions, such as Suzuki, Negishi, Stille or Sonogashira coupling reactions, Kumada cross coupling reactions continue to be used in industry due to the ability of the reaction to directly couple Grignard reagents to a wide variety of halide containing compounds.[3] The reaction provides an economic and efficient organic transformation of the Grignard reagents containing alkyl, aryl and vinyl substrates. In particular, since the reaction is not limited to $sp^2$ carbon hybridisations, the Kumada cross coupling reaction has a higher versatility over other C-C coupling reactions.[4]

Kumada cross coupling reactions provide a safer route for the formation of C-C bonds, than Stille coupling reactions, which use toxic organotin compounds.[5] Usually, nickel complexes are utilised as catalysts in Kumada cross coupling reactions, and hence provide a cheaper alternative for the same organic transformation than alternative C-C coupling reactions which generally use more expensive metals such as palladium. Additionally, a greater range of temperatures can be employed for Kumada cross couplings than alternative coupling reactions due to the thermal stability of the Grignard reagents commonly used which allows for the successful coupling of both activated and deactivated substrates.[6] Reactions such as the Stille coupling typically use reagents that are susceptible to decomposition.

Kumada cross coupling reactions are also well utilised in the pharmaceutical and commercial industries, an example is in the synthesis of the drug Aliskiren (Scheme 3.1a), which is used for the treatment of hypertension.[7] Key steps in the synthesis of polymers such as polyalkylthiophenes also utilise the Kumada cross coupling reaction (Scheme 3.1b).[8]

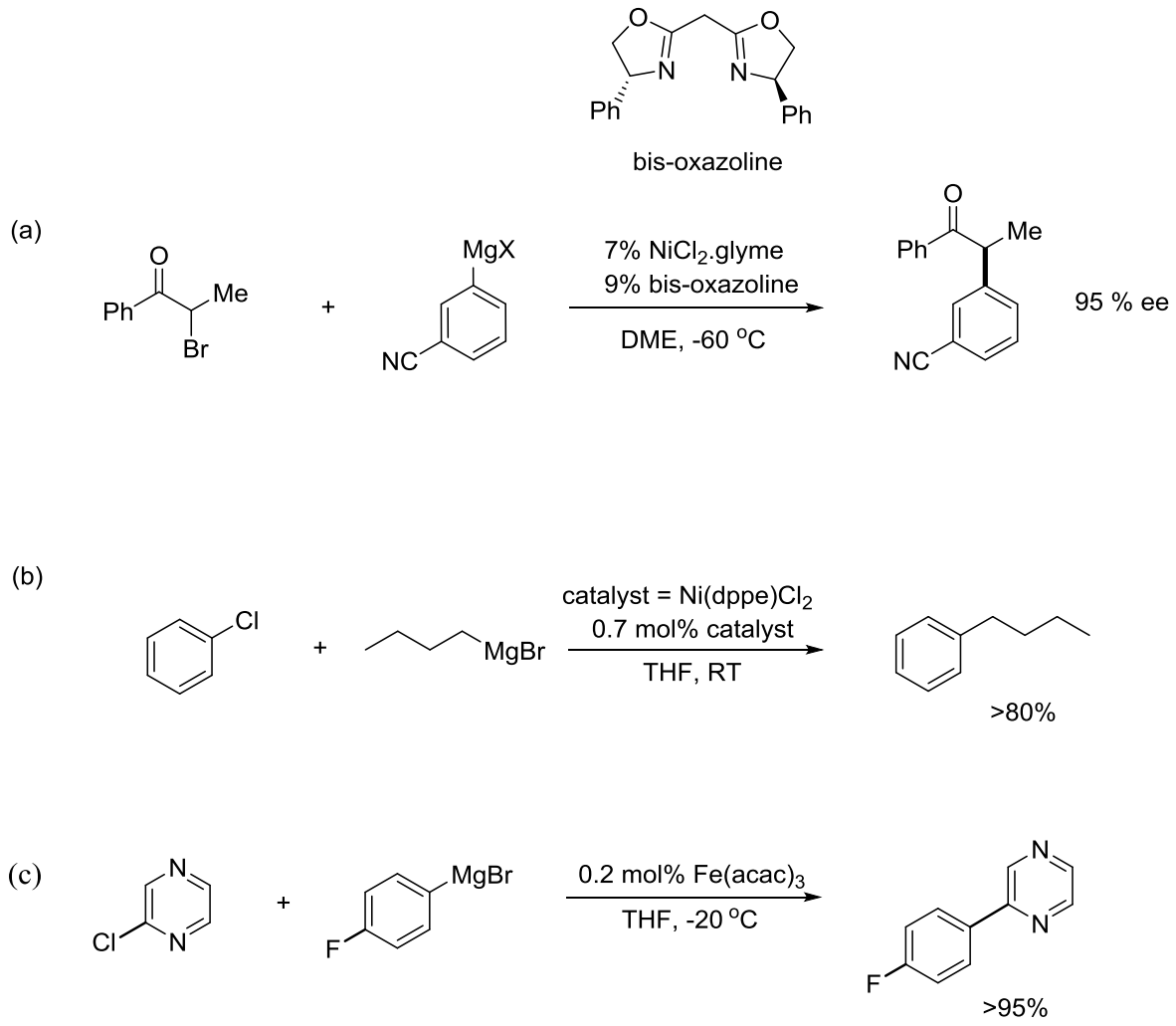



**Scheme 3.1** Kumada cross coupling as a key synthetic step in the production of (a) Aliskiren and (b) polythiophenes.

### 3.1.2. Catalysts for the Kumada cross coupling reactions

The Kumada cross coupling reaction can be catalysed by a wide range of nickel and palladium complexes. Catalytically active species can be formed *in situ* by addition of organic ligands such as bis-oxazoline to metal precursors such as $NiCl_2$ (Scheme 3.2a).[9] A disadvantage to the use of an active catalyst generated *in situ* is the unknown structure of the catalytically active species in the reaction mixture, therefore reaction pathways can be hard to determine. Therefore, isolated organometallic complexes have received increased

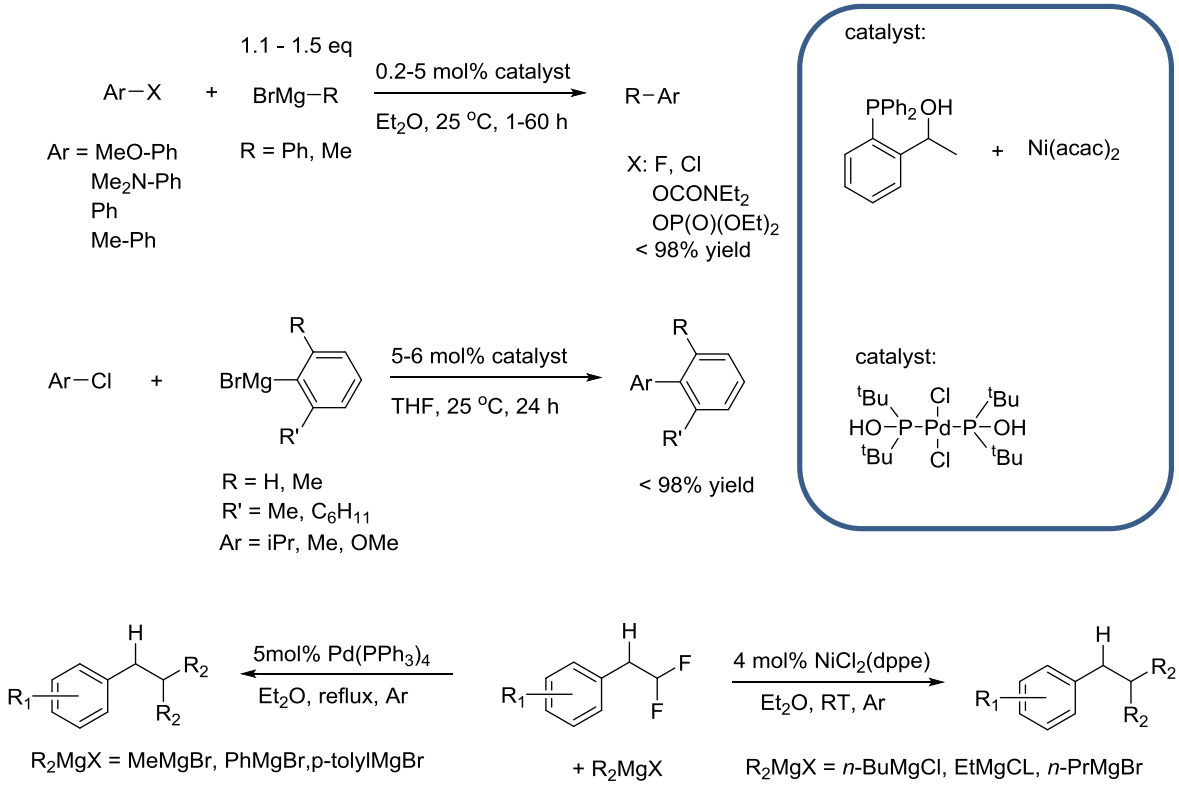
attention as catalysts for the Kumada cross coupling reaction. Among the first reported isolated organometallic complexes used for Kumada cross coupling is Ni(dppe)$Cl_2$ (dppe = 1,2-bis(diphenylphosphino)ethylene, Scheme 3.2b).[10a] This catalyst achieves near complete conversions for the Kumada cross coupling reaction of butylmagnesium bromide and chlorobenzene. Compared to *in situ* generated complexes, the isolated complex requires significantly reduced catalysts loadings to achieve high conversions. New catalysts and methods have since been developed for the Kumada cross coupling reaction with aims to achieve higher conversions at lower catalyst loadings. A “continuous flow” iron-catalysed Kumada cross coupling was recently reported which achieved high conversions for fluorinated substrates at low catalyst loadings (Scheme 3.2c).[10b]




**Scheme 3.2** Kumada cross coupling reactions catlysed by: (a) an *in situ* generated bis-oxazoline Ni(II) complex, (b) a pre-prepared Ni(II) catalyst and (c) an iron(III) catalyst.

Pd(II) and Ni(II) are the most successful and commonly used metals among the organometallic catalysts used for the Kumada cross coupling reaction. Most of the initially investigated catalysts for this type of organic transformation used Pd(II), Pd(0) and Ni(II) precursors, such as $Pd(PPh_3)_2Cl_2$, $Pd(PPh_3)_4$, $NiCl_2$ and $NiCl_2$.glyme.[11] However, most of these early complexes were susceptible to thermal and catalytic decomposition and optimization of selectivity was required. Hence, new complexes containing modified ligand structures were synthesised in order to improve catalytic activities and selectivities. Previous reports show the versatility of Ni(II) complexes used as catalysts for the cross

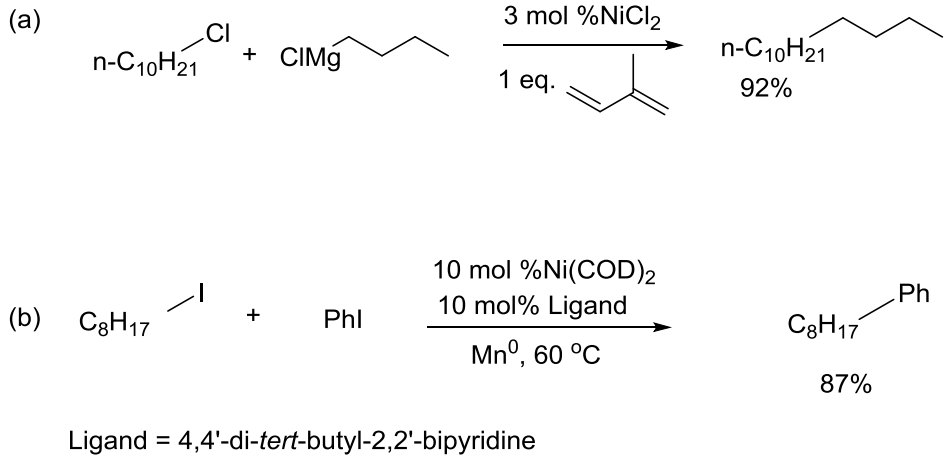
coupling reaction by using substrates with varying electronic and steric properties (Scheme 3.3).[12] The catalytic system showed high functional group tolerance, achieving moderate to high substrate conversions of a number of substrates containing electron withdrawing and electron donating groups. The versatility of Pd(II) complexes has also been demonstrated where similar functional group tolerance to that of nickel catalysts was observed (Scheme 3.3).[12, 13]




**Scheme 3.3** Recent Pd(II) and Ni(II) catalysed Kumada cross coupling reactions. [12, 13]

The coupling of alkyl halides with Grignard reagents is significantly more difficult than the coupling of aryl halides with Grignard reagents due to the presence of *β*-hydrogen atoms, which can interfere with the reaction causing the production of side products *via* competitive elimination processes.[14] However, these processes can be avoided with use of Ni(II) complexes which allows for the selective synthesis of desired products from alkyl

halides. Early examples of catalysts that suppress *β*-hydride elimination include the addition of dienes such as 1,3-butadiene to $NiCl_2$ which resulted in the production of long alkane/alkene chains with high selectivity (Scheme 3.4a).[15] The addition of the diene is hypothesised to produce a Ni(IV) intermediate which prevents the elimination processes involving *β*-hydrogen atoms.[15a] Recent examples demonstrated that the addition of diene ligands separate to nickel precursors may not be required to eliminate the formation of by-products (Scheme 3.4b).[15b]

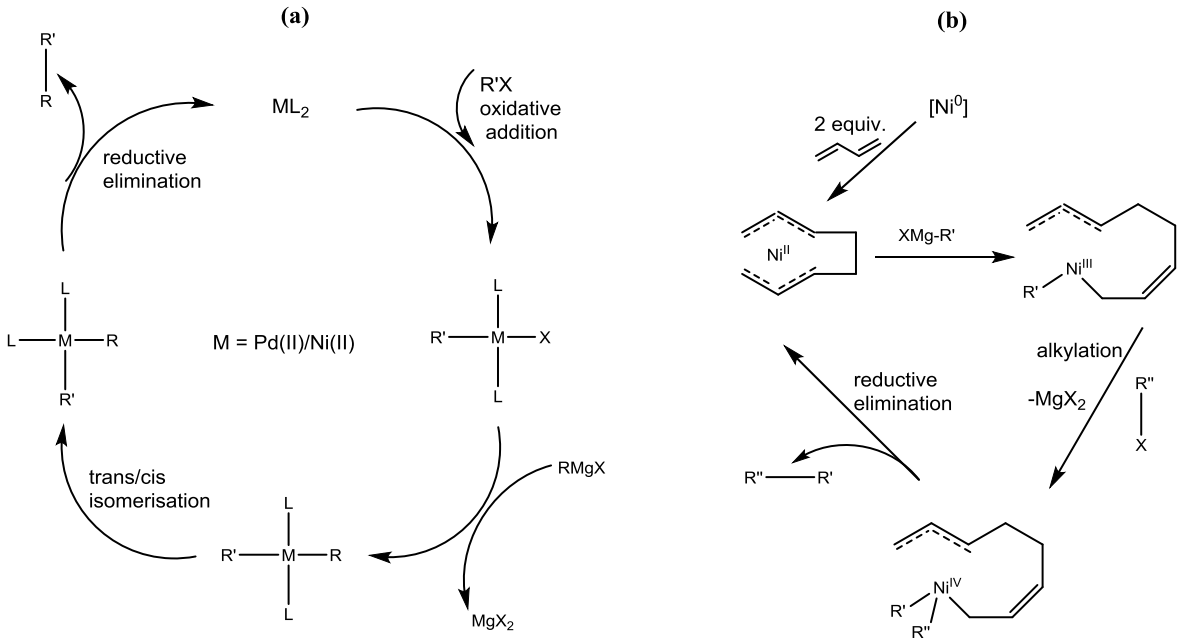



**Scheme 3.4** Selective Kumada cross coupling reactions.

### 3.1.3. The mechasims of Kumada cross coupling reactions

There are multiple proposed mechanisms for the Kumada cross coupling reaction catalysed by nickel complexes. One common example of such a mechanism is shown in Scheme 3.5a, which proceeds *via* the standard oxidative addition-transmetallation-reductive elimination pathways utilising Ni(0)/Ni(II) oxidation states.[4,16] The other example of proposed mechanisms for the Ni catalysed Kumada cross coupling reaction (Scheme 3.5b) is more specific to alkyl substrates, where it is proposed that the Ni(0) centre accesses multiple oxidation states during the reaction including Ni(0), Ni(II), Ni(III) and Ni(IV).[15,16] This

particular mechanism is based on a reaction that utilises 1,3-butadiene. Homocoupling of the 1,3-butadiene suppresses elimination processes involving *β*-hydrogen atoms of the R groups from the organohalide or the Grignard. Although palladium catalysed Kumada cross coupling reactions are also able to proceed *via* the same proposed 0/+II mechanism as proposed in Scheme 3.5a for nickel, the disadvantage of palladium is that it is susceptible to *β*-hydrogen atom elimination processes when catalysing reactions with alkyl substrates. Use of $PdCl_2$ for the reaction in Scheme 3.4 resulted in poor yield (38%) and by-products due to the *β*-hydrogen atom elimination processes were still observed.[15]




**Scheme 3.5** Kumada coupling mechanisms: a) conventional mechanism and b) mechanism with Ni(IV) intermediate.

### 3.1.4. Nickel complexes containing pincer ligands as catalysts for the Kumada cross coupling reaction: ligand effects

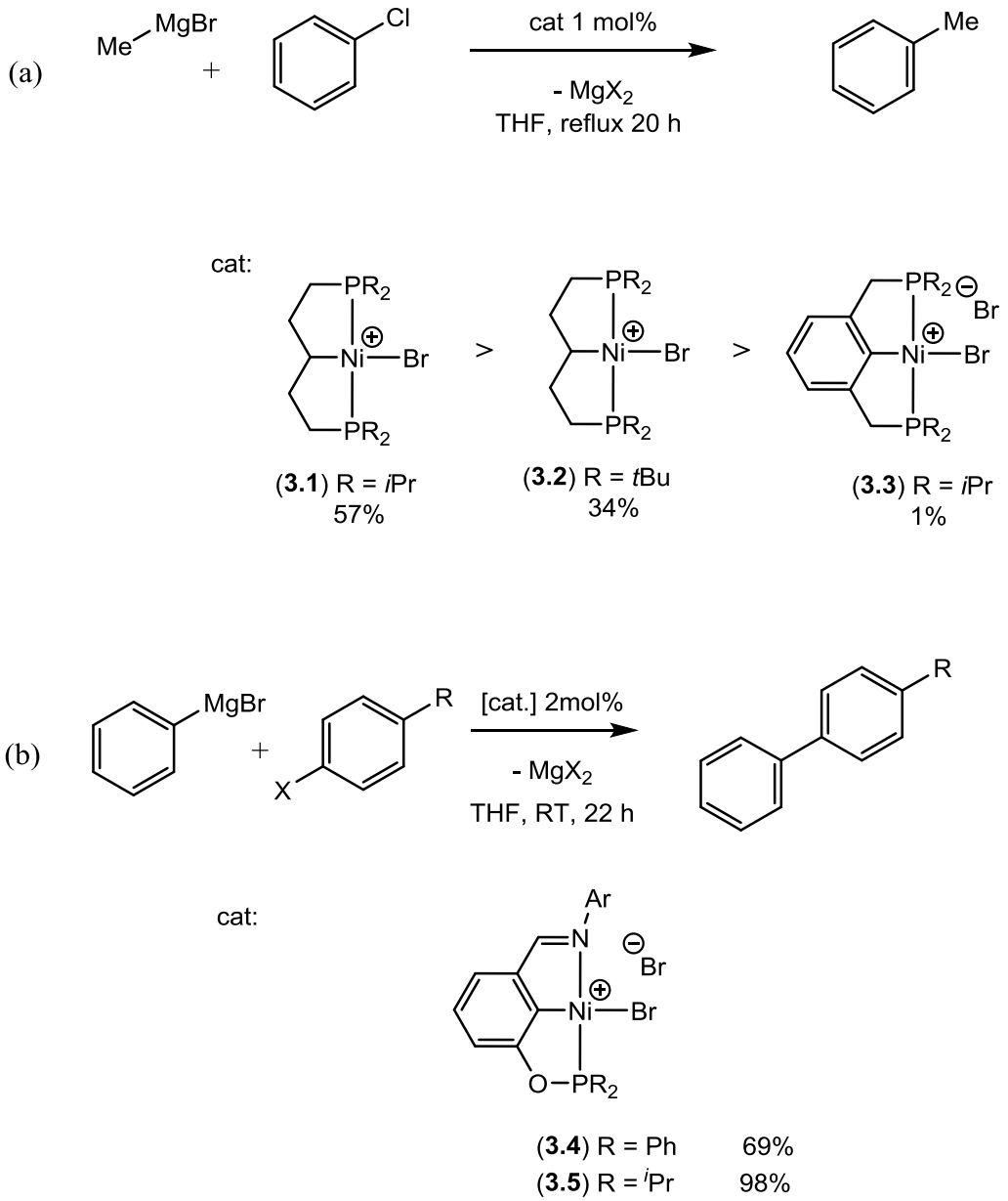
Significant attention has been focused on transition metal complexes containing pincer ligands as catalysts for C-C cross coupling reactions because complexes containing pincer

ligands can exhibit higher reactivity and increased stability over complexes containing bidentate/monodentate ligands.[17, 18] Ni complexes containing pincer ligands are widely used in C-C cross coupling reactions, particularly the coupling of aryl Grignards with aryl or alkyl halides (i.e. Kumada coupling).[3, 19]

Some of the early synthetic work in the use of complexes with pincer ligands involved the *in situ* addition of a metal precursor to a pincer ligand.[1] A wide array of transition metal complexes, mostly Ni(II) and Pd(II) containing pincer ligands have since been synthesised, aiming to achieve higher selectivities and/or activities for the Kumada cross coupling reaction.[3] The ability of the complexes bearing pincer ligands to catalyse Kumada cross coupling reactions depends on factors such as the degree of electron donation to the metal centre, and the lability of the coordinating groups to the metal centre.[3]

#### 3.1.4.1. Electron donating ability and its effects on catalytic activity

Castonguay and coworkers have demonstrated a correlation between the electron donating ability of the coordinating groups of a pincer ligand to a Ni(II) metal centre and the catalytic activity of the resulting complex.[20] The catalytic activity of complexes **3.1**, **3.2** and **3.3** (Scheme 3.6a) decreased with increasing electron donating ability of functional groups on the coordinating phosphorous or carbon atoms (**3.1** > **3.2** > **3.3**). This trend was also observed for similar pincer complexes where the authors report higher catalytic activity for complex **3.4** (Scheme 3.6b) which contains smaller electron donating isopropyl groups on the phosphorous donors in comparison to the analogous complex **3.5** containing more electron donating phenyl groups.[21]




**Scheme 3.6** Effect of varying electron donating abilities of ligands used in Ni(II) catalysed Kumada cross coupling reactions: (a) coupling of alkyl Gringard reagents; (b) coupling of aryl Grignard reagents.

### 3.1.4.2. Pincer ligands with strongly coordinating side arm donors

The most common motifs of pincer ligands used for coordination to Ni(II) include a central pyridyl donor group flanked by one or more NHC groups, a selection of which (**3.6, 3.7, 3.8** and **3.9**) are shown in Figure 3.1.[22, 23, 24, 25, 26]

Complex **3.6** (Figure 3.1) has been used as a catalyst for the Kumada cross coupling reaction of aryl bromides, chlorides and fluorides,[22] achieving moderate to good yields for most substrates with the exception of substrates containing fluorides and some chlorides. However, the use of a Ni(II) complex containing a pincer ligand (**3.9**) with only one NHC side arm led to higher yields for the coupling reaction of *para*-tolyl magnesium bromide with aryl chlorides.[23] This result suggested that combining two relatively labile donor groups with a strongly coordinating NHC donor allows increased catalytic reactivity of Ni(II) compared to pincer complexes that contain two strongly coordinating NHC donors.

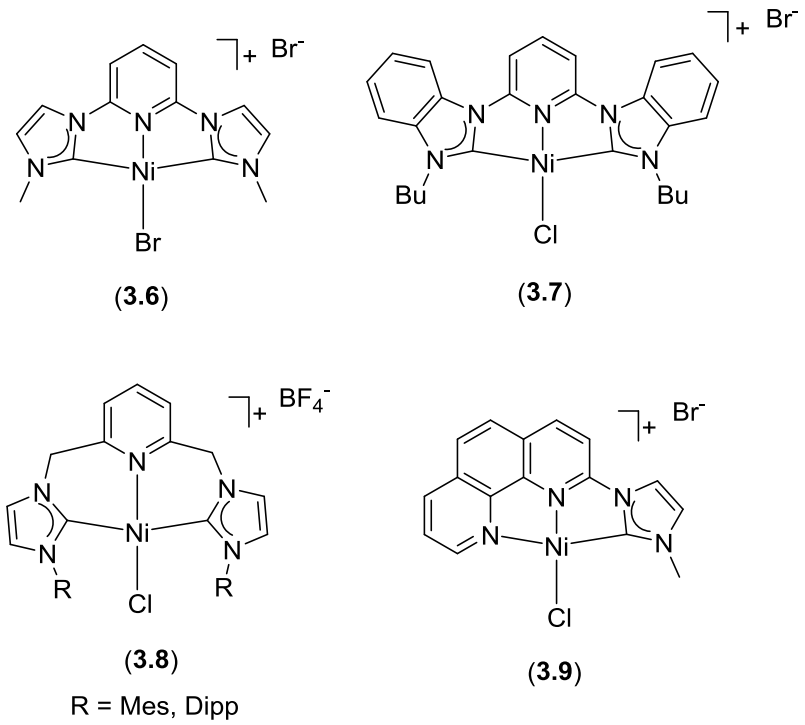
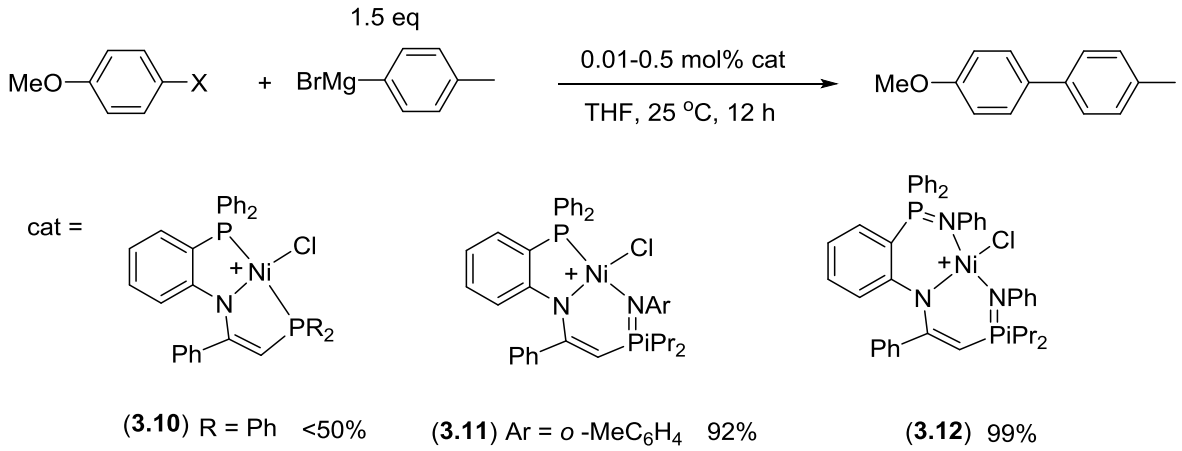



**Figure 3.1** Ni(II) complexes containing pincer ligands with strongly coordinating NHC donors.

### 3.1.4.3. Pincer ligands with weakly coordinating side arms: towards hemilability

The catalytic activity of Ni(II) complexes containing pincer ligands can be increased if strongly donating side arms are replaced with weakly coordinating side are donors such as pyrazoles and imines. Xia Wang, Ning Liu and co-workers have demonstrated this using Ni(II) complexes containing pincer ligands of the type shown in Scheme 3.7.[27] The *PNP* pincer complexes (**3.10**) containing two strongly coordinating phosphine donor groups proved to be the least active catalysts in the series. The *NNN* pincer complex (**3.12**) containing two donor atoms as shown in Scheme 3.7 exhibited superior catalytic activity for the cross coupling reaction in comparison to similar *PNN* pincer complex (**3.11**) containing only one labile donor atom.

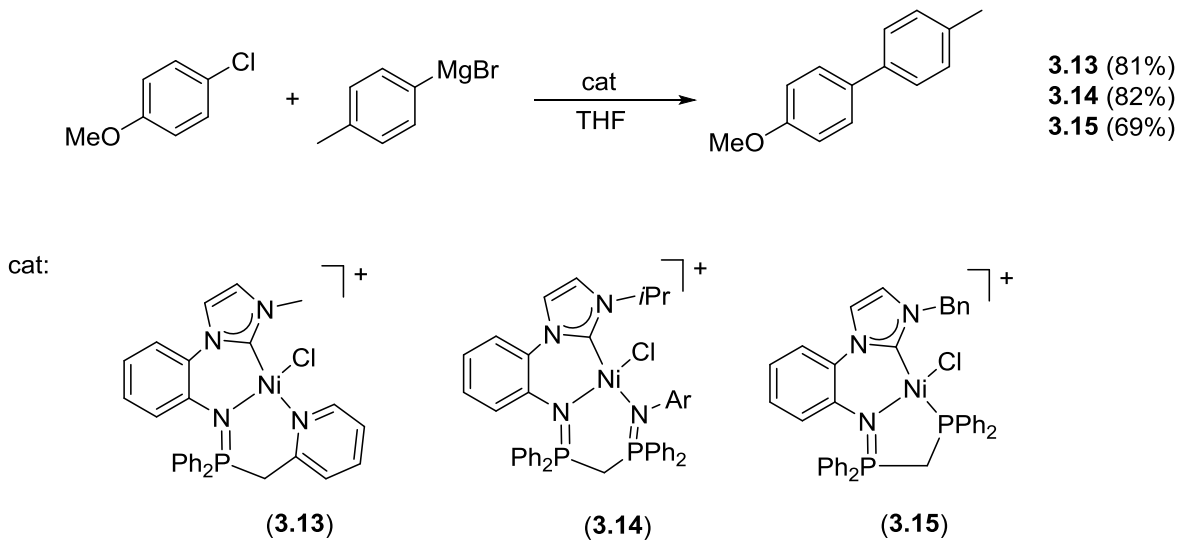



**Scheme 3.7** Ni(II) complexes containing pincer ligands with tunable catalytic properties.

Although the increased lability of selected pincer ligands proved to be effective for increasing the catalytic activity of the resulting complexes, the *PNP*, *PNN* and *NNN* pincer complexes were not stable over time when used as catalysts. Complexes containing labile donors have reduced thermal stability and are prone to destabilisation[28,29] at the elevated temperatures which are sometimes required for Kumada cross coupling reactions of certain alkyl and aryl chloride substrates, e.g. 1-chloro-4-methoxybenzene.[6] To alleviate the

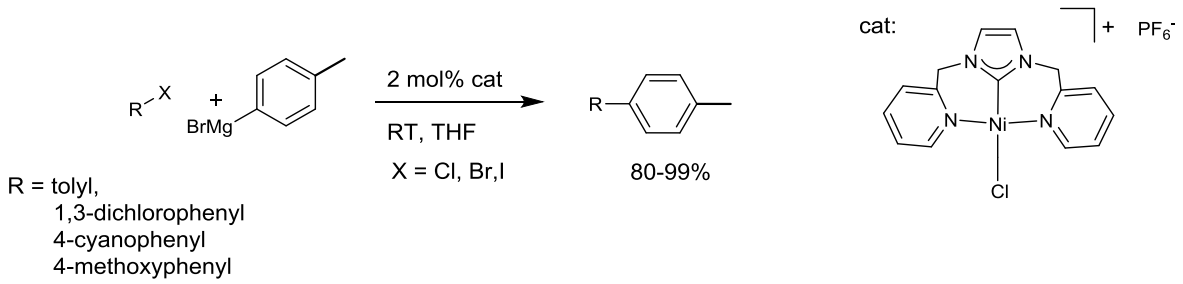
reduced catalytic and thermal stability of the pincer complexes with weakly coordinating donors, introduction of a strongly coordinating central σ-donor group (NHC) could be an answer to the instability of the complexes.

Zhang *et al*. reported the use of complexes with hemilabile pincer ligands containing $sp^2$ nitrogen ligand donors and NHC side arm donors (**3.13**, **3.14** and **3.15**, Scheme 3.8) as catalysts for the Kumada cross coupling reaction of activated aryl halides and arylmagnesium bromides with high yields at room temperature conditions.[6] However, certain unactivated substrates required the use of higher temperatures to achieve successful conversions. The complexes that contained hemilabile pincer ligands also catalysed the cross coupling reactions of unactivated chloride substrates, though the reactions had to be performed at higher temperatures (80 °C). This can be attributed to the ability of the complexes containing pincer ligands to maintain their reactivity by dissociation of one or more of the weakly coordinating ligand donors to provide vacant coordination sites for substrate binding, while retaining thermal stability owing to the strong σ-coordination of the NHC donor. The authors report high yields for the coupling of the unactivated 1-chloro-4-methoxybenzene substrate at 80 °C while no reaction occurred at room temperature. Complexes **3.13** and **3.14** (Scheme 3.8) were more active for the cross coupling of aryl chlorides with Grignard reagents in comparison to complex **3.15**, and the increased activity was attributed to the hemilability of the ligands. Complexes **3.13** and **3.14** exhibit similar reactivity due to the presence of two labile N donor groups whereas complex **3.15** contains a phosphine donor which dissociates less readily from the Ni(II) centre during catalytic reactions than the imine donors (**3.13** and **3.14**).




**Scheme 3.8** Ni(II) hemilabile complexes of pincer ligands containing a single NHC donor.

Only a few complexes containing a central NHC donor and labile donor arms have been reported in the literature. Chao Chen *et al*. have reported the use of a Ni(II) complex containing a pincer ligand with a central NHC donor and pyridyl sidearm donors (Scheme 3.9).[30] The complex achieves high conversions for the Kumada cross coupling reaction of aryl halides with aryl magnesium bromide. Heteroaryl and disubstituted aryl substrates also undergo the Kumada cross coupling reaction with tolyl magnesium bromide using the same catalyst, achieving good yields. This shows the versatility of the Ni(II) complex bearing the pincer ligand to catalyse the Kumada cross coupling reaction for a range of chlorinated substrates.




**Scheme 3.9** Ni(II) complex of a pincer ligand with a central NHC donor.

## 3.2. Aims of this chapter

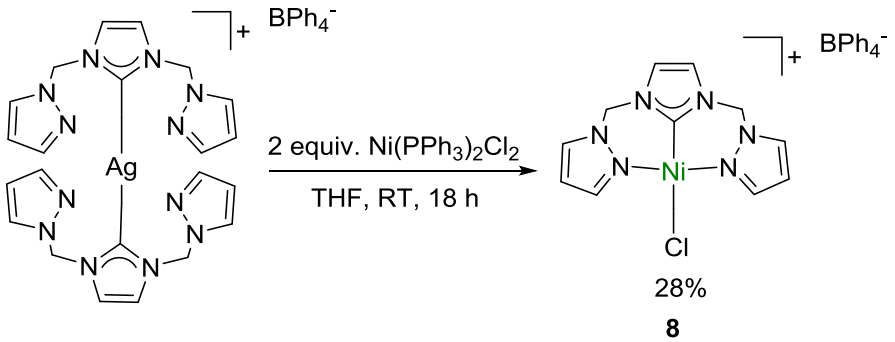
The aims of this chapter are to investigate the synthesis and coordination chemistry of a range of novel nickel(II) complexes containing hemilabile *NCN* pincer ligands, as well as their activity as catalysts for the Kumada cross coupling reaction of aryl halides. The specific goals were to:

- Prepare a range of Ni(II) complexes containing hemilabile pincer ligands composed of pyrazole-imidazolium-pyrazole motifs.
- Investigate the coordination modes of the resulting complexes with strongly coordinating co-ligands.
- Test the catalytic activities of all synthesised Ni(II) complexes for the Kumada cross coupling reaction, initially of chlorobenzene and phenylmagnesium bromide.
- Investigate the catalytic activity of the best catalyst using optimised conditions for Kumada cross coupling of a range of substituted aryl halides.

## 3.3. Synthesis of Ni(II) complexes containing an *NCN*$^{Me}$ hemilabile pincer ligand

### 3.3.1. Synthesis, characterisation and coordination study of [Ni(*NCN*$^{Me}$)Cl]$BPh_4$ (8)

The synthetic routes to the complexes presented in this chapter follow similar synthetic procedures to those used for the Ru(II) complexes presented in Chapter 2. The Ni(II) complexes of the *NCN*$^{Me}$ pincer ligand **1** were synthesised by transmetallation of the Ag(I)*NCN*$^{Me}$ complex (**2**) with two molar equivalents of $Ni(PPh_3)_2Cl_2$ to yield the complex [Ni(*NCN*$^{Me}$)Cl]$BPh_4$ (**8**) as a yellow micro-crystalline solid in 28% yield (Scheme 3.10). Multiple attempts were made to increase the yield of the product including the synthesis of the complex **8** using an external base ($NEt_3$). The complex was successfully isolated using this method, however, the yield did not improve. A mass balance analysis of the crude reaction mixture revealed the presence of three fractions. One fraction was isolated as the product **8**, the remaining two fractions proved to contain highly insoluble products and $^1$H NMR analysis of these two fractions did not yield useful information. Use of starting materials such as $Ni(DME)Cl_2$ and $Ni(OAc)_2.xH_2O$ resulted in an unreacted mix of starting material.




**Scheme 3.10** Synthesis of [Ni(*NCN*$^{Me}$)Cl]$BPh_4$ (**8**).

The $^1$H NMR spectrum obtained for complex **8** exhibited broad resonances for all protons attributed to the pincer ligand at room temperature. A single set of aromatic resonances

between 7.5 and 8.4 ppm were attributed to the protons of the pyrazolyl and imidazolyl donors. The number of resonances indicated a symmetric $\kappa^3$-*NCN* structure of the Ni(II) complex **8**.

There were significant differences between the pyrazolyl proton resonances in comparison to those observed for silver intermediate $[Ag(NCN^{Me})_2]BPh_4$ (**2**). The pyrazolyl resonances due to protons of intermediate **2** occur at 7.60 ppm and 8.13 ppm, whereas those due to the protons of the nickel complex (**8**) occur at 8.26 ppm and 8.29 ppm respectively. The downfield shift of these pyrazolyl proton resonances indicated that the transmetallation reaction was successful in coordinating the two pyrazolyl ligand arms to the nickel center unlike in Ag(I) complex **2** where the N-donors remain unbound. The ratios of the integration of ligand proton resonances to those of the $BPh_4$ counterion indicated that the ratio of ligand to counterion is 1:1. As the $^1$H NMR spectrum indicates that all ligand donors are bound to the metal centre, it is highly likely that a Cl co-ligand is also bound to the Ni metal centre.

$^{13}C\{^1H\}$ NMR and 2D NMR spectroscopy did not reveal any valuable information that explained the broad signals in the $^1$H NMR spectrum. There are different possibilities for the broad signals in the NMR spectrum including purity, paramagnetism and conformational flexibility of the complex **8** in solution state. Further characterisation was therefore carried out in aims to identify the cause of the broad signals in the NMR spectrum.

Crystals suitable for X-ray analysis were grown by vapour diffusion of diethyl ether into a saturated solution of **8** in acetone. X-ray crystal structure analysis confirmed the predicted four co-ordinate structure (Figure 3.2), with the Ni(II) centre possessing a square planar

geometry. The central NHC is twisted out of the square plane, such that the two methylene groups are positioned on opposite faces of the plane at a torsion angle of 30.1°. Mass spectrometry of complex **8** shows a dominant signal at 303.05 m/z which is attributed to the cationic fragment with formula [Ni(*NCN*$^{Me}$)OH]$^{+}$.

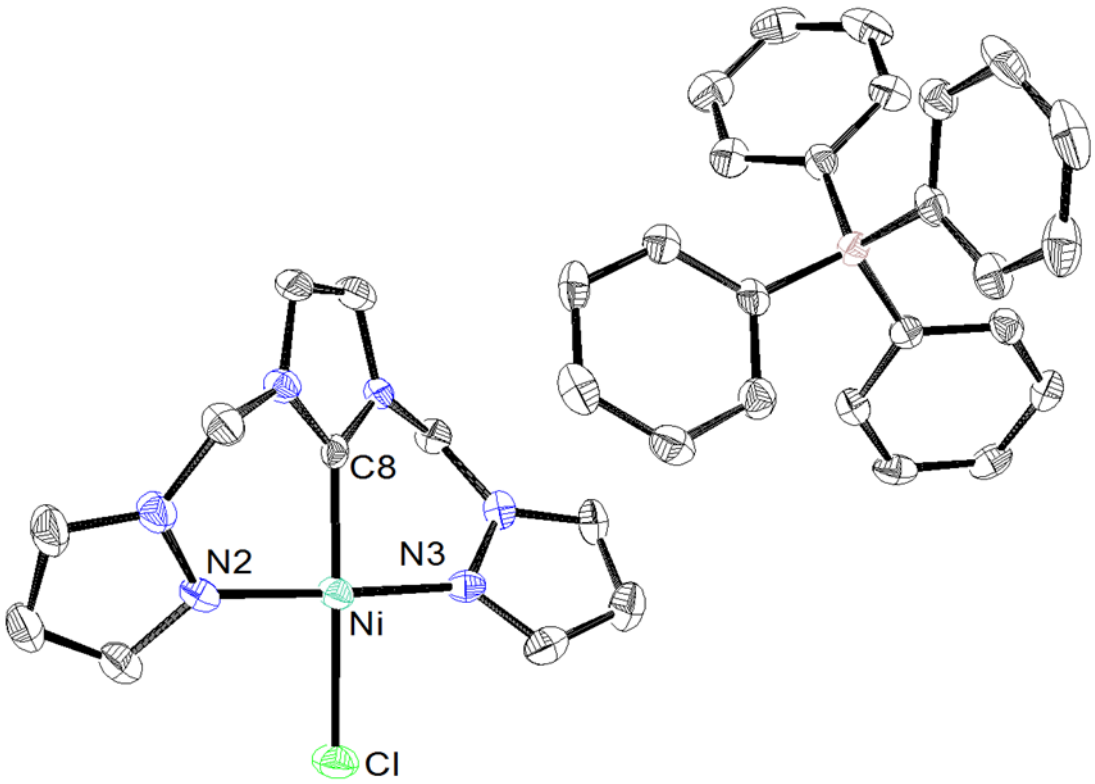



**Figure 3.2** ORTEP depiction of complex **8** with 50 % probability ellipsoids for all non-hydrogen atoms. Hydrogen atoms have been omitted for clarity.

Elemental analysis on the batch of crystals used for X-ray analysis revealed values (C, 65.54; H, 5.07; N, 13.04) nearly identical to the calculated value (C, 65.52; H, 5.03; N, 13.10) of complex **8**. However, $^{1}$H NMR analysis of the isolated crystals used for solid state structure determination of **8** and elemental analysis produced a spectrum identical to that obtained for the previously synthesised yellow powder with broad signals. The evidence indicated that the broad resonances in the NMR spectrum of **8** were not due to the presence of impurities.

Square planar Ni(II) ($d^8$, 16 valence $e^-$) complexes are diamagnetic due to the pairing of all eight d-electrons (Figure 3.3), and typically produce a sharp, well-defined $^1$H NMR spectrum. However, it is possible for four co-ordinate Ni(II) complexes to undergo an isomerization reaction in the solution state, such that the complex exists in an equilibrium between square planar and tetrahedral geometries.[31] Since tetrahedral Ni(II) ($d^8$, 16 valence $e^-$) complexes are paramagnetic due to two unpaired d-electrons (Figure 3.3), an equilibrium between pairs of square planar and tetrahedral geometric isomers in solution would result in broadening of the $^1$H NMR spectrum (Scheme 3.11). The $Ni(PPh_3)_2Cl_2$ precursor used for the synthesis of complex **8** itself exists in such an equilibrium (Scheme 3.12).[31]

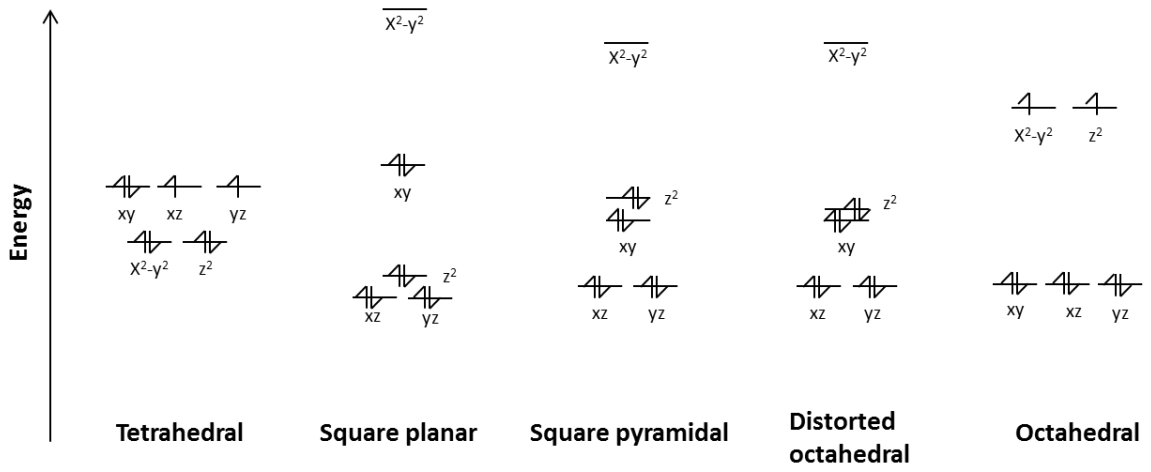
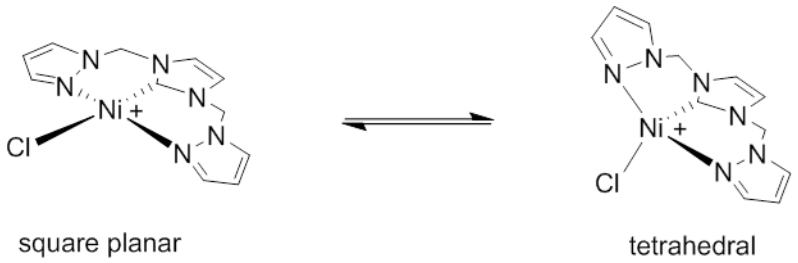
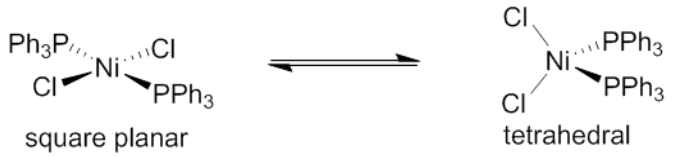



**Figure 3.3** Frontier-orbital energy level diagrams of the d-orbital electrons arising from different geometries possible for complexes of nickel(II).




**Scheme 3.11** Proposed equilibrium between the square planar and tetrahedral conformations of complex **8**.




**Scheme 3.12** Equilibrium between the square planar and tetrahedral conformations of $Ni(PPh_3)_2Cl_2$.[31]

The ligand of complex **8** can potentially undergo a conformational change, due to the flexibility of the pendant arms of the ligand, to accommodate the change in metal coordination geometry (Scheme 3.11). A tetrahedral structure of complex **8** requires a coordination of the ligand **1** to the nickel centre in a similar fashion to facial coordination observed in octahedral complexes. As presented in Chapter 2, facial coordination of ligand **1** to ruthenium(II) was shown to be possible. Complex **8** could therefore exist in an equilibrium between square planar and tetrahedral conformations. This could lead to broadened signals in the $^1$H NMR spectrum due to the contribution of the tetrahedral paramagnetic nickel(II) species.

Analysis of the complex using UV spectroscopy should provide clear evidence of the presence of a paramagnetic species since tetrahedral and square planar Ni(II) complexes are known to exhibit characteristic bands in UV visible spectroscopy. Tetrahedral Ni(II) complexes exhibit strong bands in the UV spectra at 400-500 nm and 600-800 nm, whereas analogous complexes containing a square planar geometry produce only one strong band at 400-500 nm.[32] Analysis of complex **8** in acetone solution using UV visible spectroscopy revealed the presence of only one strong band at 460 nm which is characteristic of a square planar Ni(II) compound. This suggested that the broadness observed in the $^1$H NMR spectrum was not a result of paramagnetism.

It is possible that the flexible ligand results in broadness of the $^{1}$H NMR spectrum. Evidence of the flexibility in the ligand is evident from the X-ray crystal structure analysis where the methylene groups are significantly bent out of plane about the Ni(II) centre and *NCN*$^{Me}$ donor atoms. To test this hypothesis, complex **8** was analysed using variable temperature $^{1}$H NMR spectroscopy (Figure 3.4).

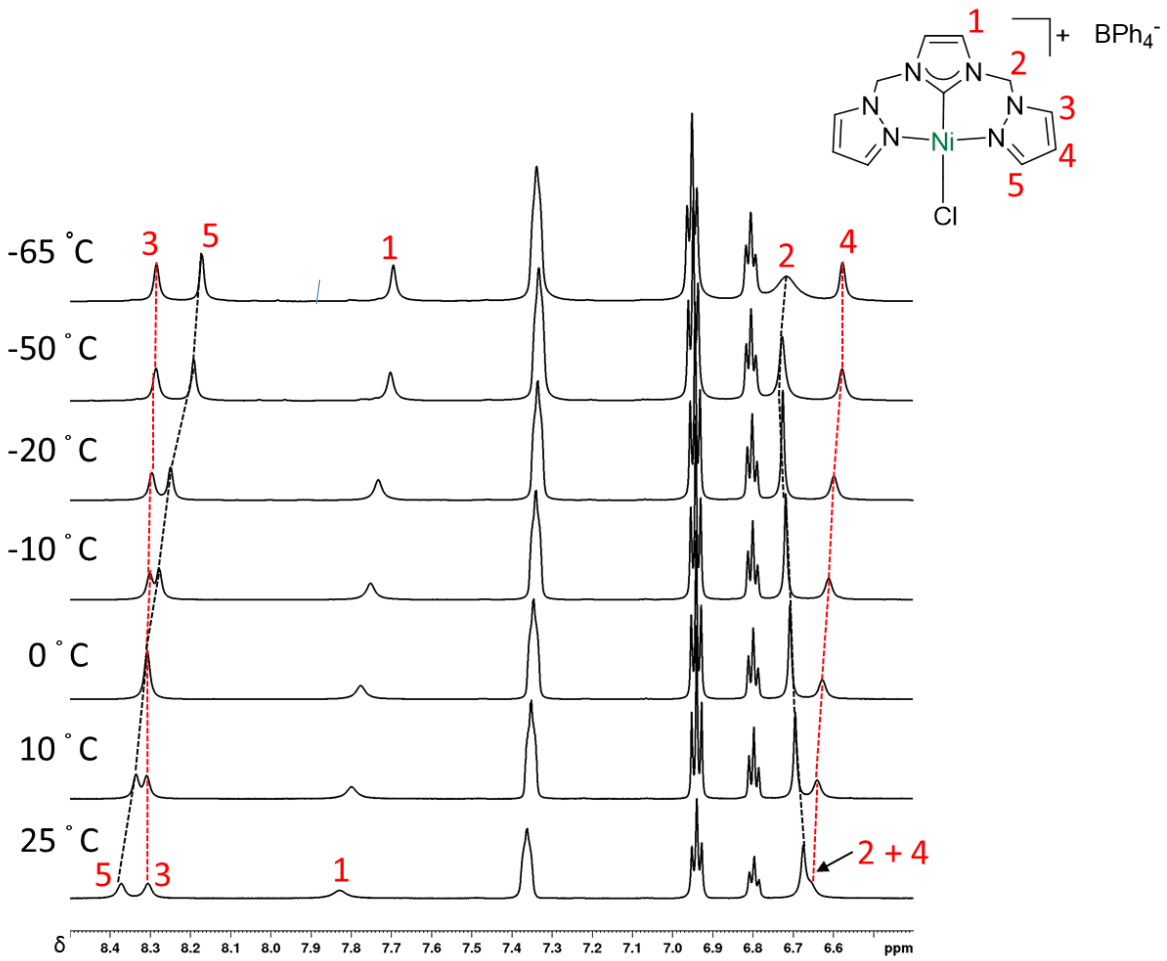



**Figure 3.4** Variable temperature NMR (600 MHz, acetone-$d_6$) of complex **8**.

Characterisation using $^{13}$C{$^{1}$H} NMR and 2D NMR techniques were possible at -65 °C. Characterisation of complex **8** at the reduced temperature of -65 °C showed the presence of eight proton resonances, five of which are attributed to the ligand, indicative of a single species with a symmetric structure. This is typical of a $\kappa^3$ coordination of the ligand to the

nickel metal centre and the changing chemical shifts confirmed that the broadness in the $^{1}$H NMR spectrum of complex **8** resulted from conformational flexibility (Figure 3.5) of the complex rather than paramagnetism or presence of impurities.

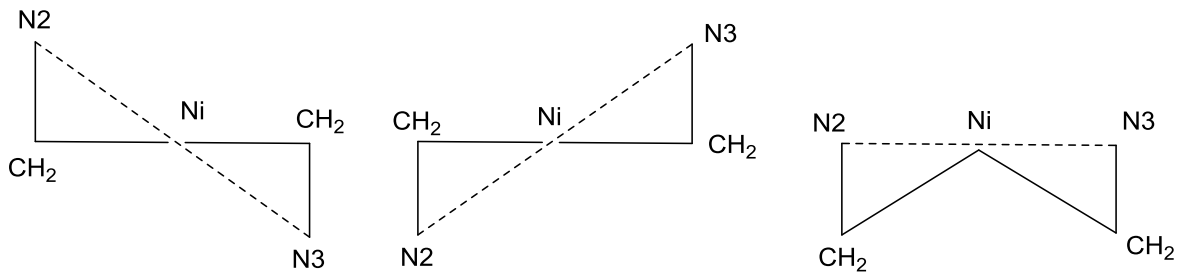



**Figure 3.5** Different conformations possible for complex **8**.

### 3.3.2. Coordination chemistry of [Ni(*NCN*$^{Me}$)Cl].BPh$_4$

Four coordinate Ni(II) complexes can be converted into more conformationally stable diamagnetic square pyramidal or octahedral complexes upon additional coordination of hard-donor ligands.[33] Hence, NMR scale reactions of complex **8** with a range of hard donor ligands were carried out with the aim of gaining better understanding of the complex in terms of geometric character (spin state) and coordination chemistry (Figure 3.6).

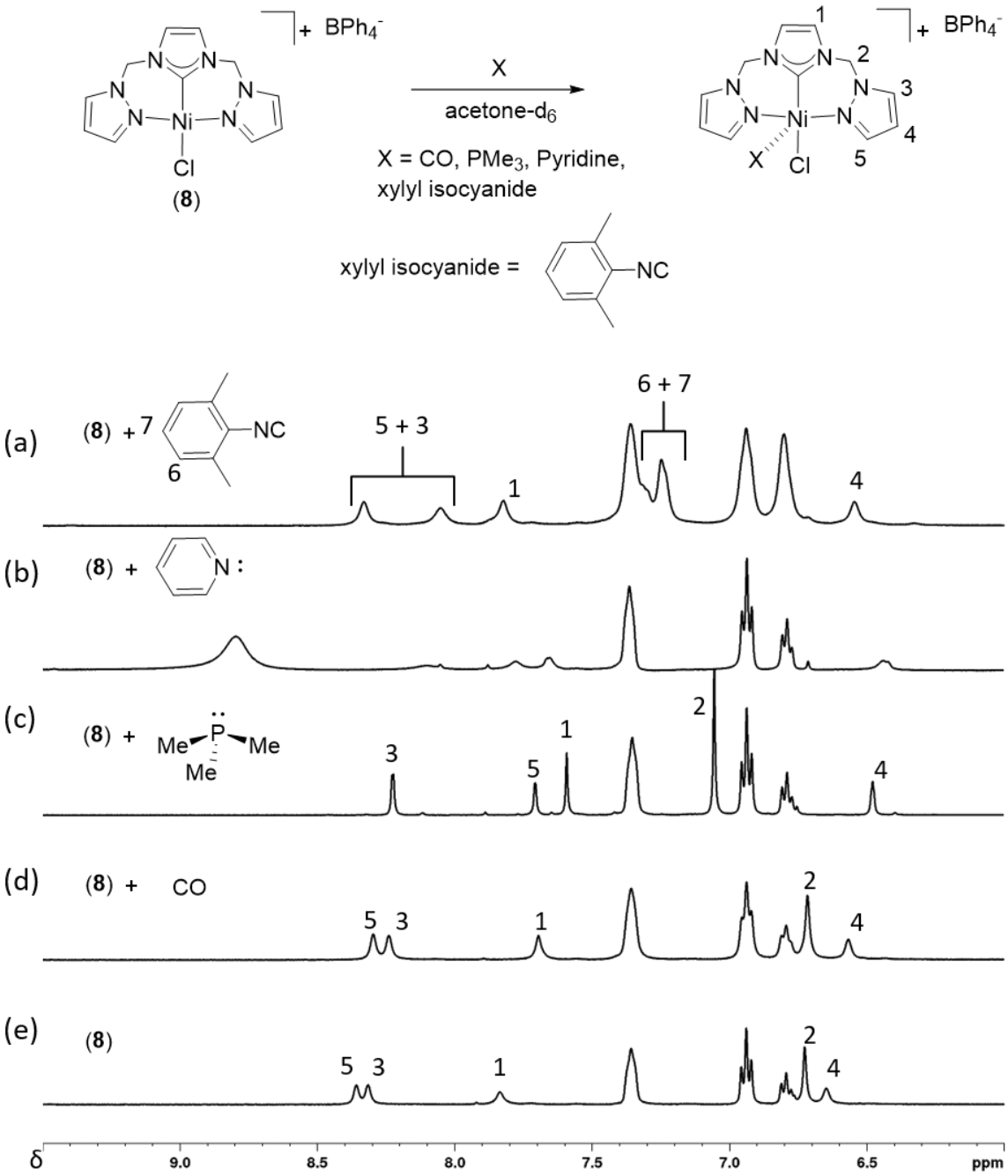



**Figure 3.6** $^{1}$H NMR (500 MHz, acetone-$d_6$, 25 °C) stacked plots of **8** reacting with hard donor ligands. (a) xylylisocyanide, (b) pyridine, (c) $PMe_3$, (d) CO, (e) four-coordinate complex **8**.

Carbon monoxide, trimethylphosphine, pyridine and xylylisocyanide were used as donor ligands to investigate their effect on the Ni(II) complex upon coordination. The $^{1}$H NMR spectra of Ni(II) complex **8** in the presence of the additional donors show clear evidence of

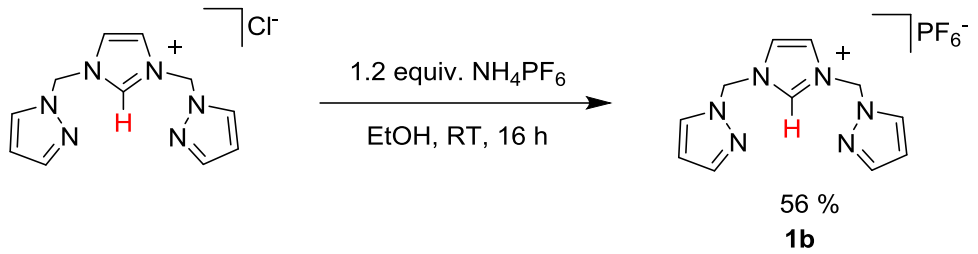
coordination of each except CO. The $^{1}$H NMR spectra of complex **8** before and after exposure to $CO_{(g)}$ shows little difference in the chemical shifts of proton resonances and IR (ν(CO)) spectra were not obtained as a $CO_{(g)}$ atmosphere would be required for the analysis. Addition of pyridine and xylylisocyanide resulted in successful coordination to the nickel metal centre, this was evident from significant shifts of the ligand proton resonances in comparison to the $^{1}$H NMR spectrum of the parent nickel complex **8** (Figure 3.6a and b). However, the $^{1}$H NMR spectra of **8+pyridine** and **8+xylyl isocyanide** remain broad suggesting structural flexibility of these *in situ* complexes in solution. Upon addition of $PMe_3$ to **8**, the broad $^{1}$H NMR resonances became sharp, well-defined peaks (Figure 3.6c). A single resonance at 6.2 ppm was observed in the $^{31}$P NMR (free $PMe_3$ = -62 ppm) spectrum indicating successful addition of the phosphine co-ligand to the nickel metal centre. Unlike the spectrum upon addition of pyridine and xylylisocyanide to **8**, the resonances in the $^{1}$H NMR spectrum of **8+PMe$_3$** were sharp indicating that the nickel species was conformationally stable on the NMR time scale. The chemical shift of the pyrazolyl ($H^5$) proton resonance moves from 8.3 ppm to 7.6 ppm which is likely due to the increased electron density on the pyrazolyl groups due to the $PMe_3$. A significant change in the chemical shift of the pyrazolyl ($H^5$) proton resonance is expected as it lies closest in proximity to the nickel metal centre. The $^{1}$H NMR spectrum of complex **8** after the addition of $PMe_3$ retains its $\kappa^3$-*NCN* geometry symmetry as indicated by the five distinct $^{1}$H resonances attributed to a symmetrically coordinated ligand **1**.

The integration ratio of *NCN*-ligand proton resonances to $PMe_3$ proton resonances is 12 : 18, demonstrating that two $PMe_3$ co-ligands are bound to the nickel metal centre. However, an octahedral geometry is unlikely since it would result in a paramagnetic

complex (Figure 3.3). It is possible that the complex exists in a distorted octahedral geometry whereby Jahn-Teller distortion causes splitting of the $x^2$-$y^2$ and $z^2$ orbitals, resulting in pairing of all d-orbital electrons (Figure 3.3). This distortion can also occur for the pyridine and xylyl isocyanide analogues, however, ligand **1** likely retains its flexibility resulting in spectra with broad resonances. Pyridine and xylyl isocyanide are sterically bulkier than $PMe_3$ and CO. Congestion at the nickel center may also cause more fluctionality in the pincer ligand resulting in broad $^1$H NMR spectra. In comparison, the $PMe_3$ bound Ni(II) species, similar to complex **3**, which also contains two phosphine co-ligands *trans* to each other, exhibits a sharp singlet resonance for the $CH_2$ protons in the $^1$H NMR spectrum. The evidence shows that the flexibility of the ligand while coordinated to a metal center can be controlled by careful selection of co-ligands.

### 3.3.3. Synthesis and characterisation of ($NCN^{Me}$)$PF_6$ (1b)

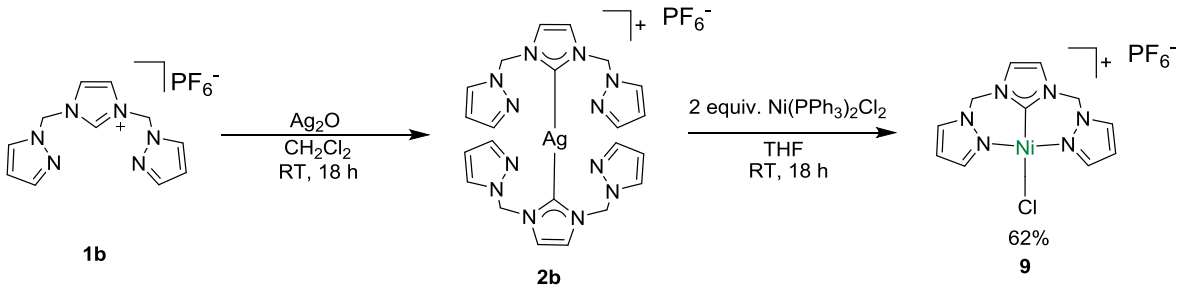
Complex **8** proved to be difficult to synthesise in reasonable yields and required a number of steps in purification and since the choice of counter ion used in a metal complex can significantly affect catalytic activity,[34] the analogous $PF_6^-$ derivative of complex **8** was synthesised. The imidazolium ligand (**1b**) was synthesised following a similar method reported previously.[35] However, the counterion exchange reaction of the ($NCN^{Me}$)Cl salt was performed with 1.2 equiv. of ammonium hexafluorophosphate instead of $NaBPh_4$. The pro-ligand ($NCN^{Me}$)$PF_6$ (**1b**) was isolated as a crystalline white solid in 56% yield (Scheme 3.13). The $^1$H NMR spectrum of ligand **1b** was analogous to that of ligand (**1**), exhibiting six $^1$H resonances with the characteristic imidazolium proton signal appearing in the expected region at 9.56 ppm.




**Scheme 3.13** Synthesis of *NCN* pincer ligand ($NCN^{Me}$)$PF_6$ (**1b**)

### 3.3.4. Synthesis and characterisation of [Ni($NCN^{Me}$)Cl]$PF_6$ (9)

The $NCN^{Me}$ pincer ligand **1b** was reacted with excess $Ag_2O$ (2 equiv.) to produce [Ag($NCN^{Me}$)$_2$].$PF_6$ as a pale brown solid (Scheme 3.14), to which $Ni(PPh_3)_2Cl_2$ was added *in situ* to afford [Ni($NCN^{Me}$)Cl].$PF_6$ (**9**) as an orange powder in 62% yield.




**Scheme 3.14** Synthesis of [Ni($NCN^{Me}$)Cl]$PF_6$ (**9**)

The $^1$H NMR spectrum of **9** was similar to the analogous Ni(II) $BPh_4$ complex **8**, the $^1$H NMR spectrum of the $PF_6^-$ derivative (**9**) exhibited five broad ligand resonances. Complex **9** could not be characterized at 25 °C using $^{13}$C NMR or 2D NMR techniques as the resonances were too broad. Analysis of complex **9** using UV visible spectroscopy produced a single peak at 460 nm, similar to the UV/Vis spectra of complex **8** which suggested that the broadness was not a result of any paramagnetic species. Low temperature NMR spectroscopy at -50 °C allowed characterisation of the complex to be achieved using $^{13}$C NMR and 2D NMR techniques.

The presence of only five resonances in the $^{1}H$ NMR spectrum of **9** at -50 °C suggested symmetry in the structure in the solution state and is likely to contain a $\kappa^3$-*NCN* geometry analogous to complex **8**. The resonances due to the methylene linker protons ($CH_2$) and pyrazolyl protons (Pz4) are well separated in complex **9** even at 25 °C compared to those of complex **8** suggesting that the change in counterion altered the chemical shifts of the Ni(II) complex bearing the $NCN^{Me}$ ligand **1**. The resonance due to $CH_2$ protons at -50 °C shows a doublet pattern typical of diastereotopic coupling which has been observed previously for the Ru(II) complexes of ligand **1**, synthesised in chapter 2.

Crystals of **9** suitable for X-ray analysis were grown by vapour diffusion of diethyl ether into a saturated solution of **9** in acetone. Analysis using X-ray crystallography confirmed the expected $\kappa^3$-*NCN* symmetric structure with the Cl co-ligand terminally bound to the Ni metal centre and in a *trans* position relative to the central carbene (Figure 3.7). Mass spectrometry shows a dominant signal at 303.05 m/z which was attributed to the cationic fragment with formula $[[Ni(NCN^{Me})OH]^+$. The structure with the exemption of the counter ion proved to be isostructural to complex **8**.

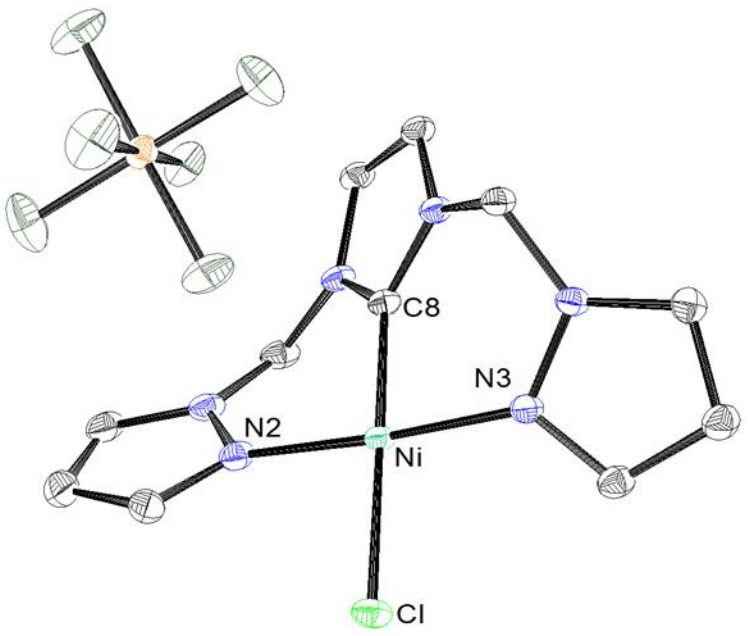
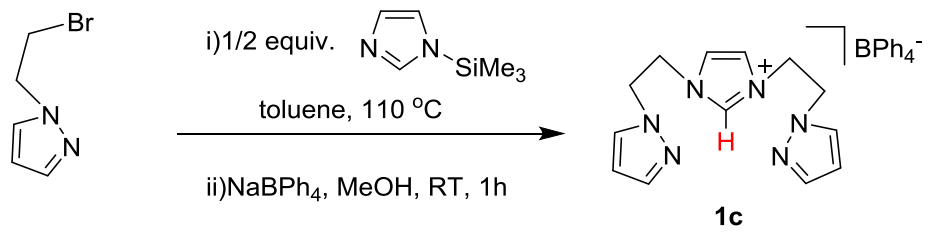



**Figure 3.7** ORTEP depiction of complex **9** with 50 % probability ellipsoids for all non-hydrogen atoms. Hydrogen atoms have been omitted for clarity.

### 3.3.5. Synthesis and characterisation of $[Ni(NCN^{Et})_2](BPh_4)_2$ (10)

The use of a pincer ligand containing a longer alkyl linker between the central imidazolyl and pendant pyrazolyl moieties can affect the coordination of the ligand to a metal centre. Therefore, the pincer ligand $(NCN^{Et})BPh_4$ (**1c**) was synthesised according to a previous literature procedure using bromoethylpyrazole and half an equivalent of trimethylsilylimidazole in refluxing toluene. [35] This was followed by counterion exchange with $NaBPh_4$ to yield **1c** as a white solid at a yield of 72% (Scheme 3.15).[35] Crystals suitable for X-ray analysis were grown by slow evaporation of a saturated solution of **1c** in acetone. The X-ray analysis confirms the conformational flexibility of the ligand as expected due to the ethylene linkers with one pendant pyrazolyl arm nearly linear in conformation whereas the second pendant arm is rotated nearly 90° away from linearity (Figure 3.8).




**Scheme 3.15** Synthesis of ($NCN^{Et}$) $BPh_4$ **(1c)**.

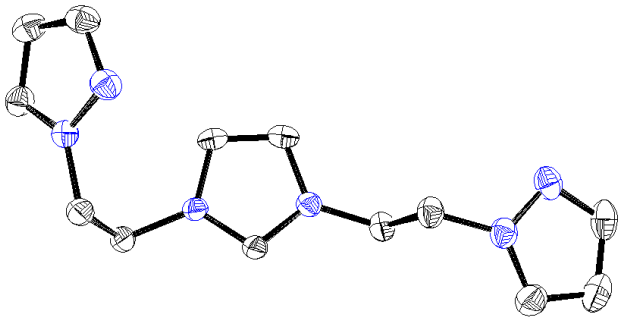
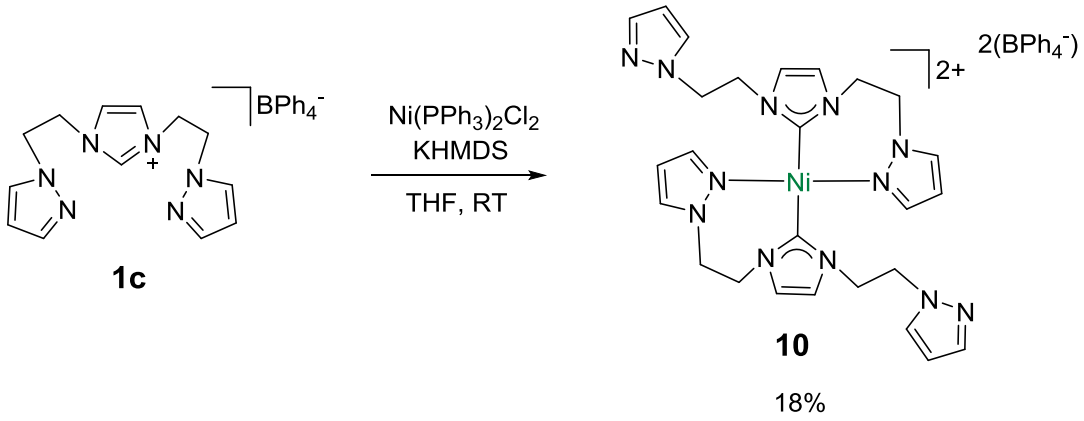


**Figure 3.8** ORTEP depiction of ligand **1c** with 50% probability ellipsoids for all non-hydrogen atoms. Hydrogen atoms and $BPh_4$ have been omitted for clarity.

The silver complex [Ag($NCN^{Et}$)$_2$].$BPh_4$ (**2c**) was prepared as a white solid by reaction of ligand **1c** with excess $Ag_2O$. The $^1$H NMR spectrum of the white solid contained nine proton resonances, six of which were attributed to the ligand protons and the remaining three resonances are assigned to the $BPh_4^-$ protons. In a similar fashion to the $^1$H NMR spectrum of [Ag($NCN^{Me}$)$_2$]$BPh_4$ (**2**), the absence of the imidazolium proton resonance in the $^1$H NMR spectrum of **2c** indicates successful complexation of silver to the ligand. The ratio of the integrals of the proton resonances indicate that the ligand to $BPh_4^-$ ratio is 2 : 1 which is indicative of a homoleptic structure for the silver complex [Ag($NCN^{Et}$)$_2$]$BPh_4$ (**2c**).

With the aim of synthesising a Ni(II) complex of ligand **1c** containing longer alkyl linkers linker between the central imidazole and pendant pyrazolyl moieties, two equiv. of $Ni(PPh_3)_2Cl_2$ were added to the silver intermediate (**2c**). This approach had been used previously for the transmetallation synthesis of Ni(II) complexes **8** and **9** containing ligands

**1a** and **1b** respectively. However the reaction of **2c** and $Ni(PPh_3)_2Cl_2$ resulted in a mixture of unreacted starting material and insoluble silver salts, so this method proved to be unsuccessful. An alternate approach to the synthesis of a Ni(II) complex with ligand **1c** was to use an external base to deprotonate the imidazolium salt (**1c**) *in situ* prior to addition of the nickel precursor ($Ni(PPh_3)_2Cl_2$). Triethylamine, $K_2CO_3$ and potassium hexamethyl-disilazide (KHMDS) were tested as bases for this reaction, however only KHMDS was successful at deprotonating **1c.** The precursor $Ni(PPh_3)_2Cl_2$ was reacted with ligand **1c** in the presence of excess KHMDS producing $[Ni(NCN^{Et})_2](BPh_4)_2$ (**10**) as a yellow solid in 18% yield (Scheme 3.16). Many attempts were made to improve the yield of complex **10**, by altering the reaction temperatures and ligand to metal ratios. However, any deviations from the synthetic method shown in Scheme 3.16 resulted in unsuccessful reactions which did not show evidence of any single isolable species.




**Scheme 3.16** Synthesis of $[Ni(NCN^{Et})_2](BPh_4)_2$ (**10**).

The $^1H$ NMR spectrum of the nickel(II) complex **10** revealed that **10** exists as an asymmetric species in solution. The $^1H$ NMR spectrum contains 19 distinct proton resonances, 16 of which were assigned to the protons of two ligands which suggested the complex had two NHC donors. The analysis of the NMR spectrum indicates that each pincer ligand of

complex **10** has only two coordinating donors and one free pyrazolyl arm giving rise to the unsymmetric structure. Two sets of proton resonances with coupling patterns that are typical of resonances due to diastereotopic proton pairs were attributed to the ethylene protons. One set consists of four multiplets within close proximity (4.35-4.72 ppm; $^{3}J$ = 13.8 Hz) while the second set of resonances due to diasterotopic protons contains four separate multiplet signals (5.04, 5.42, 6.11 and 7.05 ppm; $^{3}J$ = 13.8 Hz); which is characteristic of an asymmetric geometry of the ligand about the metal centre. The ratio of the integrals of resonances due to the ligand and $BPh_4$ indicates that the ratio of ligand to $BPh_4$ is 1:1, again indicating a likely *bis*-NHC structure. The *bis*-NHC structure was further confirmed by an absence of $PPh_3$ proton resonances in the $^{1}H$ NMR spectra of complex **10**, which indicates that the two phosphine co-ligands have been displaced from the nickel centre. Analysis of complex **10** by variable temperature $^{1}H$ NMR spectroscopy revealed the presence of another species at low concentrations (Figure 3.9). The resonance of $H^{8a}$ markedly shifts to high ppm at lower temperatures (Figure 3.9), this indicates a strong C-H $\pi$-interaction with a pyrazole from the second *NCN* ligand.

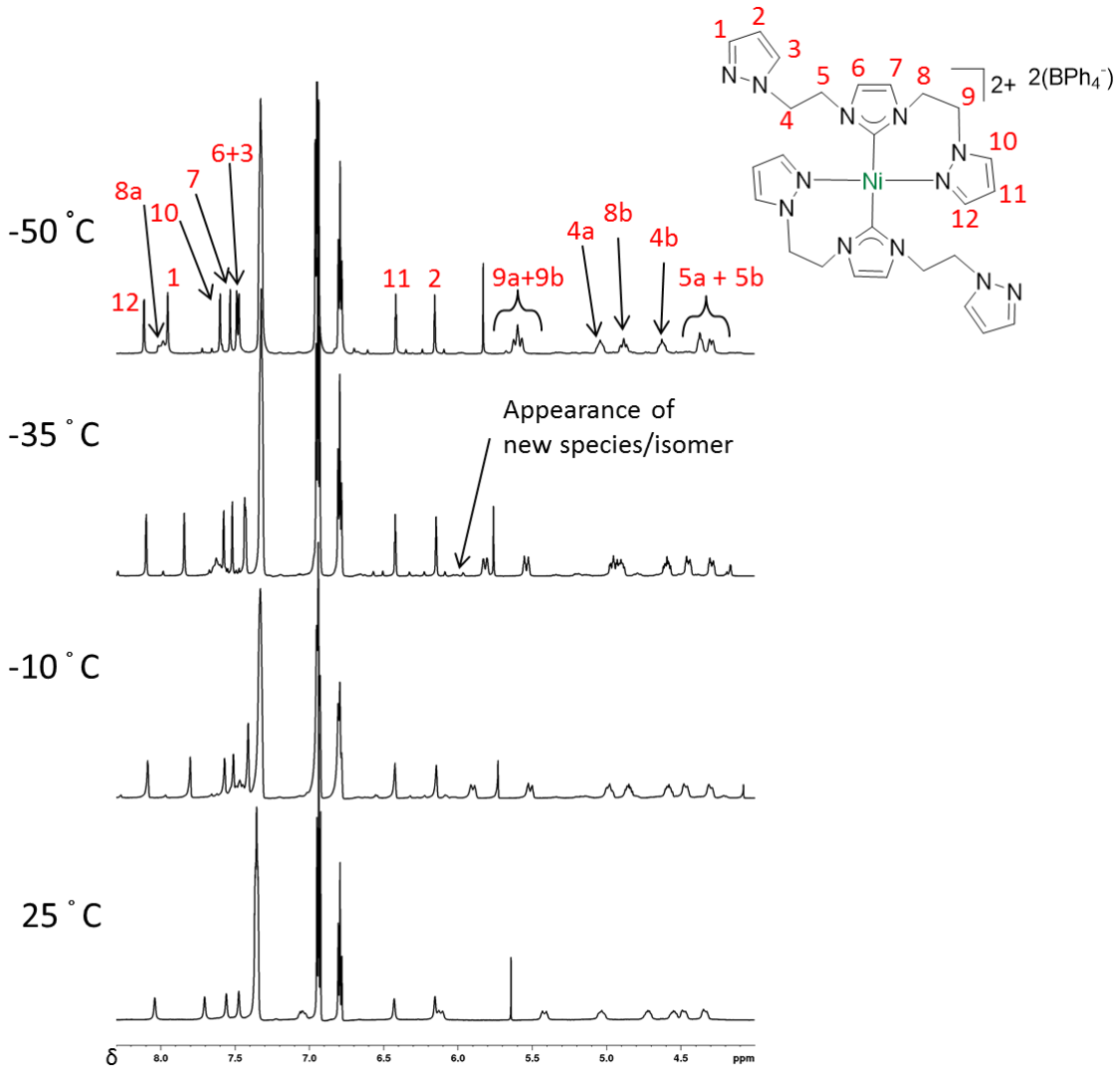



**Figure 3.9** Variable temperature $^{1}$H NMR spectra (600 MHz, acetone-$d_6$) of complex **10**. (a and b = diastereotopic hydrogens of ethylene linkers).

Crystals of **10** suitable for X-ray analysis were grown by vapour diffusion of diethyl ether into a saturated solution of **10** in acetone. X-ray crystal structure analysis confirmed that Ni(II) had a square planar geometry in complex (**10**) and that the *bis*-NHC ligands were asymmetrically $\kappa^2$-*NCN* coordinated (Figure 3.10). The significant shift of the resonances due to $H^{8a}$ to higher ppm ranges as observed in $^{1}$H NMR (Figure 3.9) was confirmed by X-ray analysis to be due to C-H $\pi$-interaction of the proton to a pyrazolyl ring with an interaction distance of 2.845 Å. This distance is typical of C-H $\pi$- interactions of hydrogen atoms to an

aryl ring.[36] A similar *bis*-NHC geometry was reported previously by Mancano *et al.* for a complex containing ligand **1c**,[35] where the Ir(I) compound contained two ligands *trans* to each other similar to complex **10**. However complex **10** shows a bidentate coordination of the ligand **1c** to the metal centre whereas the Ir(I) counterpart had a monodentate coordination of the ligand to the metal centre.

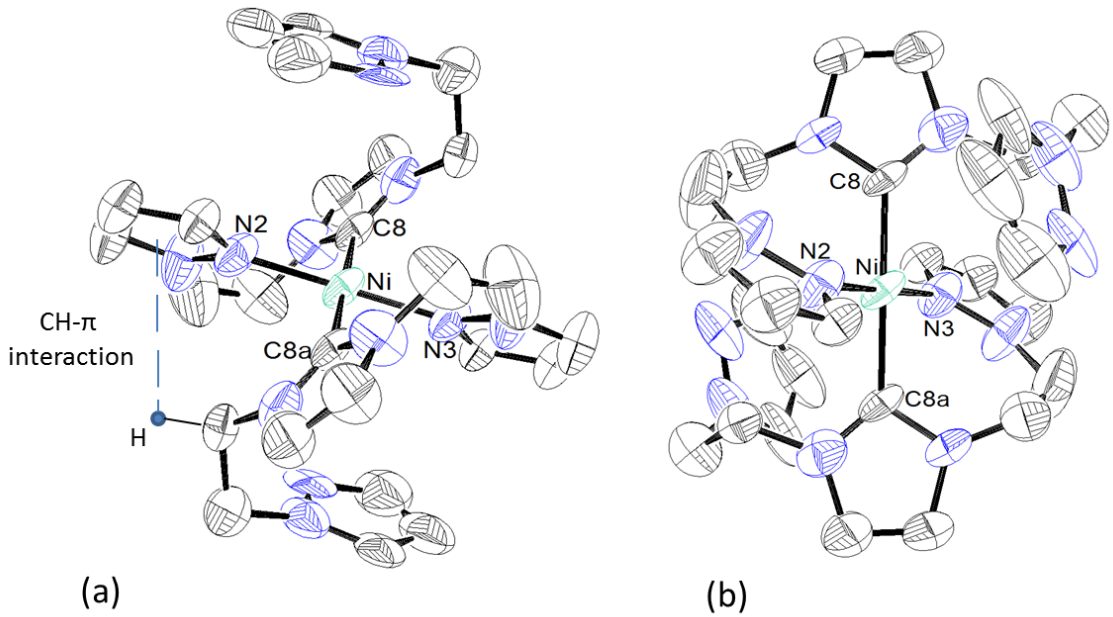



**Figure 3.10** ORTEP depiction of complex **10** with 50% probability ellipsoids for all non-hydrogen atoms. Hydrogen atoms and $BPh_4$ have been omitted for clarity. (a) Viewed along C8a-Ni-C8 axis. (b) Viewed along N2-Ni-N3 axis.

### 3.3.6. Comparison of the inner coordination sphere of complexes 8, 9 and 10.

| | Atoms | 8 | 9 | 10 |
|---|---|---|---|---|
| Bond lengths | Ni(1)-C(8)(carbene) | 1.850(4) | 1.847(2) | 1.899(1) |
| | Ni(1)-C(8a) | ---- | ----- | 1.899(1) |
| | Ni(1)-N(2) | 1.887(3) | 1.902(2) | 1.909(8) |
| | Ni(1)-N(3) | 1.908(3) | 1.900(2) | 1.909(8) |
| | Ni(1)-Cl | 2.200(1) | 2.220(1) | ----- |
| Bond angles | C(1)-Ni(1)-N(3) | 89.8(2) | 88.6(1) | 91.9(2) |
| | C(1)-Ni(1)-N(2) | 88.2(2) | 88.4(1) | 88.1(2) |

**Table 3.1** Selected bond lengths (Å) and angles (°) for **8, 9** and **10**.

All three Ni(II) complexes **8**, **9** and **10** under investigation here adopt a square planar geometry, with the main difference between the structures being that there are two *NCN* ligands bound to the Ni(II) centre in a bidentate coordination mode in complex **10** (Figure 3.10) where there is only one $NCN^{Me}$ ligand bound to nickel in **8** and **9**. The bond lengths of the inner coordination sphere of complexes **8** and **9** are nearly identical as expected due to their isostructural solid state structures. Analogous Ni(II) square planar carbene complexes in the literature where the NHC ligand contains pyridine side arms have similar nickel-carbene (1.837Å) and Ni(1)-Cl (2.236 Å) bond lengths to those of complexes **8** and **9**.[30] The nickel-carbene bond length in complex **10** is slightly longer than that observed for **8** and **9**. Complexes **8** and **9** contain a Cl co-ligand *trans* to the NHC carbene which has a weaker *trans* effect than an NHC carbene. Since all three complexes consist of two pyrazolyl groups *trans* to each other, the Ni(1)-N(2) and Ni(1)-N(3) bond lengths are similar in all three complexes; where the maximum variation in Ni(1)-N bond lengths is 0.012 Å. The two carbene carbons (C8 and C8a) and two pyrazolyl nitrogens (N2 and N3) in complex **10** show no distortion from linearity as the Ni atom lies in an inversion centre (C-Ni-C/N-Ni-N:

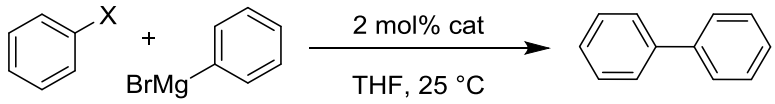
180.00(2)°). However, similar alignments in complexes **8** and **9** exhibit slight distortion from linearity (complex **8**: N-Ni-N: 176.02(2)°, complex **9**: N-Ni-N: 175.68(2)°) which is likely due to decreased ring strain in complex **10** enabled by bidentate coordination of ligand **2** to the Ni(II) metal centre. There are also significant rotations of the NHC ligands out of the square plane in all three complexes, giving a torsion angle (N3-Ni-C8-Imidazolium N5) of 30° in complexes **8** and **9** and 46° in complex **10**.

### 3.4. Catalytic activity of Ni(II) complexes for Kumada cross coupling of aryl halides

Ni(II) square planar complexes are known to be efficient catalysts for the Kumada cross coupling reaction. Among the best nickel catalyst systems for the Kumada cross coupling reaction include the addition of nickel metal ions to calixarene ligands. The catalytic systems achieve complete conversions of substrate at room temperature within 1 h, and can catalyse the reaction at catalyst loadings as low as 0.1-0.02 mol%.[37] However, only a few of the Ni complexes of weakly coordinating ligands such as calixarene maintain high activity at elevated temperatures without suffering catalyst decomposition.[6] Thus, complexes [Ni($NCN^{Me}$)Cl]($BPh_4$) (**8**), [Ni($NCN^{Me}$)Cl]($PF_6$) (**9**) and [Ni($NCN^{Et}$)$_2$Cl]($BPh_4$)$_2$ (**10**) synthesised here that contain hemilabile ligands composed of pyrazolyl and imidazolyl carbene donors, were tested as catalysts for the Kumada cross coupling reaction of aryl halides. The reactions were carried out under Schlenk conditions using distilled THF at 25 °C with a catalyst loading of 2 mol% unless otherwise stated. The glassware was flame dried and catalysts were predried under vacuum prior to the catalysis reactions. GC-MS analysis was used to monitor the reaction progress by taking aliquots at regular intervals. For complete experimental details, refer to Chapter 6.

### 3.4.1. Catalytic activity of 8, 9 and 10 for Kumada cross coupling reactions of chlorobenzene and bromobenzene

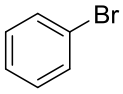
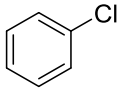
Complexes **8**, **9** and **10** were initially tested as catalysts for the Kumada cross coupling reactions of chlorobenzene and bromobenzene and with phenylmagnesium bromide (Scheme 3.17).




X = Cl, Br

**Scheme 3.17** Kumada cross coupling reactions of PhBr and PhCl with PhMgBr catalysed by **8**, **9** and **10**.

**Table 3.2** Kumada cross coupling reactions of PhBr and PhCl with PhMgBr catalysed by **8**, **9** and **10**.

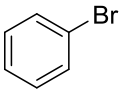
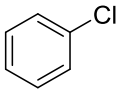
| entry | substrate | catalyst | %conv. (3.5 h) |
|---|---|---|---|
| **1** |  | **8** | 87 |
| **2** | | **9** | 89 |
| **3** | | **10** | 40 |
| **4** |  | **8** | >99 |
| **5** | | **9** | 40 |
| **6** | | **10** | 40 |

Conditions - Temperature: 25 °C. Catalyst loading: 2 mol%. Substrate: (0.5 mmol). Phenylmagnesium bromide: (1.5 mmol).

Complex **10** proved to be the least active catalyst of the three catalysts tested, achieving low conversions for the Kumada cross coupling reactions of both chlorobenzene and bromobenzene. Both reactions with chlorobenzene and bromobenzene terminate at 40% conversion (entries 1 and 2, Table 3.2) which suggested that deactivation of the catalyst occurs. The deactivation and thus the reduced catalytic activity of complex **10** compared to complexes **8** and **9** is likely due to complete coordinative saturation of the nickel center by ligand **1c**. Any conversion of substrate promoted by **10** likely occurred due to the lability of the weakly coordinating pyrazolyl groups allowing substrate access to the active metal center. The pyrazolyl groups are positioned *trans* to each other along with the central NHC groups. Previous work reported in the literature has demonstrated that nickel *bis*-carbenic systems have reduced activity for the Kumada cross coupling reaction in relation to mono carbonic systems. Zhang *et al*. have synthesized Ni(I)(IMes)Br and Ni(II)(IMes)$Br_2$ complexes which were tested as catalysts for the Kumada cross coupling reaction of aryl bromides.[38] The Ni(I) complexes fail to achieve complete conversions with reactions terminating at 60-80% even at 3 mol% catalyst loading. Very low yields were reported for the Ni(II)(IMes)$Br_2$ systems.[38]

Complex **8**, containing the $BPh_4^-$ counterion, proved to be the most effective catalyst overall for the Kumada cross coupling reactions of chlorobenzene and bromobenzene, achieving high conversions for both substrates within 3.5 h (entries 1 and 4, Table 3.2). Due to the high conversions achieved using complex **8**, the reactions were repeated at a lower catalyst loading of 1 mol% to determine whether the catalyst maintains the activity at lower loadings.

Table 3.3 Catalysed Kumada cross coupling of PhCl and PhBr using **8** at different catalyst loadings.

| entry | substrate | Catalyst loading | %conv. (4 h) |
|---|---|---|---|
| **1** |  | **1 mol%** | 80 |
| **2** | | **2 mol%** | 87 |
| **3** |  | **1 mol%** | 43 |
| **4** | | **2 mol%** | >99 |

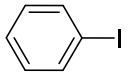
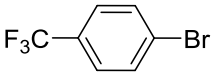
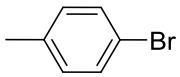
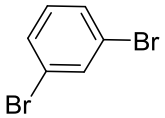
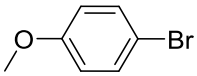
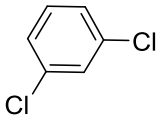
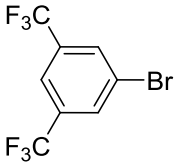
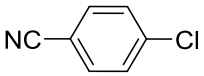
Conditions - Temperature: 25 °C. Catalyst loading: 1 or 2 mol%. Substrate: (0.5 mmol). Phenylmagnesium bromide: (1.5 mmol).

Decreasing the catalytic loading of complex **8** to 1 mol% for the conversion of the chlorobenzene substrate to biphenyl resulted in a significant reduction in catalytic activity, where only 43% conversion of chlorobenzene was achieved (entries 3 & 4, Table 3.3). Surprisingly, the coupling reaction of bromobenzene using 1 mol% of **8** did not result in a significant reduction in catalytic activity compared to the reaction catalysed by 2 mol% of **8**. Catalyst loadings of 1 mol% and 2 mol% achieve 80% conversion and 87% conversion respectively (entries 1 & 2, Table 3.3). All reactions shown in Table 3.3 were reproducible. There is currently no established mechanism to explain the higher reactivity of **8** for the conversion of chlorobenzene compared to bromobenzene.

### 3.4.2. Substrate scope of complex 8 for the Kumada cross coupling reaction

As complex **8** proved to be the most effective catalyst under investigation here for the cross coupling reactions of bromobenzene and chlorobenzene, it was tested as a catalyst for the transformation of a selection of substrates. (Table 3.4)

Table 3.4 Range of substrates catalysed by **8** for Kumada cross coupling reactions.

| entry | R-X | % conv. | entry | R-X | % conv. |
|---|---|---|---|---|---|
| **1** |  | >99 | **5** |  | 90 |
| **2** |  | 78 | **6** |  | 67(m) |
| **3** |  | 50 | **7** |  | 16(d) |
| **4** |  | 68 | **8** |  | 0 |

Conditions - Temperature: 25 °C. Catalyst loading: 2 mol%. Substrate: (0.5 mmol). Phenylmagnesium bromide: (1.5 mmol). Time : 4h. (m = monosubstituted product, d= disubstituted product)

Of all the bromo-substrates tested (Table 3.4) for conversion to biphenyl products using **8**, the highest conversions were achieved for the substrate containing an electron withdrawing $CF_3$ substituent on the aryl ring. In comparison, substrates with mesomerically electron donating substituents (*i.e.* methoxy) and more electron donating functional groups (methyl) achieve lower conversion to product. The tolyl bromide with increased electron donating character showed reduced activity for the Kumada cross coupling reaction compared to the phenyl counterparts with the reaction terminating at 78% conversion. Increasing the catalyst loading did not improve the catalytic activity, with a higher loading of 5 mol% achieving nearly identical results (76% conversion) within 4 h. Increasing the number of functional groups resulted in lower conversions for the cross coupling; since disubstitution of $CF_3$ groups located at the *meta* positions on the aryl ring relative to the bromine resulted in a reduced substrate conversion (68%) compared to the mono-*para*

substituted $CF_3$ reaction (90%). It was interesting to observe that the choice of halide altered the selectivity of cross coupling reactions to form biphenyl or triphenyl products. The catalysed reaction of phenylmagnesium bromide with the 1,3-dibromobenzene resulted in selective formation of the monosubstituted 1-bromo-3-phenylbenzene. However, the catalyzed reaction of the analogous 1,3-dichlorobenzene with phenylmagnesium bromide using **8** results in the selective production of the disubstituted 1,3-diphenylbenzene. This result was unexpected considering 1,3-dibromobenzene is more likely to produce the disubstituted product due to the propensity of bromide groups to be more readily substituted in comparison to chloride groups. However, as expected, substrates containing bromide groups produced higher overall yields in comparison to the substrates containing chloride groups.

## 3.5. Conclusions

This chapter describes the coordination chemistry of *NCN* pincer ligand precursors **1**, **1b** and **1c** with Ni(II) and Ag(I) metal centres and the investigation of the activity of the resulting Ni(II) complexes **8**, **9** and **10** as catalysts for the Kumada cross coupling reaction.

- Choice of ligand affected the nature of the coordination observed in the resulting complexes. Both bidentate and tridentate coordination of the *NCN* ligands to the Ni(II) metal centre were observed.
- Complex **8** containing the pincer geometry was found to be the most active catalyst for the Kumada cross coupling reaction in comparison to complexes **9** and **10**. The coordinatively saturated complex **10** was found to be nearly inactive as a catalyst for the organic transformation.
- Changing the counterion from $BPh_4^-$ to $PF_6^-$ (complexes **8** and **9**) resulted in reduced activity for promoting the transformation of the chlorinated substrate chlorobenzene, and similar activity for the Kumada cross coupling reaction of bromobenzene with phenylmagnesium bromide.
- Complex **8**, being the most active catalyst under investigation here was tested as a catalyst for a wide range of substrates to test functional group tolerance and ability to perform more difficult di-substitution reactions. Complex **8** catalysed the Kumada cross coupling reaction for a wide range of substrates with higher activities achieved for substrates with electronegative substituents. The investigation showed that the catalytic activity was dependent on the type of substituents present on the aryl substrates.

- Complex **8** proved to be moderately active for the Kumada cross coupling reaction compared to other Ni(II) complexes in literature. Other Ni(II) complexes containing NHC pincer ligands achieve similar conversions to those of complex **8** for the Kumada cross coupling reaction.
- The air stable complex **8** may prove to be useful in catalysed reactions such as Suzuki- Miyura cross coupling.

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# Chapter 4. Gold(I) and Gold(III) complexes of hemilabile pincer ligands for catalysed activation of alkynes

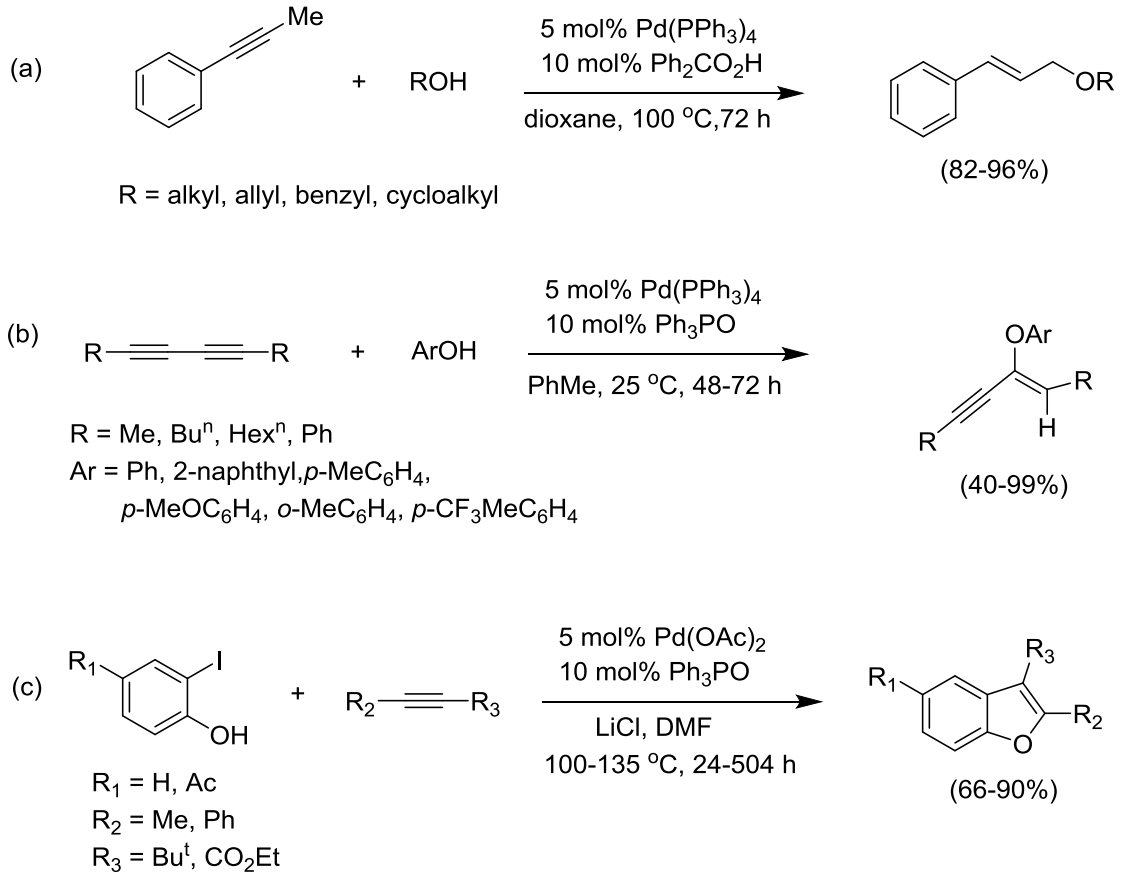
## 4.1. Introduction

### 4.1.1. Transition metal catalysed addition of X-H bonds to alkynes

The addition of X-H bonds to an alkyne functional group, where X= O, N, Si, B, or P, has proven to be important in the field of chemistry,[1, 2, 3] as it is an efficient and atom economical method for the synthesis of X-C bonds resulting in little to no production of wasteful by-products when compared to traditional synthetic/retrosynthetic methods.[1] The production of many organic compounds vital to the pharmaceutical industry often relies on the economic hydroelementation reaction as a key step in the synthetic process.[4, 5] Transition metal complexes have proven to be the ideal choice as catalysts for the addition reactions of X-H bonds to alkynes in comparison to main group elements, due to increased product selectivity.[2] The efficacy of the complexes as catalysts for the hydroalkoxylation (X = O) and hydroamination (X = N) reactions is described below.

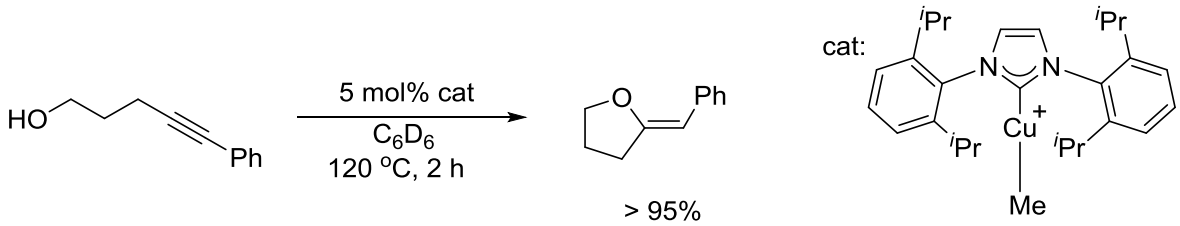
#### 4.1.1.1. Transition metal catalysed hydroalkoxylation reactions

A large number of transition metal complexes have been used for the addition of O-H bonds to alkynes (hydroalkoxylation reaction), which include Rh(I), Ir(I), Ag(I), Hg(I), Au(I), Au(III) and Pd(II).[1] Up to 2004, Pd(II) complexes were the preferred choice for this type of organic transformation. A selection of hydroalkoxylation reactions catalysed by Pd(II) are shown in Scheme 4.1.[6, 7, 8]



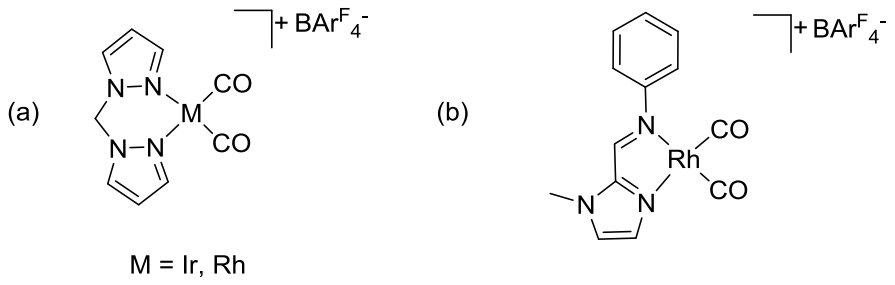

**Scheme 4.1** Examples of Pd(II) catalysed hydroalkoxylation reactions.(a) aromatic alkynes,[6] (b) aromatic and alkyl substituted alkynes,[7] (c) disubstituted aromatic alcohols.[8]

Other metal complexes have since been synthesised with the aims of achieving higher turnover number (TON) and turnover frequency (TOF) for the hydroalkoxylation reaction. Recently, a copper(I) NHC complex was found to be an active catalyst for the intramolecular hydroalkoxylation reaction of alkynyl alcohols, achieving near complete conversions within two hours (Scheme 4.2).[9]

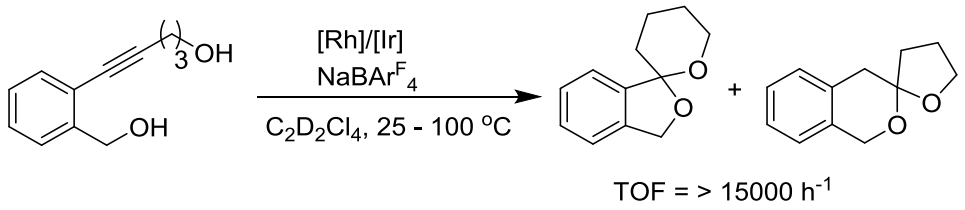



**Scheme 4.2** Cu(I) catalysed intramolecular hydroamination of alkynyl alcohols.[9]

Messerle *et al.* have extensively investigated the hydroalkoxylation reaction using Rh(I) and Ir(I) complexes (Scheme 4.3), in particular, the intramolecular dihydroalkoxylation reaction of alkyne diols (Scheme 4.4).[10] The complexes containing carbonyl co-ligands, $[M(bpm)(CO)_2]BAr^F{}_4$ (M = Rh, Ir) were highly efficient catalysts for this double cyclisation reaction.[10]



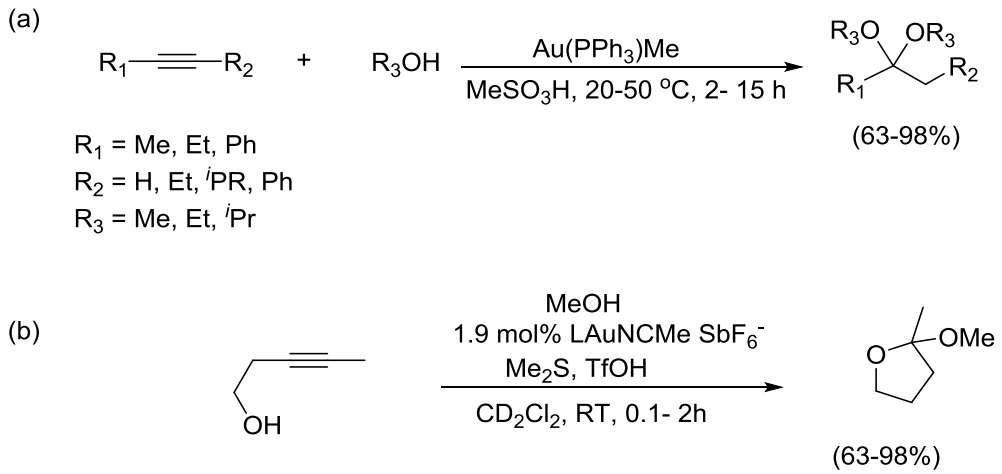

**Scheme 4.3** Rh(I) and (Ir) catalysts synthesised in the Messerle group for the dihydroalkoxylation reaction.[10]




**Scheme 4.4** Catalysed dihydroalkoxylation of alkyne diols.

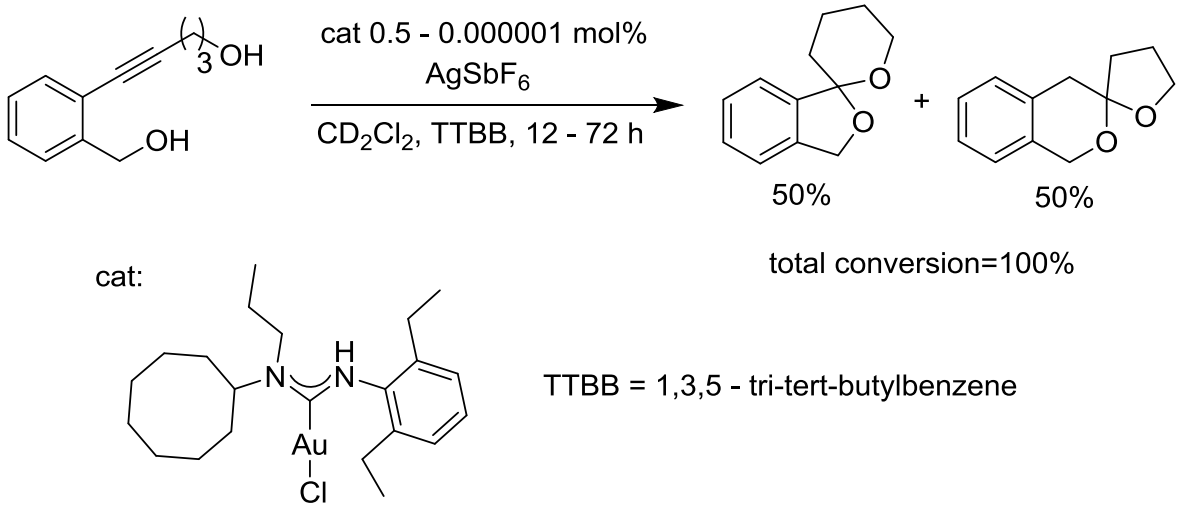
Gold complexes have received significant attention as catalysts for the activation of alkynes, including hydroalkoxylation reactions,[11] due to the ability of the complexes to achieve high catalytic conversions at very low catalyst loadings without being air or moisture sensitive. Teles *et al.* have reported the use of an *in situ* generated Au(I) complex from $Au(PPh_3)Me$ and methanesulfonic acid, which achieved TON values up to $10^5$ and TOF of 5400 $h^{-1}$ for the intermolecular dihydroalkoxylation reaction of asymmetric alkynes (Scheme 4.5a).[12a, 12b] Gold complexes are also able to achieve complete conversions for the hydroalkoxylation reaction at ambient conditions within short reaction times. For example,

a gold complex containing an acetonitrile co-ligand for selected intramolecular hydroalkoxylation reactions within 12 minutes (Scheme 4.5b)[12c]




**Scheme 4.5** (a) Intermolecular hydroalkoxylation catalysed by $Au(PPh_3)Me$. (b) Intramolecular hydroalkoxylation catalysed by LAuNCMe.

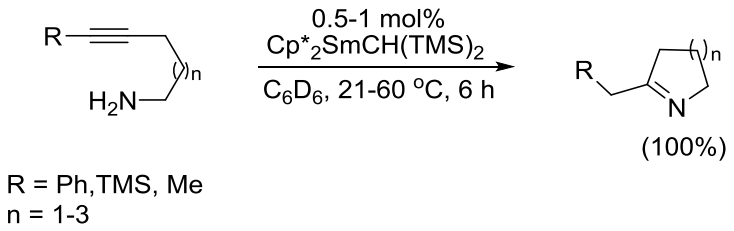
Gold complexes that are stabilised by strong donors have proven to be highly stable over longer periods of time, achieving unmatched catalytic TON (turnover numbers) values for the hydroalkoxylation reactions. Hashmi *et al.* have recently reported the use of a Au(I)-carbene complex which achieved a TON value of 970 000 for the dihydroalkoxylation reaction of alkyne diols when used as a homogeneous catalyst. Remarkably, the complex when attached to a silica based support achieved over 32 000 000 TON for the organic transformation (Scheme 4.6).[11a]




**Scheme 4.6** Au(I) catalysed intramolecular dihydroalkoxylation of alkyne diols.

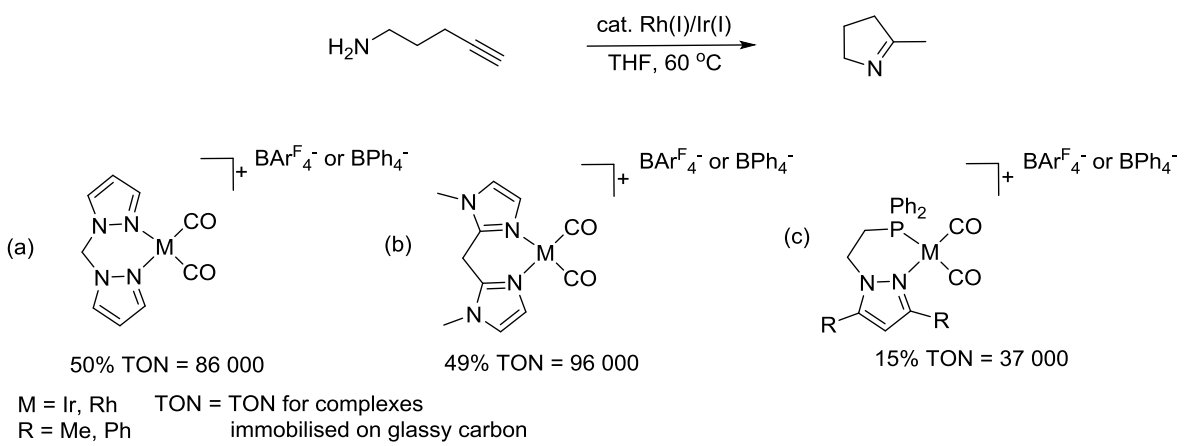
#### 4.1.1.2. Transition metal catalysed hydroamination reactions

Early examples of hydroamination reactions, the addition of an N-H bond across unsaturated C-C bonds, involved the use of lanthanide and actinide complexes.[2] A lanthanide complex, $Cp_2SmCH(TMS)_2$ kept under rigorously inert conditions (moisture and oxygen free) was shown to be a highly active catalyst for the intramolecular hydroamination reaction of a series of aminoalkynes achieving TOF values up to 7600 $h^{-1}$.[13]



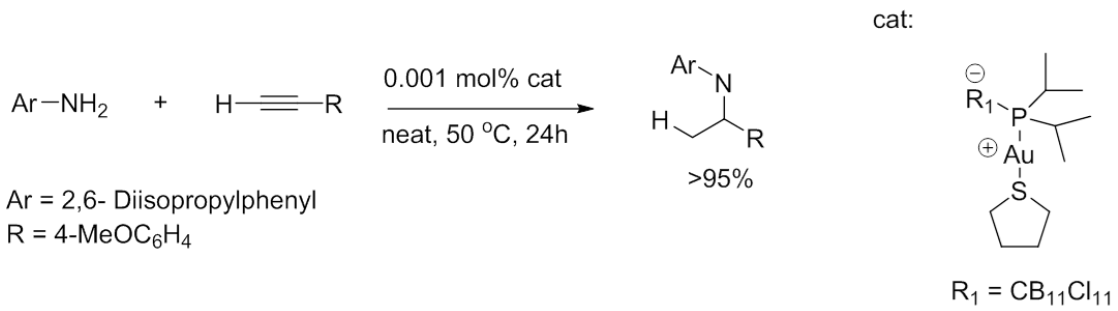

**Scheme 4.7** Samarium catalyst for the intramolecular hydroamination of aminoalkynes. [13]

Recently reported catalysts that are highly active for the hydroamination reaction include Rh(I) and Ir(I) complexes containing *NN* and *NP* bidentate ligands(Scheme 4.8).[14] Messerle *et al.* have synthesised a number of Rh(I) and Ir(I) catalysts,[10, 14] some of which achieved TON up to 96 000 for the intramolecular hydroamination of 4-pentyn-1-amine.[14a]




**Scheme 4.8** Rh(I) and Ir(I) catalysts for the hydroamination reaction of 4-pentyn-1-amine.[14]

The high TON values achieved by using the Rh(I) catalysts require a heterogeneous system. Simple homogeneous gold complexes catalyse hydroamination reactions at low catalyst loadings under mild conditions. Lavallo *et al.* have demonstrated the high efficiency of a boron cluster containing a zwitterionic gold complex and a phosphine donor group (Scheme 4.9). This catalyst has the highest reported TON value (95 000) for the intermolecular hydroamination reaction.[15]




**Scheme 4.9** Highly active Au(I) catalyst for the intermolecular hydroamination reaction.

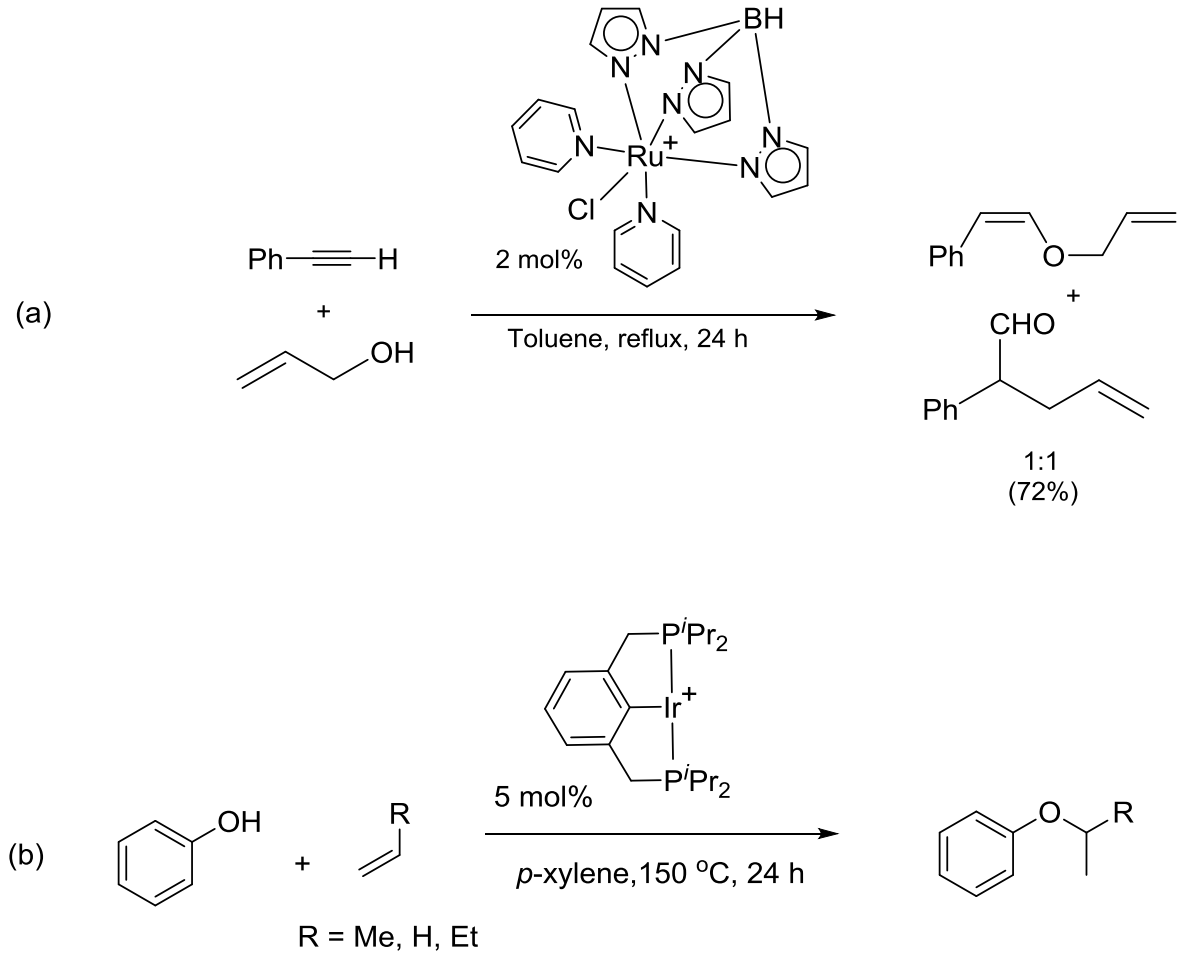
### 4.1.2. Transition metal complexes containing pincer ligands for catalysed addition of X-H bonds to alkynes

Transition metal complexes containing monodentate and bidentate ligands can be effective catalysts for X-H addition to alkynes for selected substrates as described above. However,

monodentate and bidentate complexes can suffer from reduced catalytic and thermal stability resulting in reduced activity due to decomposition of the catalysts. Transition metal complexes bearing pincer ligands tend to have increased catalytic and thermal stability owing to the $\kappa^3$ co-ordination of the ligands allowing successful catalytic conversions even at elevated temperatures.[16]

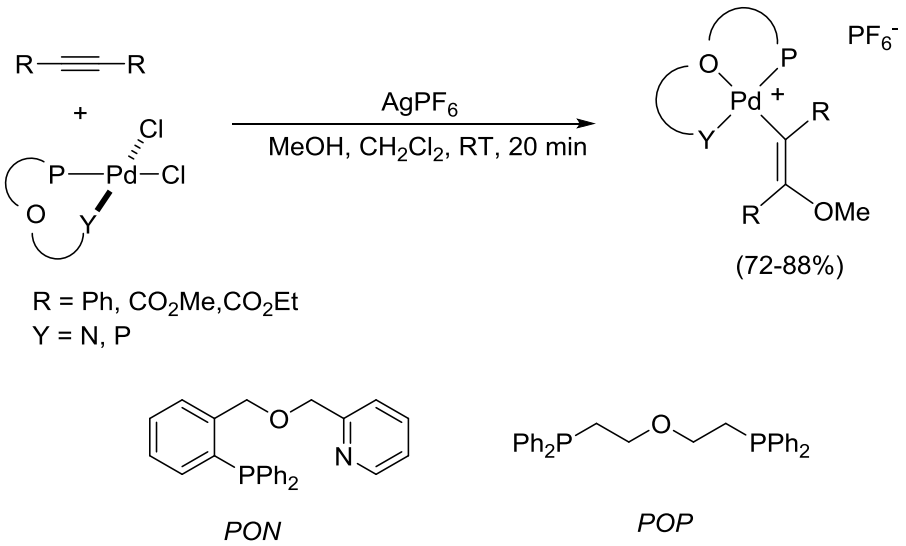
#### 4.1.2.1. Transition metal complexes containing pincer ligands as catalysts for hydroalkoxylation reactions

A Ru(II) complex synthesised by Kirchner *et al.* containing tridentate co-ordination of a *tris*(pyrazolyl) borate ligand to the metal centre was the first reported case for the intermolecular addition of allyl alcohols to acetylenes by ruthenium. The complex maintains stability at elevated temperatures (110 $^{o}$C) over an extended period of time (24 hours), achieving a consistent ratio of 1:1 of the *cis*-allyl vinyl ether and the aldehyde shown in Scheme 4.10a.[17a] A significant number of pincer complexes with different metals has since been investigated as catalysts for hydroalkoxylation reactions. Goldman *et al* has recently reported the catalytic activity an iridium complex bearing a *PCP* pincer ligand for the hydroaryloxylation reaction of olefins (Scheme 4.10b).[17b]




**Scheme 4.10** (a) First example of a Ru(II) catalysed intermolecular addition of allyl alcohols to acetylenes. (b) An iridium complex bearing a *PCP* pincer ligand for the hydroaryloxylation reaction of olefins [17]

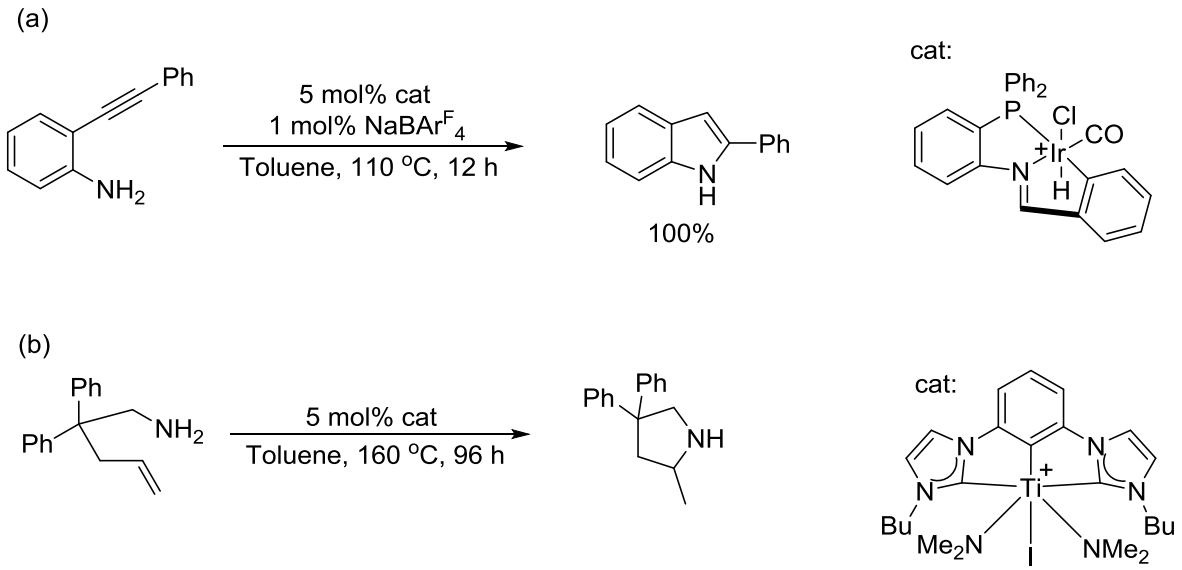
Mechanistic investigations using palladium complexes containing *PON* and *POP* tridentate ligands have provided vital information on the reaction pathway of the stereoselective addition of methanol to activated acetylenes.[18] This was made possible by isolating key Pd(II) intermediates in the reaction, which were stabilised by the $\kappa^3$ chelate effect of the pincer ligands (Scheme 4.11).




**Scheme 4.11** Key Pd(II) intermediate stabilised by the tridentate coordination of *PON* or *POP* pincer ligands.[18]

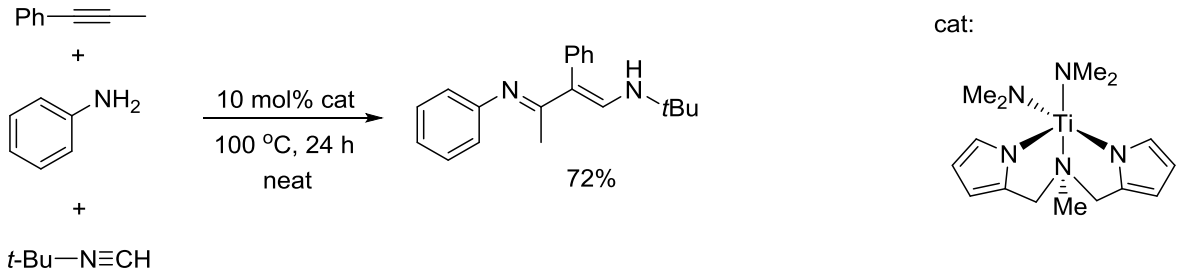
#### 4.1.2.2. Transition metal catalysts containing pincer ligands for hydroamination reactions

Transition metal complexes with pincer ligands have also been utilised as catalysts for the hydroamination reaction.[19] For example, an Ir(III) complex bearing a *PNC* pincer ligand proved to be an effective catalyst for the intramolecular hydroamination of 2-alkynylanilines to produce indoles (Scheme 4.12a). The catalyst achieved complete conversion of substrates, avoiding thermal decomposition at high temperatures (110 $^{o}$C) for over 12 hours.[19a] Recent work has also expanded the investigation of complexes containing pincer ligands for the hydroamination reaction to metals such as titanium. As shown in Scheme 4.12b, a titanium complex of a *CCC* pincer ligand achieved high conversions for the intramolecular hydroamination of alkenes.[19b]




**Scheme 4.12** (a) Ir(III) catalyst with a pincer ligand for the hydroamination of 2-alkynylanilines. (b) Ti catalyst with a pincer ligand for the hydroamination of alkenes. [19]

It is difficult to achieve high yields for catalysed three component reactions, and often high temperatures are required to produce successful conversions.[20] A titanium complex containing a tridentate *NNN* pincer ligand achieved good conversions for the three component intermolecular hydroamination of alkynes with aromatic amines and *tert*-butyl isonitrile at temperatures of up to 100 °C, with exclusive selectivity for α,β-unsaturated β-aminoimine (Scheme 4.13).[21]

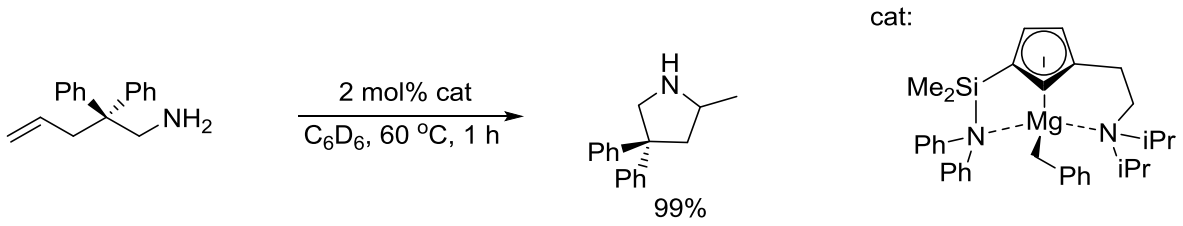



**Scheme 4.13** Ti catalyst used for three component intermolecular hydroamination reactions. [21]

#### 4.1.2.3. Metal complexes containing hemilabile pincer ligands for the addition of X-H bonds to the C-C multiple bond of alkenes or alkynes

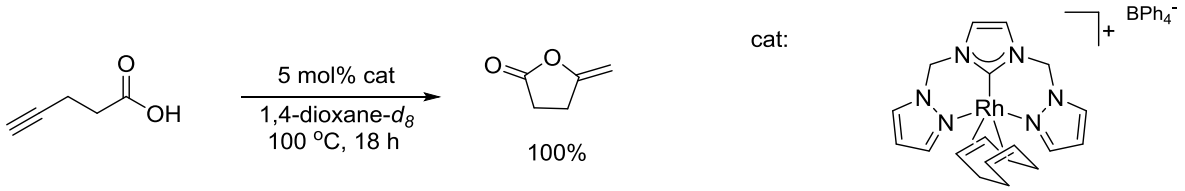
Pincer ligands that contain a combination of strong and weak donor groups (hemilabile ligands) can offer additional advantages in metal catalysis; the strong donors are able to stabilise the complex by forming a robust metal-ligand bonds while weaker donors are able to temporarily dissociate from the metal opening up reactive coordination sites during the catalytic cycle.[22] Therefore hemilabile pincer complexes are able to maintain catalytic and thermal stability without sacrificing high reactivity.

A hemilabile magnesium complex containing *NN* pendant donor arms and a strongly coordinating central aryl group was found to be a highly active catalyst for the intramolecular hydroamination of aminoalkenes.[23] The catalyst achieves complete conversion for the organic transformation within one hour (Scheme 4.14).




**Scheme 4.14** Hemilabile magnesium pincer catalyst for the hydroamination of aminoalkenes.

Messerle *et al.* have recently synthesised Rh(I) and Ir(I) complexes containing the hemilabile pincer ligand **1** as presented in Chapter 2.[24] The Rh(I) complex bearing the pincer ligand **1** and a COD co-ligand achieved complete conversion for the hydroalkoxylation reaction of 4-pentynoic acid to ϒ-methylene-ϒ–butyrolactone (Scheme 4.15). The catalyst remained active at elevated temperatures over an extended period of time.




**Scheme 4.15** Rh(I) catalyst containing the hemilabile pincer ligand **1** for the hydroalkoxylation of 4-pentynoic acid.

## 4.2. Aims of this chapter

The work presented in this chapter focuses on pincer ligands containing a central *N*-heterocyclic carbene donor and labile pyrazole pendant donors. Gold complexes have proven to be highly active catalysts for a range of organic transformations, however, tend to lack thermal stability. The coordination of a gold centre to hemilabile pincer ligands should provide an advantageous combination of stable and highly active catalysts for hydroalkoxylation and hydroamination reactions.

The aim of this chapter was to investigate the synthesis and co-ordination chemistry of novel gold complexes containing an hemilabile $NCN^{Me}$ pincer ligands, and their activity as catalysts for the dihydroalkoxylation and hydroamination reactions. The specific goals were to:

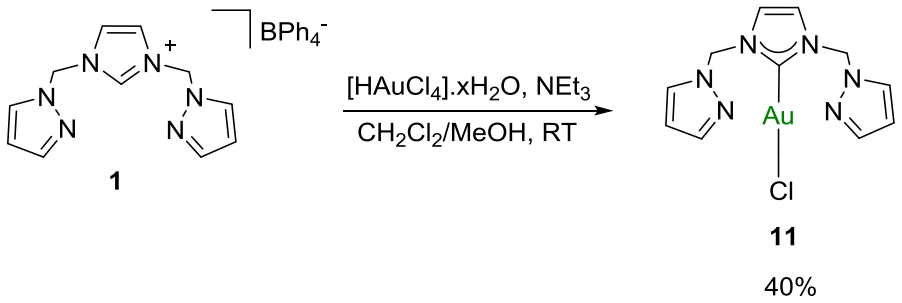
- Synthesise gold complexes containing oxidation states +I or +III using different reagents and deprotonation methods.
- Characterise and investigate coordination chemistry of these novel gold complexes using NMR spectroscopy, mass spectrometry, elemental analysis and X-ray crystallography.

- Investigate dihydroalkoxylation reactions of alkyne diols catalysed by the novel Au(I) and Au(III) complexes containing pincer ligands.
- Test the Au(I) and Au(III) complexes as catalysts for intramolecular and intermolecular hydroamination reactions.

## 4.3. Synthesis of Gold(I) and Gold(III) complexes containing an *NCN*$^{Me}$ hemilabile pincer ligand

### 4.3.1. Synthesis and characterisation of [Au(I)(*NCN*$^{Me}$)Cl]$BPh_4$ (11)

There is literature precedence for the synthesis of Au(I) carbene complexes using mild bases, such as carbonates as deprotonating agents.[25] Therefore, initial attempts to synthesise the Au(I) complex of ligand **1** were carried out by reacting Au(I)($SMe_2$)Cl with the *NCN*$^{Me}$ ligand **1** using $NaHCO_3$ and $K_2CO_3$ as the deprotonating agents. However, these reactions resulted in no formation of **1** leaving an unreacted mixture of reactants. It was likely that the carbonates were not sufficiently basic to deprotonate the imidazolium proton of the ligand. Triethylamine was therefore employed as an alternative deprotonating agent. Complex **11** was successfully prepared by stirring a suspension of chloroauric acid in the presence of excess triethylamine, dichloromethane, methanol and ligand **1** at room temperature for 16 hours (Scheme 4.16). The resulting reduced gold(I) complex was isolated as a grey solid. The complex can also be synthesised using a silver transmetallation route, by reacting Au($SMe_2$)Cl with the silver intermediate **2** (Chapter 2) in dichloromethane. Interestingly, the yield of the desired Au(I) complex *via* the silver transmetallation route was significantly reduced compared to the earlier carbene deprotonation route. Further details are provided in the experimental section, Chapter 6.




**Scheme 4.16** Synthesis of [Au(I)(*NCN*$^{Me}$)Cl] (**11**).

The $^{1}$H NMR spectrum of complex **11** exhibited five resonances indicating a symmetric environment in the gold complex. All five resonances were attributed to the ligand protons. The absence of $BPh_4^-$ proton resonances suggested that the resulting Au(I) complex was neutral in character with a terminally bound Cl to balance the +1 charge. The structure containing monodentate coordination of the *NCN* pincer ligand, and exhibiting a linear geometry typical of Au(I) complexes was confirmed using X-ray crystal structure analysis (Figure 4.1). Mass spectrometry provided further evidence of the linear conformation of the Au(I) metal centre with a single ligand showing a dominant signal at 425.0778 m/z, which is attributed to the loss of the terminally bound Cl co-ligand.

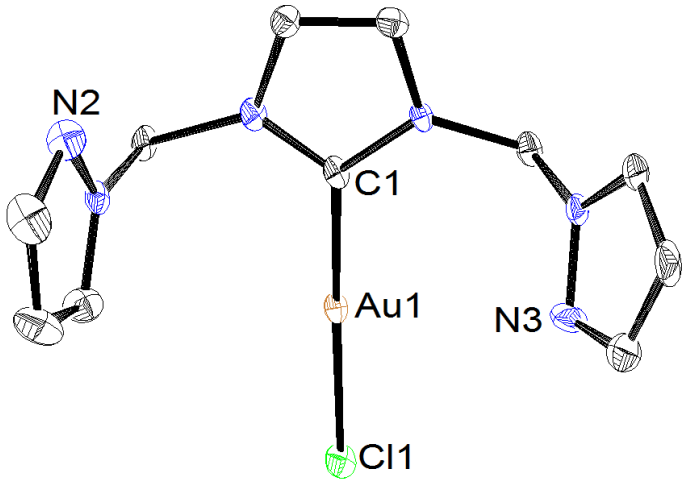
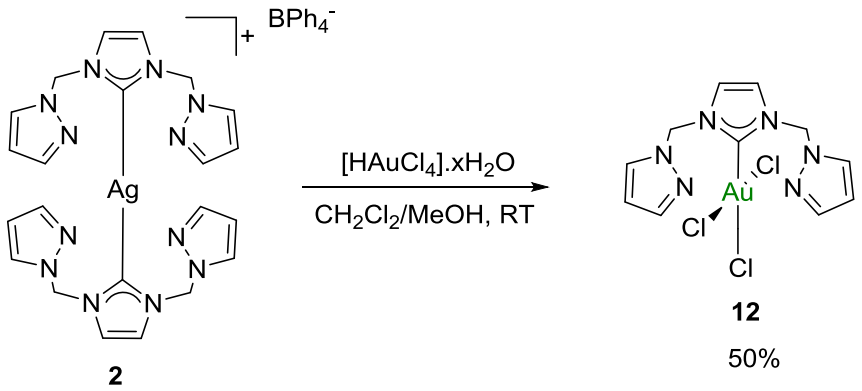



**Figure 4.1** ORTEP depiction of the solid state structure of complex **11** at 50% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

### 4.3.2. Synthesis and characterisation of [Au(III)(*NCN*$^{Me}$)Cl]$BPh_4$ (12)

Few Au(III) carbene complexes have been reported in the literature and most of those reported have been synthesised using a mercury or silver transmetallation route under mild conditions.[26] This method was therefore employed for the synthesis of the Au(III)

complex of ligand **1**. The Au(III) compound was prepared by transmetallation of the ligand to Au(III) from the silver intermediate [Ag(I)($NCN^{Me}$)$_2$]$BPh_4$ (**2**) using chloroauric acid in dichloromethane (Scheme 4.17). Stirring the reaction mixture at room temperature followed by addition of pentane resulted in the isolation of [Au(III)($NCN^{Me}$)Cl]$BPh_4$ (**12**) as a yellow solid.




**Scheme 4.17** Synthesis of [Au(III)($NCN^{Me}$)Cl] (**12**)

Similar to the $^1$HNMR spectrum of Au(I) complex **11**, the $^1$H NMR of [Au(III)($NCN^{Me}$)Cl] (**12**) shows that the complex is symmetric with a line of symmetry along the carbene-gold-chloride axis. Only five resonances were observed in the spectrum which were all attributed to the ligand protons. As observed for complex **11**, the absence of resonances due to protons of $BPh_4^-$ suggested the loss of the counterion and that the 3+ charge of the Au(III) compound was balanced by three terminally bound Cl atoms. X-ray analysis of a single crystal of **12** (Figure 4.2) confirmed the expected square planar geometry of the Au(III) complex with a monodentate co-ordination of the $NCN^{Me}$ ligand to the Au(III) metal centre *via* the carbene donor. Mass spectrometry of the isolated yellow solid revealed the presence of a dominant signal at 495.0155 m/z which was assigned to the loss of one terminally bound Cl co-ligand.

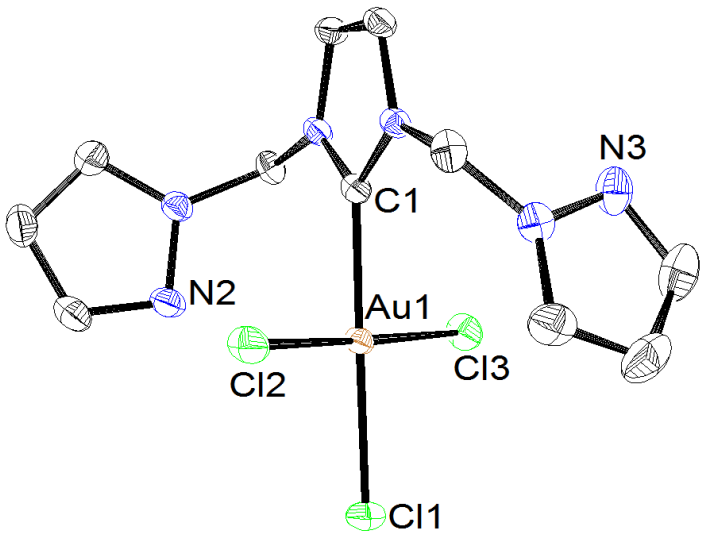



**Figure 4.2** ORTEP depiction of the solid state structure of complex **12** at 50% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

### 4.3.3. Comparison of the solid state structures of 11 and 12

The Au(I) complex **11** and Au(III) complex **12** both have similar planar structures. However, the metal centres Au(I) and Au(III) are linear and square planar respectively, see Figure 4.1 and Figure 4.2, and the Au(III) complex contains two extra Cl co-ligands. In both structures the gold ions are coordinated to the carbon atom on the NHC unit and the $(C2\text{-}C3)_{centroid}$-C1-Au angle is close to linear. The slight elongation of the gold-carbene bond length in complex **12** compared to that of complex **11**, is attributed to the square planar geometry of complex **12** with combined *cis* effects from the two additional Cl atoms. The pendant pyrazole donors remain uncoordinated to both Au(I) and Au(III) centres in both **11** and **12**, N-Au distances are greater than 3.1 Å, though in the Au(III) example the N-atom from the pyrazole would be available for hemilabile binding upon displacement of a chloride ion by a suitable counterion such as $NaBAr^{F}_{4}$.

| Atoms | **11** | **12** |
|---|---|---|
| Au(1)-C(1) | 1.973(5) | 2.007(2) |
| Au(1)-Cl(1) | 2.285(1) | 2.3116(8) |
| Au(1)-Cl(2) | ----- | 2.2807(7) |
| Au(1)-Cl(3) | ----- | 2.2780(7) |
| C(1)-Au(1)-Cl(2) | ----- | 89.37(6) |
| C(1)-Au(1)-Cl(3) | ----- | 89.02(6) |
| C(2)-C(3)$_{centroid}$-C(1)-Au(1) | 175.57(6) | 178.71(6) |

**Table 4.1** Selected bond lengths(Å) and angles(°) for **11**, and **12**.

Both pendant pyrazole arms are not coplanar with the central imidazole. For complex **11** a cavity bearing an N•••N distance of 6.626 Å was observed. This has the potential to coordinate a second metal center to form a bimetallic complex containing a shared ligand moiety (Figure 4.3).

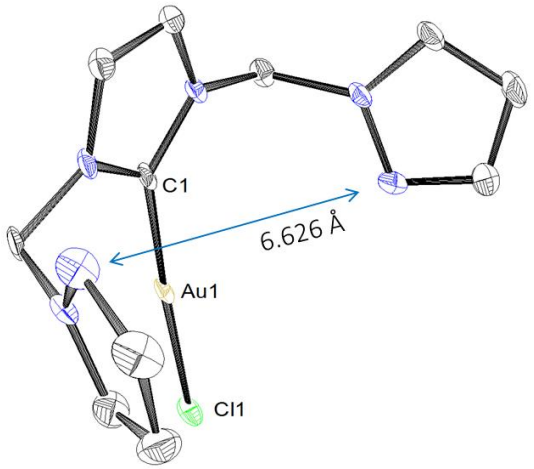
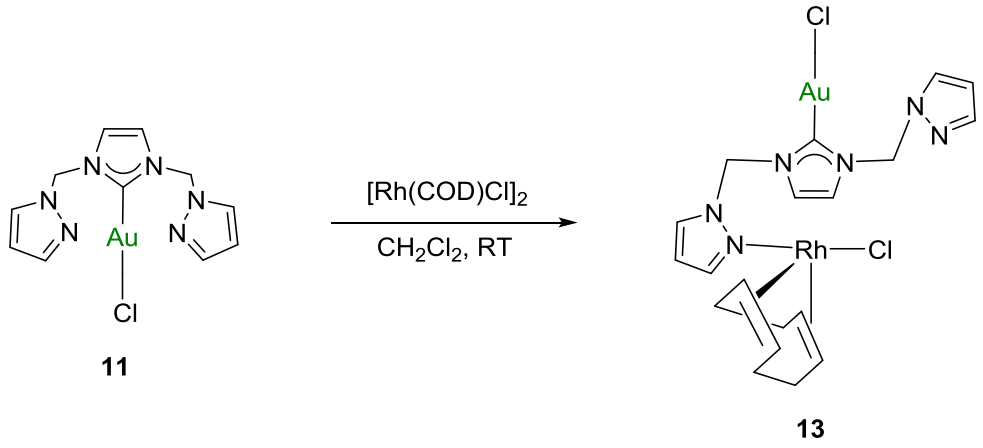



**Figure 4.3** ORTEP depiction of complex **11** showing the distance between pyrazole nitrogens.

### 4.3.4. Attempted synthesis of Au(I)/Rh(I) bimetallic complexes

As the X-ray analysis of the structure of complex **11** revealed a close proximity of the two pendent pyrazole arms, the distance between the pyrazoles provided an ideal "pocket" for an additional and different metal such as Rh(I) (Scheme 4.18).

Bimetallic complexes have been shown to enhance the catalytic activity for a number of organic transformations.[10b,27] Heteronuclear bimetallic complexes can also promote tandem catalytic reactions where the different metals can catalyse the different individual reaction steps respectively in a multi-step reaction.[28] Therefore, an attempt was made to synthesise an Au(I)/Rh(I) bimetallic complex. Complex **11** was mixed with a half molar equivalent of $[Rh(COD)Cl]_2$ in dichloromethane. Addition of pentane resulted in the isolation of complex **13** as a yellow solid. ($^1$H NMR of **11** shown in Figure 4.4 for comparison to **13** in Figure 4.5)




**Scheme 4.18** Synthesis of a heterobimetallic Au(I)/Rh(I) complex (**13**).

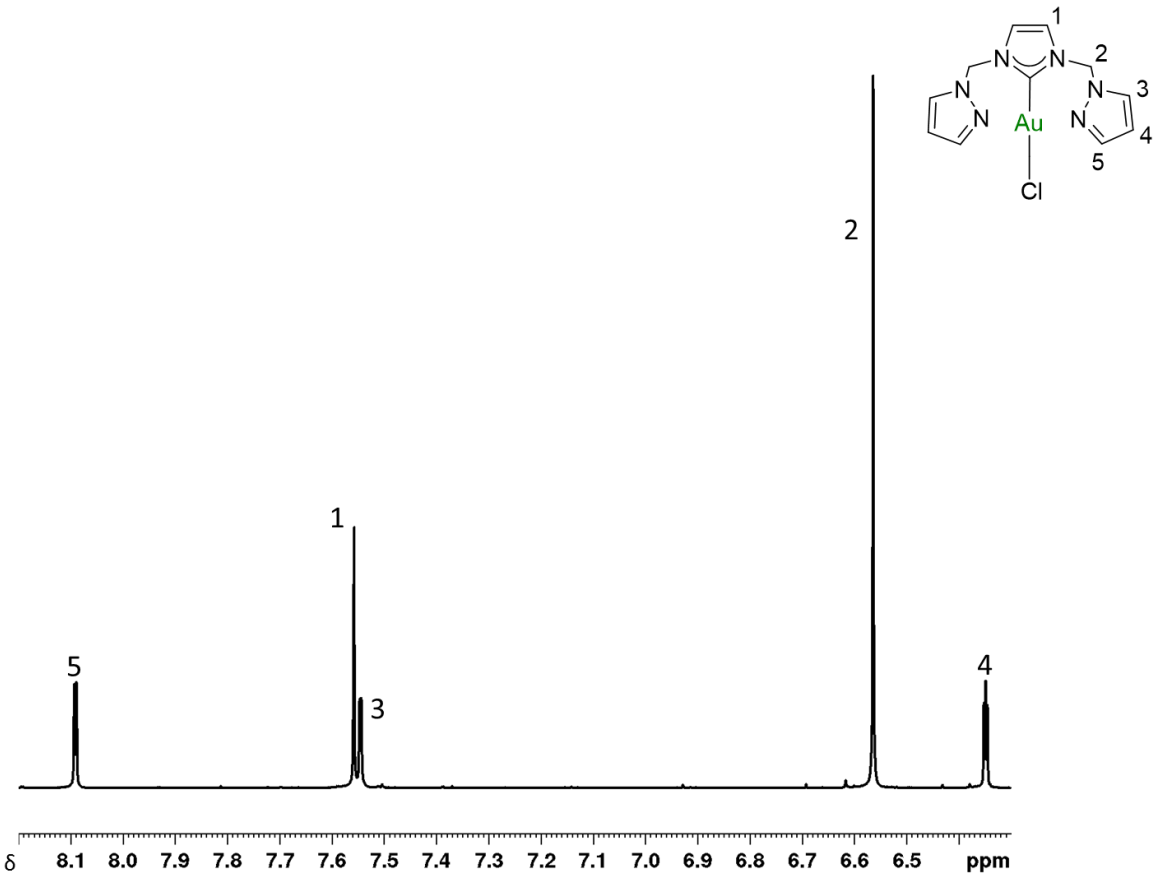



**Figure 4.4** $^{1}$H NMR (600 MHz, acetone-$d_6$) of complex **11**.

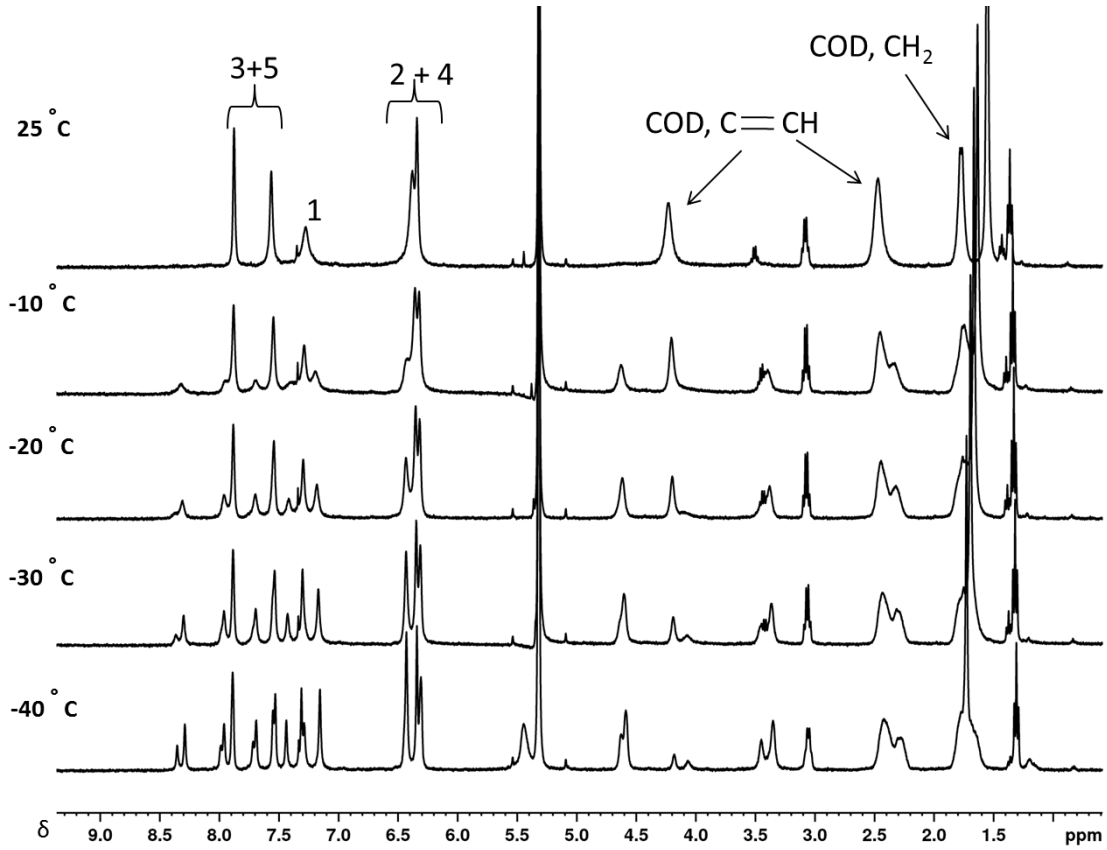



**Figure 4.5** Variable temperature $^{1}$H NMR (400MHz, acetone-$d_6$) of heterobimetallic complex **13**.

The $^{1}$H NMR spectrum of the complex **13** at room temperature exhibited five broad resonances that were unresolved. The broadening of the signals was attributed to fluctionality of the *NCN*$^{Me}$ ligand **1** on the NMR time scale. Analysis of the sample using variable temperature $^{1}$H NMR revealed the presence of 12 resonances between 6 and 9 ppm (Figure 4.5) which were attributed to protons on the ligand and counter ion. The asymmetry revealed by the $^{1}$H NMR suggested successful coordination of the pyrazolyl donors of the *NCN*$^{Me}$ ligand to the Rh(I) metal centre. However, further characterisation proved to be difficult due to the decomposition of the complex over time even at reduced temperatures and under inert conditions.

Decomposition of the heterobimetallic complex may occur *via* dissociation of labile pyrazole nitrogen ligand donors from the rhodium. To alleviate the problem, the complex **13** was treated with abstracting agents such as $NaBPh_4$ and $NaBAr^F_4$ in a DCM solution, which can promote removal of a terminally bound chloride from either the Au(I) or Rh(I) centres promoting coordination of the free pyrazole pendant arm. This bidentate coordination of the ligand to the Au(I) or Rh(I) centre should significantly reduce the rate of dissociation by increasing the chelate effect of the complex. However, analysis of the reaction of **13** with $NaBAr^F_4$ and $NaBPh_4$ by $^1$H NMR spectroscopy indicated the formation of an intractable mix of products. It is likely that the Cl co-ligand on the Au(I) metal can undergo abstraction, which could result in decomposition of complex **13**.

### 4.4. Catalysed hydroalkoxylation reactions using complexes 11 and 12.

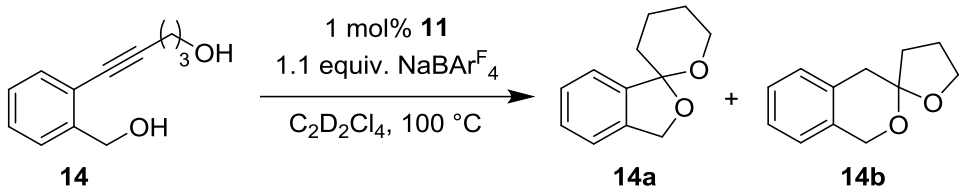
Au(I) and Au(III) complexes have proven to be excellent catalysts for the activation of alkynes.[11, 29] Therefore,[Au(I)(*NCN*$^{Me}$)Cl] (**11**) and [Au(III)(*NCN*$^{Me}$)Cl] (**12**) were tested as catalysts for the dihydroalkoxylation reaction of the alkyne diols **14**, **15** and **16**. The reactions were carried out in $C_2D_2Cl_4$ at various temperatures as stated using a catalyst loading of 1 mol% unless otherwise stated. $NaBAr^F_4$ was also used as an additive for the catalysis reactions. For further details, refer to the experimental section in Chapter 6.

#### 4.4.1. Catalysed dihydroalkoxylation of 2-(5-hydroxypent-1-ynyl)benzylalcohol (14).

Gold complex **11** was an efficient catalyst for the dihydroalkoxylation of 2-(5-hydroxypent-1-ynyl)benzylalcohol **14** (Chart 4.1). On using **11** to promote dihydroalkoxylation of **14**, two isomeric spiroketalproducts **14a** and**14b** were observed in equivalent proportions. The isomers can be separated using methods such as HPLC, however, this work is focused only

on the catalytic conversion and selectivity of the catalyst. Previous reports have shown that regioselectivity between these two spiroketal isomers is difficult to control.[10,30]

The reaction was first attempted at 100 °C in $C_2D_2Cl_4$ using Au(I) complex **11** with a catalyst loading of 1 mol% to which was added $NaBAr^F{}_4$ (1.1 mol%) and alkyne diol **14**. The reaction was monitored at regular intervals using $^1H$ NMR spectroscopy. Catalytic efficiency was established using the TOF ($h^{-1}$) calculated at the time of 50% conversion of substrate to product, as the amount of product formed per mole of catalyst per hour.



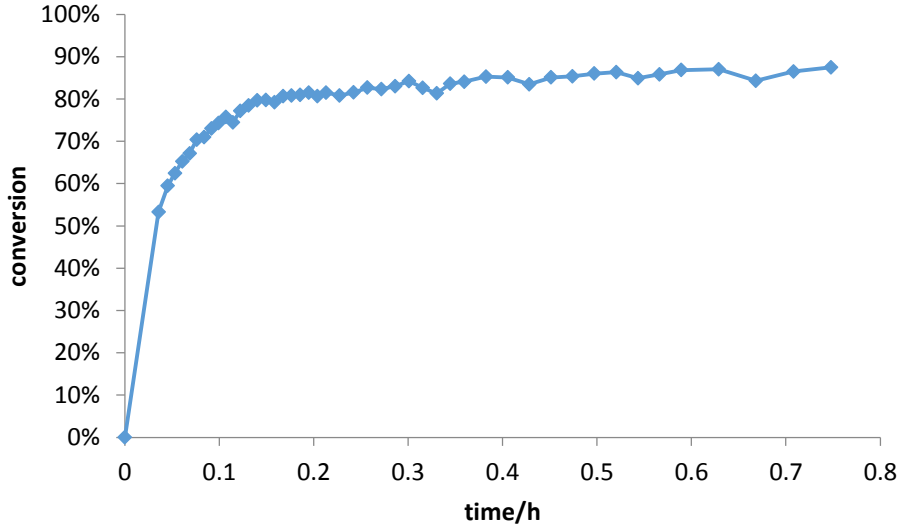
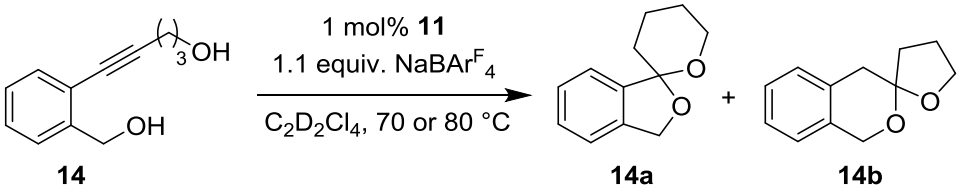




**Chart 4.1** Time course profile for the dihydroalkoxylation of **14** catalysed by **11** at 100 °C (equiv. = equivalent relative to catalyst).

The reaction of **14** catalysed by **11** at 100 °C achieves a high TOF of 1241 $h^{-1}$, however, there was a reduction of the rate of conversion after 0.2 h, with a maximum of 85% conversion reached. This suggested rapid decomposition of the Au(I) catalyst which was in

agreement with the physical observation of the formation of a purple precipitate/mixture indicative of the formation of gold nanoparticles. Navarro *et al.* reported similar findings using UV spectroscopy.[31] Reducing the temperature to 80 °C resulted in complete conversion of the dihydroalkoxylation and the reaction reaches > 98% conversion within two min. Formation of a purple mixture at this temperature was only observed after completion of reaction. Since the catalyst is highly active at 80 °C, monitoring of the organic transformation proved to be difficult and a further reduction in temperature to 70 °C was required to attain reliable kinetic data (Chart 4.2). The Au(I) catalyst **11** promoted full conversion of **14** after 12 min at 70 °C as shown in Chart 4.2.



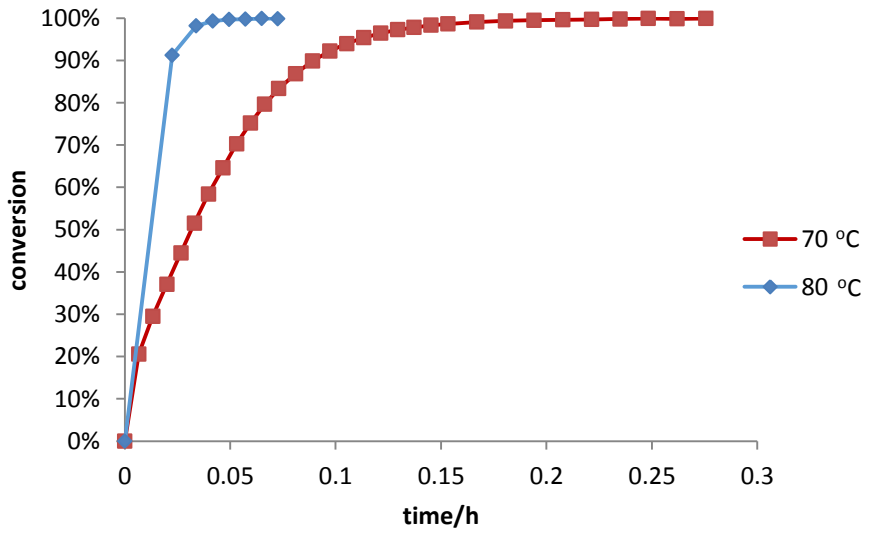




**Chart 4.2** Time course plots for the dihydroalkoxylation reaction of **14** catalysed by **11** at 70 °C and 80 °C. (equiv. = equivalent relative to catalyst).

Au(III) complex **12** was also investigated as a catalyst for the dihydroalkoxylation of alkyne diol **14**. Surprisingly, the Au(III) catalyst reached complete conversion of **14** to **14a** and **14b** by the time the first NMR spectra had been acquired (< 1 min) at 70 °C. Given the excellent activity of **12** at 70 °C, the temperature was lowered to ambient (25 °C) and the reactions repeated. Again the Au(III) complex **12** was found to be a more efficient catalyst than Au(I) complex **11**, with complexes **12** and **11** achieving complete conversion of **14** within 9.3 min and 145 min respectively (Table 4.2, entries 3 and 5, Chart 4.3). These gold(III) catalysed reactions at room temperature are the fastest reported for 2-(5-hydroxypent-1-ynyl)benzyl alcohol (**14**). [10b, 11a,]

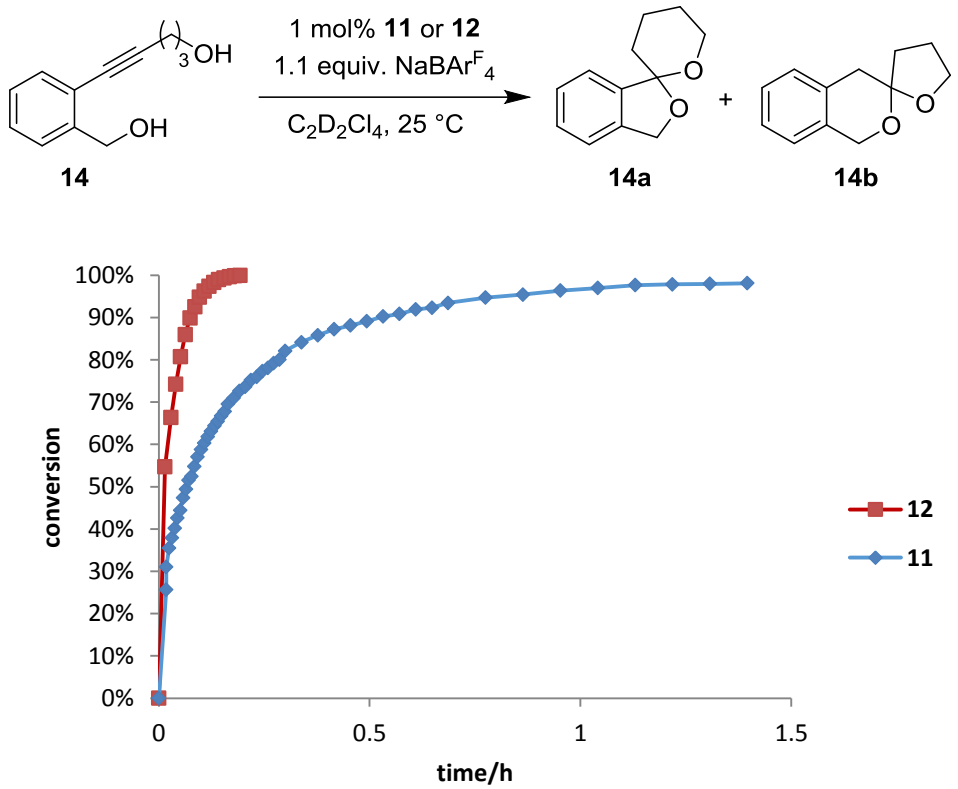
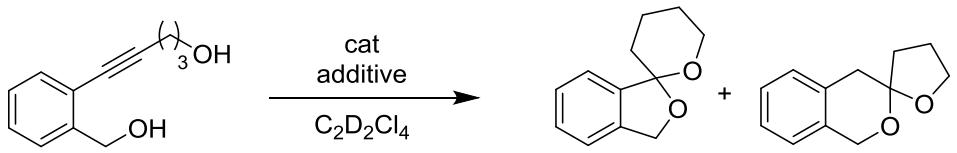



**Chart 4.3** Time course plots for the catalysed dihydroalkoxylation of **14** using **11** and **12** at 25 °C. (equiv. = equivalent relative to catalyst).

**Table 4.2** Comparison of Au(I) vs Au(III) catalysts and the effect of counterion. [a]Determined by $^1$H NMR spectroscopy. [b]Conversion refers to substrate to combined spiroketal products a and b. [c] Time taken to reach stated conversion.




**14** **14a** **14b**

| entry | catalyst | additive | temp, °C | conv, %[b] | time, min.[c] | TOF, $h^{-1}$ | TON |
|---|---|---|---|---|---|---|---|
| 1 | **11** (1 mol%) | $NaBAr^F_4$ (1.1 mol%) | 70 | >99 | 12 | >1600 | 99 |
| 2 | **12** (1 mol%) | $NaBAr^F_4$ (1.1 mol%) | 70 | >99 | <1 | >15000 | 99 |
| 3 | **11** (1 mol%) | $NaBAr^F_4$ (1.1 mol%) | 25 | 97 | 145 | >58 | 97 |
| 4 | **12**(1 mol%) | - | 25 | 98 | 67.8 | >800 | 98 |
| 5 | **12**(1 mol%) | $NaBAr^F_4$ (1.1 mol%) | 25 | >99 | 9.3 | >2100 | 99 |
| 6 | **12**(1 mol%) | $NaBAr^F_4$ (2.2 mol%) | 25 | >99 | 10.7 | >4400 | 99 |
| 7 | **12**(1 mol%) | $NaBAr^F_4$ (3.3 mol%) | 25 | >99 | 5 | >5200 | 99 |
| 8 | **12**(0.1 mol%) | $NaBAr^F_4$ (0.11 mol%) | 25 | 30 | 2.2 | - | 361 |
| 9 | **12**(0.01 mol%) | $NaBAr^F_4$ (0.011 mol%) | 25 | 10 | 3.3 | - | 1033 |
| 10 | **12**(1 mol%) | $AgSbF_6$ (1.1 mol%) | 25 | 93 | 39.9 | >2000 | 93 |
| 11 | **12**(0.1 mol%) | $AgSbF_6$ (0.11 mol%) | 25 | 0 | - | - | - |

### 4.4.2. Counterion dependence:

The impact of the amount of $NaBAr^F_4$ on reaction rate was also investigated (Table 4.2, entries 4-7) to establish the effect of displacing the strongly coordinating $Cl^-$ ions with a weakly coordinating counterion. Messerle *et al.* has shown that $NaBAr^F_4$ alone will not catalyse the dihydroalkoxylations of **14**.[10b,10c] However, as the amount of added $NaBAr^F_4$ was increased from 0 to 3.3 mol%, a marked improvement in the turnover rate was observed, Chart 4.4. A two-fold increase in TOF was observed for the reaction conducted using 2.2 mol% $NaBAr^F_4$ compared to that using 1.1 mol% $NaBAr^F_4$ additive (Table 4.2, entries 5 & 6). Furthermore, addition of 3.3 mol%. of $NaBAr^F_4$ increasingly enhanced the initial rate of the dihydroalkoxylation reaction. The steady enhancement in catalytic activity with

increasing $NaBAr^F_4$ concentrations for the conversion of **14** to **14a** and **14b** catalysed by **12** was attributed to the increasing substitution of the coordinated chloride ions in **12** by the weakly coordinating $BAr^F_4$ counter anion.

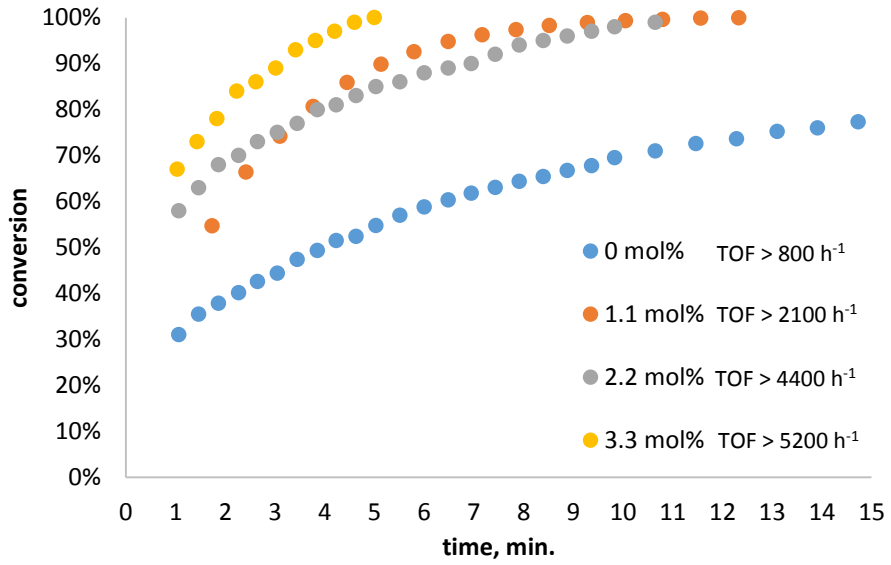
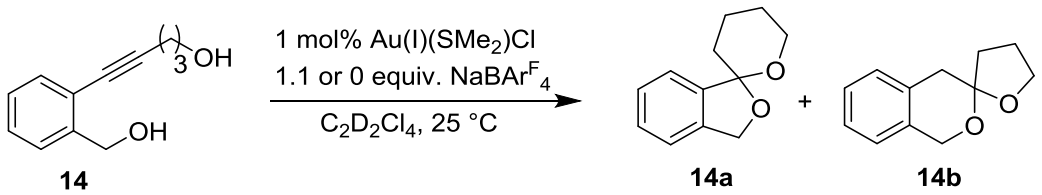



**Chart 4.4** Time course plots for varying quantity of $NaBAr^F_4$ additive, see Table 4.2, entries 4-7. Reaction conditions: pre-catalyst (1 mol%), 25 °C, $C_2D_2Cl_4$.

To assess if this enhanced reaction rate was due to any decomplexed metal present in solution, control reactions were performed using various gold salts at room temperature. $Au(SMe_2)Cl$ in the presence of $NaBAr^F_4$ gave quantitative conversion after 15.6 min, whereas $Au(SMe_2)Cl$ by itself gave a lower conversion (70%) after a much longer time (166 min). $HAuCl_4$ gave no reaction at room temperature, with or without $NaBAr^F_4$ present. Catalysis of similar reactions using the simple gold(I) and gold (III) salts has been reported in the literature.[32]



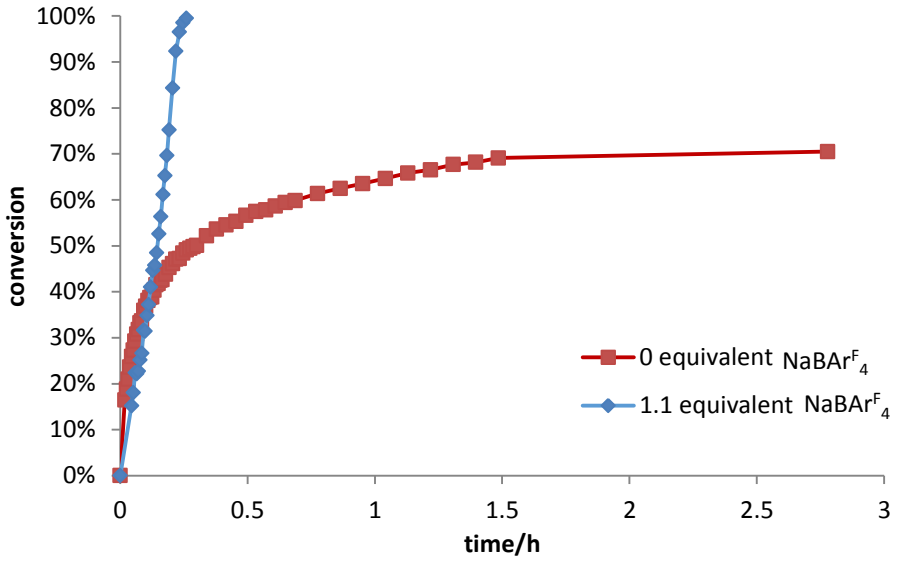




**Chart 4.5** Time course plots showing catalytic activity of Au(I)(SMe$_2$)Cl for the conversion of **14**. (equiv. = equivalent relative to catalyst).

It was interesting to note that the rate at which the gold(III) complex (**12**) catalysed the reaction was faster than any other reported analogous reaction, especially given the absence of catalytic activity using $HAuCl_4$. Gold complexes are well known to be the most active species for alkyne activation reactions, which are attributed to the metal's relativistic effects, high acidity and low oxyphillicity. However, the Au(III) complex **12** greatly outperforms the Au(I) counterpart **11** for the dihydroalkoxylation reaction of **14**. This is likely due to the increased Lewis acidity of the Au(III) metal centre in **12** compared to the Au(I) metal centre in **11** and the increased number of coordination sites available in **12** due to its square planar geometry, in comparison, **11** only contains one vacant coordination site due to its linear geometry. Only a few complexes in literature achieve high TOF values for

the dihydroalkoxylation reaction at lower temperatures (25 or 40 °C) and complete the reaction in a time scale of minutes. Hashmi *et al.* has reported the highest TOF values for the dihydroalkoxylation reaction, however, the reaction required 72 hours to achieve complete conversion.

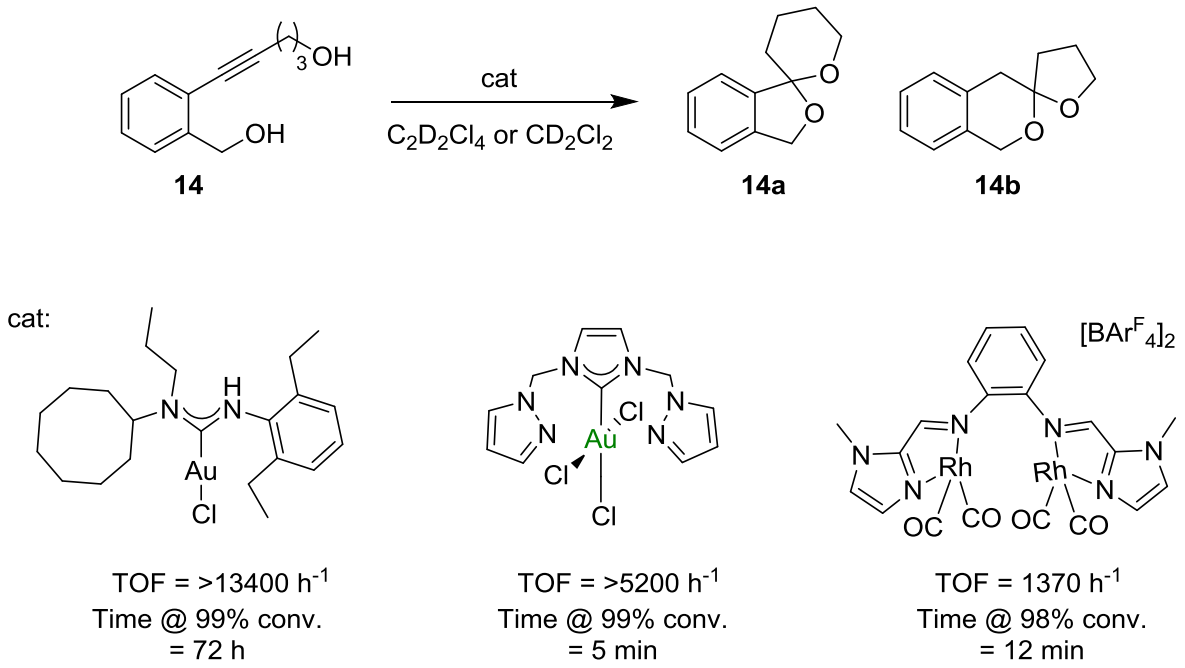



**Figure 4.6** Comparison in catalytic activity of **12** with complexes in literature. [11, 33]

### 4.4.3. Oxidation state:

To investigate if the Au(III) complex **12** catalysed reaction was strictly a gold(III) catalysed process and that no redox transformation between (I) and (III) oxidation states transpired , these catalysis reactions were monitored by UV/Vis spectroscopy (Chart 4.6 and Chart 4.7). The gold(I) complex **11** gave an absorption at 258 nm and gold(III) complex **12** gave a similar absorption at 258 nm with a second absorption appearing between 270 nm to 330 nm. Over time (>6 min) a broad absorption appeared in the gold(III) spectrum between 500 nm to 580 nm, indicative of a surface plasmon resonance, most likely caused by the formation

of nanoparticles.[34] No such peak appeared on using the gold(I) system (**11**), even after 40 min at 25 °C.

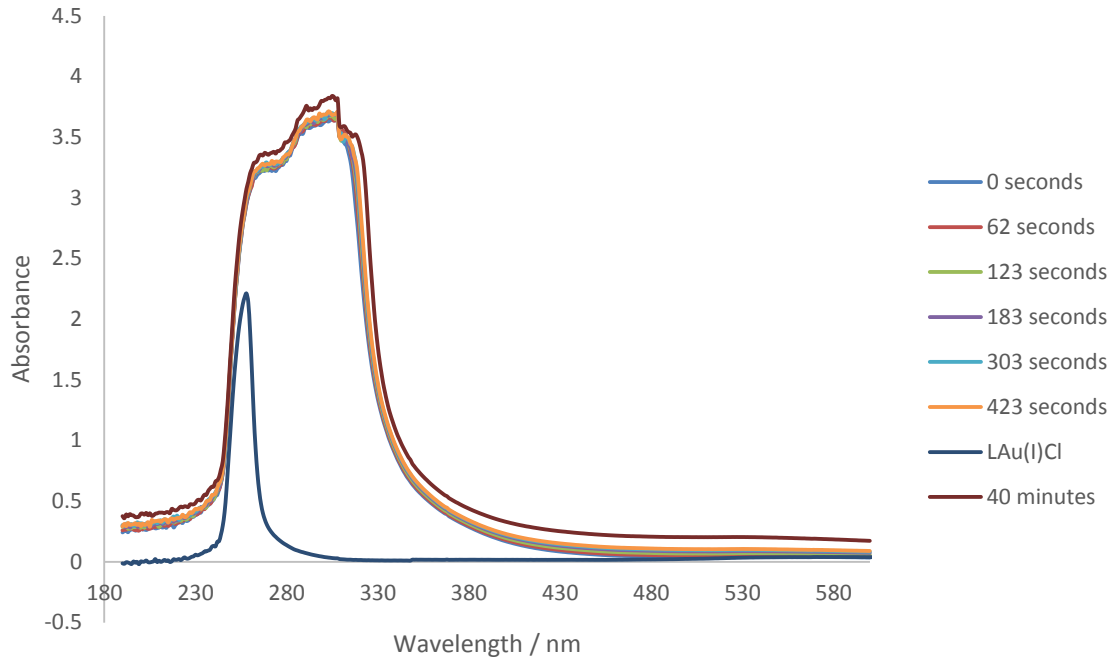



**Chart 4.6** UV/Vis Spectra for Au(I) (**11**) catalysed dihydroalkoxylation of **14**

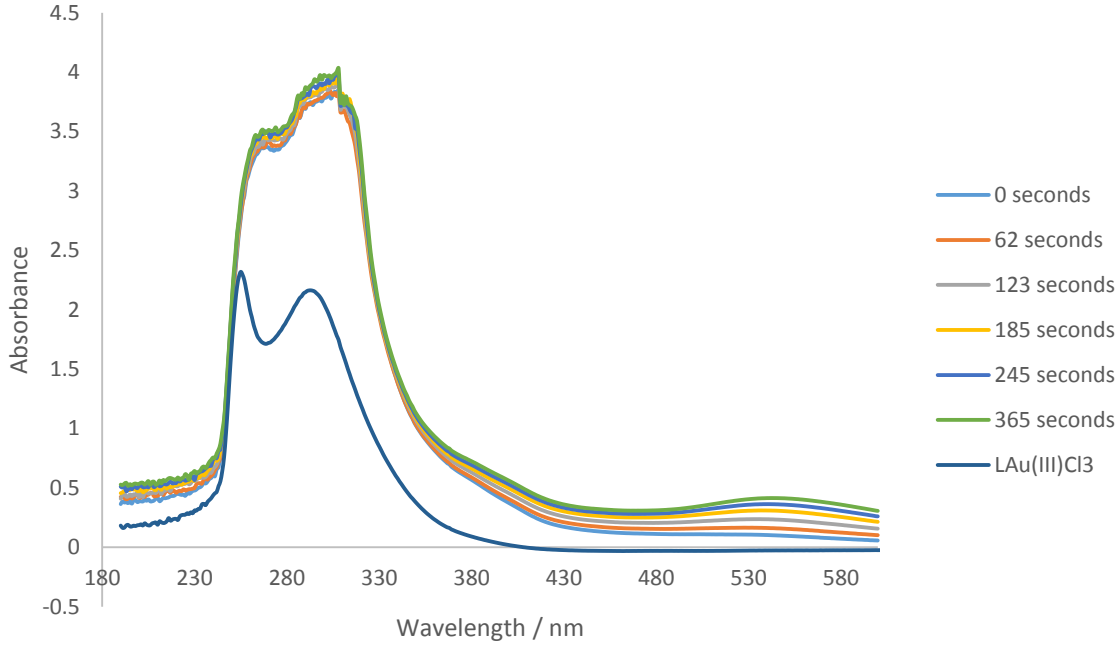



**Chart 4.7** UV/Vis Spectra for Au(III) (**12**) catalysed dihydroalkoxylation of **14**

These results indicate that the gold catalysts **11** and **12** decompose to a certain extent over time. Although both spectra look similar after 62 seconds, only the spectra of **12** shows bands at 380 nm and 500 to 580 nm regions. To rule out catalysis caused by nanoparticle formation, a mercury drop test was conducted, by adding mercury to the dihydroalkoxylation reactions catalysed by both the gold(I) and gold(III) catalysts **11** and **12** for substrate **14**; using the conditions stated in Table 4.2, (entries 3 and 5) and monitored by $^{1}$H NMR spectroscopy. In both cases the reactions reached the same conversions at the same times as those conducted in the absence of mercury (Table 4.2, entries 3 and 5). This confirmed that the catalytic activities observed were promoted by complexes **11** and **12** and not due to any nanoparticles that may have formed.

### 4.4.4. Catalyst loading dependence:

Encouraged by the results of the initial reactions and the control reactions, lower catalyst loadings of the gold(III) catalyst **12** were used to further investigate the dihydroalkoxylation reaction of **14** (Table 4.2, entries 8-11). Lowering the catalyst loadings to 0.1 mol% resulted in a significant decrease in catalytic activity, with the reaction progressing up to 30% conversion after 2.2 min (Table 4.2, entry 8). Further decreasing catalyst loading of **12** to 0.01 mol% resulted in a 10% conversion of **14** to **14a** and **14b** after 3.3 minutes. The time course plots show both reactions essentially plateau after the first NMR spectra were recorded (Chart 4.8). It would seem that the gold(III) catalyst **12** suffers from inhibition during reactions at these low catalyst loadings, possibly from either substrate or product binding.

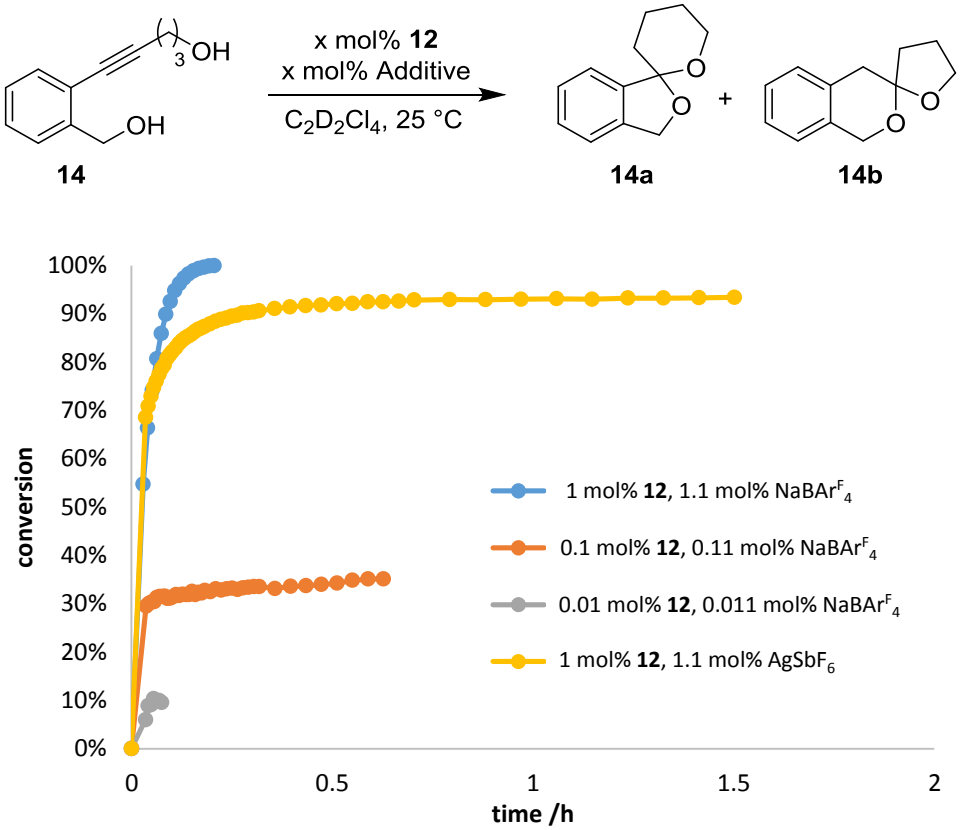



**Chart 4.8** Time vs conversion plots of the dihydroalkoxylation of **14** by **12** showing the effect of catalyst loading and counterion.

The role of the counterion proved to be vital for increasing catalytic activity, hence the dihydroalkoxylation reaction of **14** was examined using $SbF_6^-$ instead of $BAr^F{}_4^-$(Table 4.2, entries 10, 11). At 1 mol% of **12** the reaction proceeded to 93% conversion of **14** after almost 40 minutes, nearly four times slower than when using the $BAr^F{}_4^-$ counterion. Lowering the catalyst loading to 0.01 mol% whilst using $SbF_6^-$ as an additive gave no conversion to spiroketal products. These results would indicate that for the dihydroalkoxylation reaction of **14**, $BAr^F{}_4^-$ outperforms $SbF_6^-$. Screenings of other weakly coordinating anions were deemed unnecessary given the excellent performance of $BAr^F{}_4^-$.

### 4.4.5. Catalyst scope-investigating substrates with varying structure (15, 16)

To increase the scope of alkyne diols, substrates with different lengths of alkyl chain between the alkyne and the aliphatic alcohol were investigated. The substrate with the shorter alkyl chain 2-(4-hydroxybut-1-ynyl)benzyl alcohol (**15**) cyclised to give the 5,5-spiroketal product **15a** in a similar time (>99% conv., 15 min) to the reaction of **14** when using **12** as the catalyst (Chart 4.9). For comparison, the gold (I) catalyst **11** took almost two hours to reach quantitative conversion (96%) for the cyclisation of **14**. The use of $SbF_6^-$ as the counterion for catalyst **12** for the cyclisation of **15** also produced similar results compared to the catalysed reaction of **14** (Chart 4.10), which is consistent with the similarity in results observed for the two substrates when using $BAr^F{}_4^-$ as the counterion.

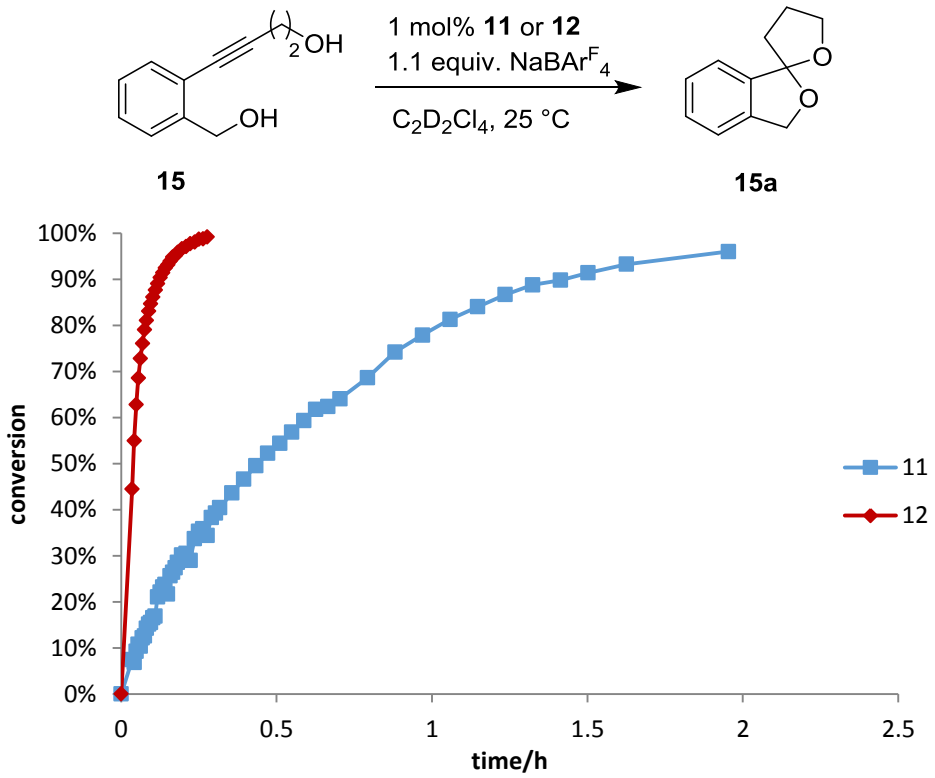
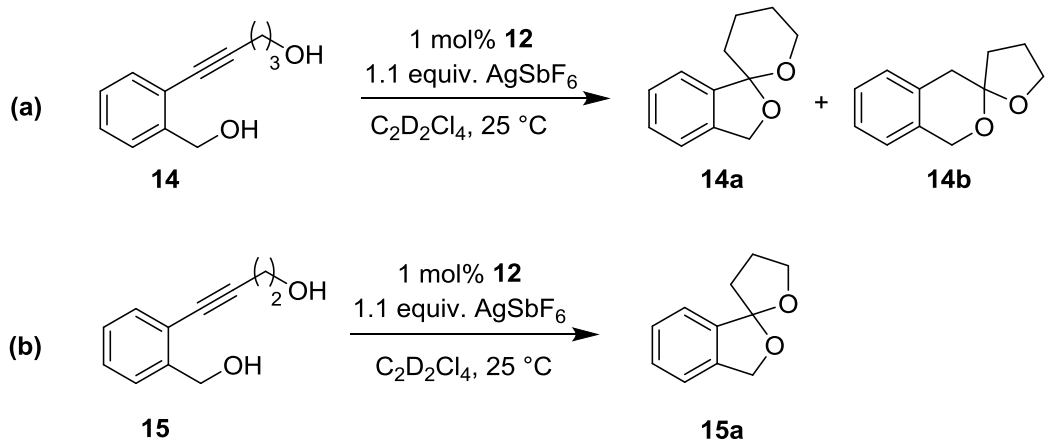



**Chart 4.9** Time vs conversion plots showing conversion of alkyne diol **15** catalysed by 1 mol% **11** and **12** at 25 °C. (equiv. = equivalent relative to catalyst).



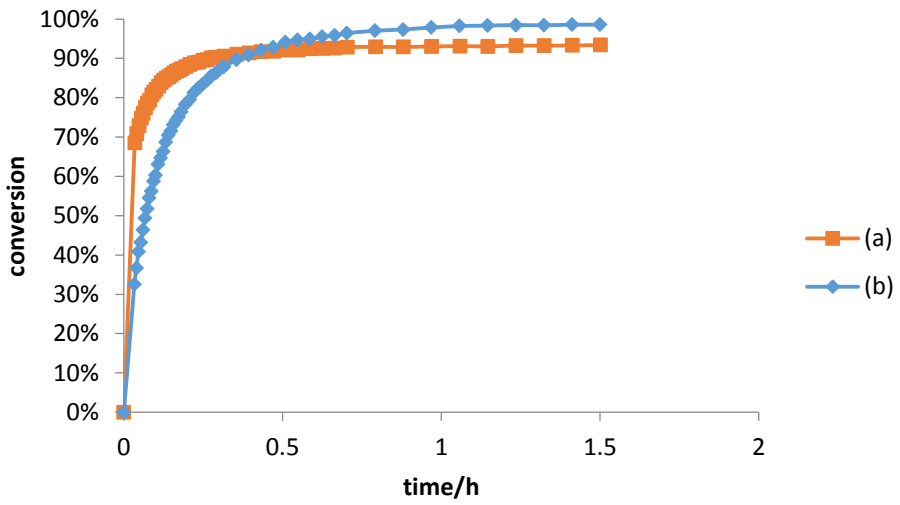
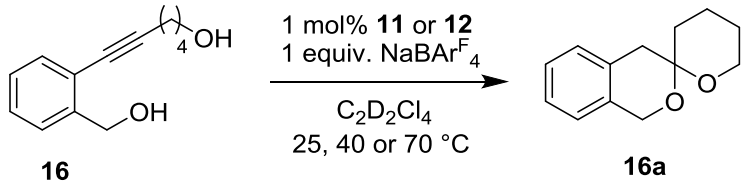




**Chart 4.10** Time vs conversion plots showing catalytic conversion of **14** and **15** using 1 mol% complex **12** and $SbF_6^-$ as counterion at 25 °C. (equiv. = equivalent relative to catalyst).

Catalysed dihydroalkoxylation of 2-(6-hydroxyhex-1-ynyl)benzyl alcohol (**16**) gave no conversion at room temperature in the presence of the gold(III) catalyst **12**, conversion of **16** was only achieved after heating to 40 °C. Catalyst decomposition was recorded to occur at elevated temperatures from previous experiments and the transformation reactions of **16** were carried out at 40 °C rather than 70 °C. The time course plot of the gold(III) catalyst **12** shows the first data point at 38% conversion to the 6,6-spiroketal product **16a**, and no further reaction beyond this point (Chart 4.11), indicating that the catalyst had likely

decomposed or become inhibited prior to the first NMR spectrum being recorded. No reaction was observed for the gold(I) analogue (**11**) catalysed reaction of **16** at either 25 °C or 40 °C.



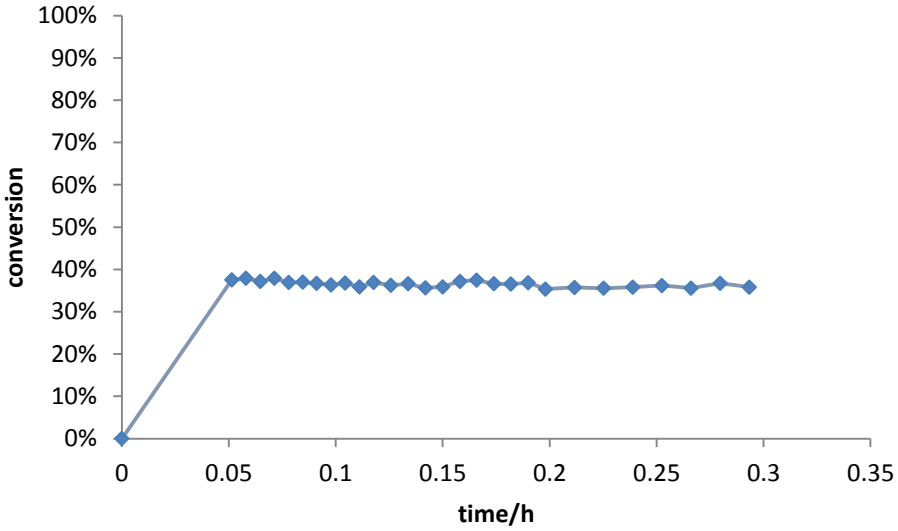




**Chart 4.11** Time vs conversion plot showing catalysis of the cyclisation of substrate **16** by 1 mol% complex **12** at 40 °C. (equiv. = equivalent relative to catalyst).

## 4.5. Catalysed hydroamination reactions using complexes 11 and 12.

Hydroamination reactions involve the addition of an N-H bond across an unsaturated C-C bond and are typically atom economical processes.[2,5] Alkynes usually react faster than alkenes due to less electron density in the C=C bond, and intramolecular cyclisation outpaces intermolecular reactions.[2] Having shown that gold complexes containing an *NCN*$^{Me}$ ligand proved to be excellent catalysts for dihydroalkoxylation reactions, we set out to investigate their activity as hydroamination catalysts.

### 4.5.1. Intramolecular hydroamination reactions catalysed by complexes 11 and 12.

Initially the catalytic activity of the intramolecular cyclisation of 4-pentyn-1-amine (**17**) to 2-methyl-1-pyrroline (**17a**) at room temperature was investigated using catalysts **11** and **12**. Given the typically slower progress of hydroamination reactions compared to the dihydroalkoxylation reactions, a catalyst loading of 2 mol% was used in toluene-$d_8$, and the reactions monitored using $^1$H NMR spectroscopy. Over the course of 90 minutes, the catalysed reactions of **17** progressed slowly and a conversion of 25% was reached when using the Au(III) catalyst **12** and a maximum of 18% was reached using the Au(I) catalyst **11** (Chart 4.12 and Chart 4.13). Heating the reaction to 70 °C saw the initial reaction rate accelerate, with conversion plateauing at 69% after 30 minutes using the Au(I) complex **11**. and 81% conversion using Au(III) complex **12** after 90 minutes. Increasing the temperature to 100 °C resulted in 97% conversion after 15 minutes using complex **12** and 93% conversion after 20 minutes using complex **11**.

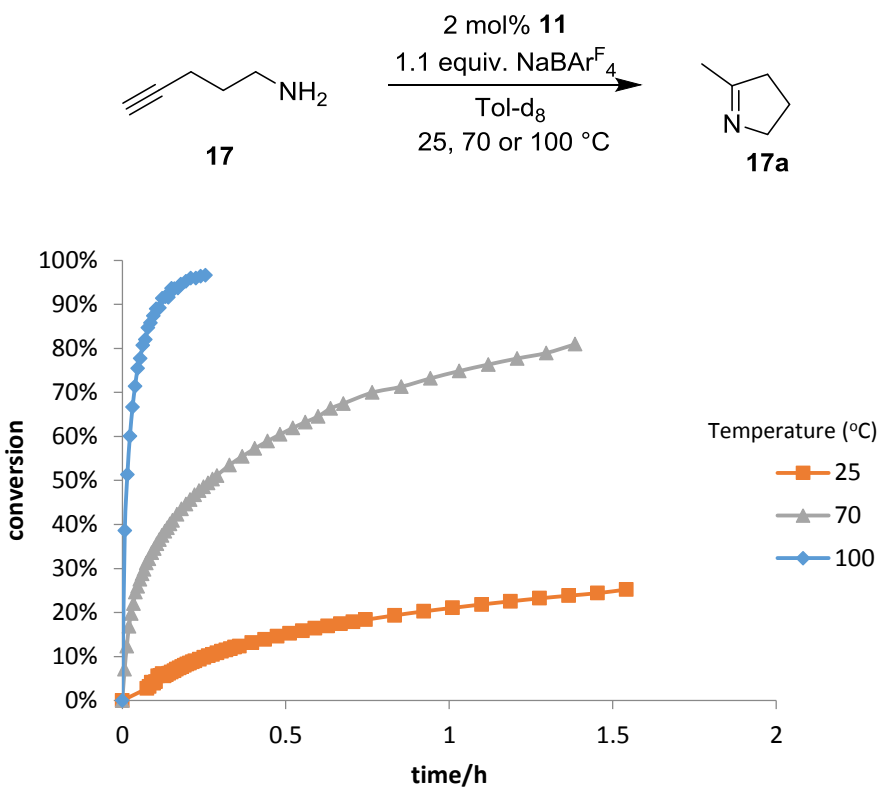
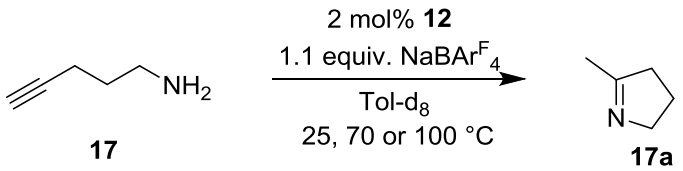



**Chart 4.12** % Time vs conversion plot for the hydroamination of **17** using 2 mol% of **11**. (equiv. = equivalent relative to catalyst).



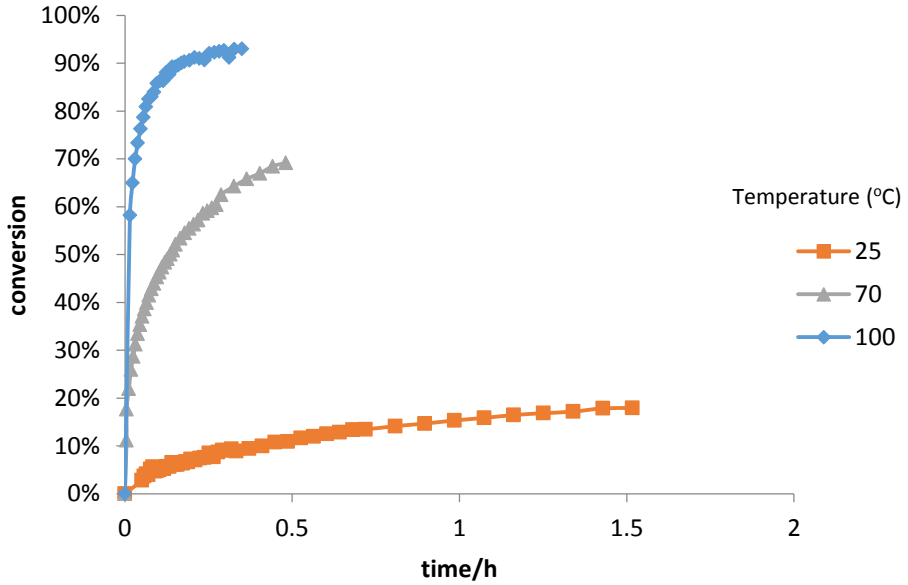
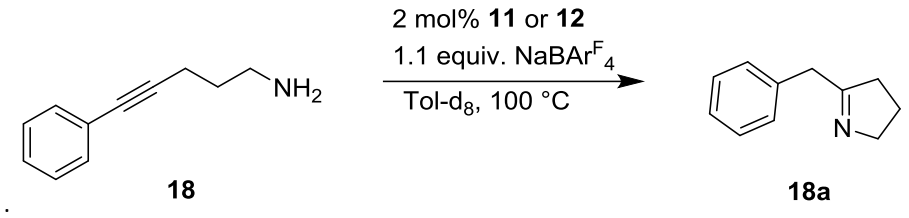




**Chart 4.13** % Time vs conversion plots showing hydroamination of **17** using **12.** (equiv. = equivalent relative to catalyst).

The efficiency of conversion of 5-phenyl-4-pentyn-1-amine (**18**) proved to be similar to that of **17** at 100 °C with quantitative conversions on using both gold catalysts after 24 minutes. The TOFs for 5-phenyl-4-pentyn-1-amine (**18**) proved to be about half that of the substrate possessing the terminal alkyne (**17**), confirming that addition to a terminal alkyne is faster than addition to an internal alkyne.



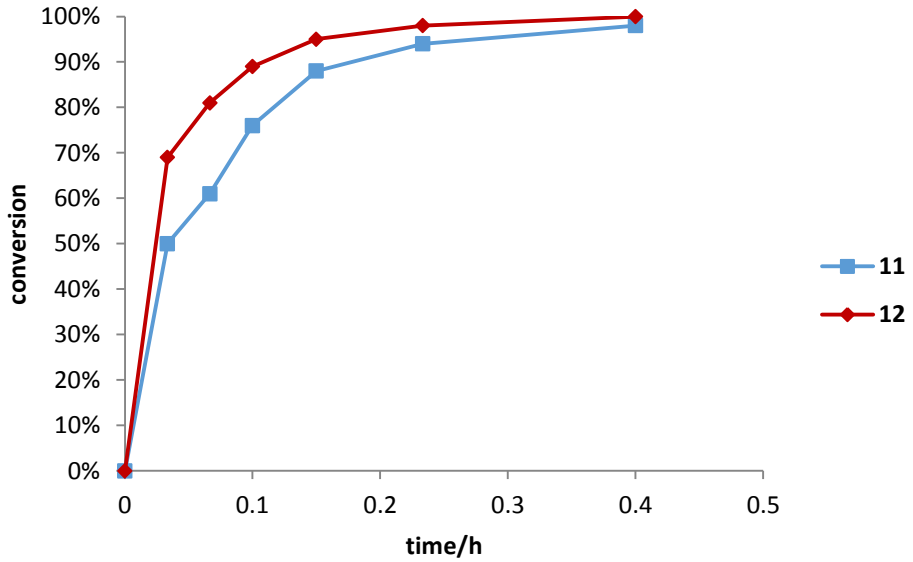
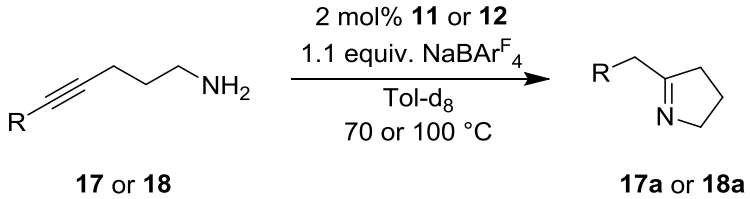




**Chart 4.14** Time course plots showing hydroamination of **18** at 100 °C using complexes **11**

**Table 4.3** Summary of intramolecular hydroamination reactions of **17** and **18** using complexes **11** and **12**. (equiv. = equivalent relative to catalyst).




| entry | R | catalyst | temp, °C | % conv(+/-0.5%). | time, min | TOF, $h^{-1}$ |
|---|---|---|---|---|---|---|
| 1 | H | **11** | 70 | 69 | 29 | 179 |
| 2 | H | **12** | 70 | 81 | 83 | 95 |
| 3 | H | **11** | 100 | 93 | 18 | 1952 |
| 4 | H | **12** | 100 | 97 | 15 | 1668 |
| 5 | Ph | **11** | 100 | 96 | 24 | 893 |
| 6 | Ph | **12** | 100 | 98 | 24 | 758 |

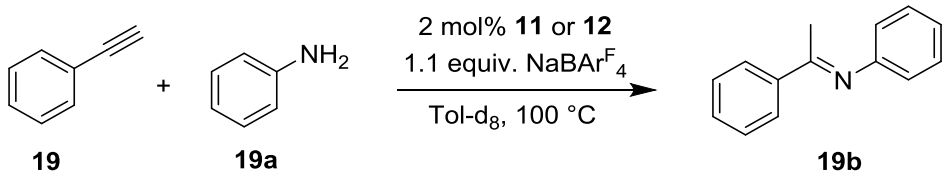
### 4.5.2. Intramolecular hydroamination of alkenes:

Alkenes are harder to cyclise than alkynes due to the potential inability of the alkyl gold species to undergo protodeauration,[35] though hydroamination reactions of alkenes are known despite reports that anilines and amines inhibit the reaction.[36] Routes to circumvent this have included using benzyl or carbobenzyloxy protected amines,[37] carboxamides,[38] ureas,[39] and sulphonamides.[40] As such, a reaction using a primary amine, specifically the cyclisation of 2,2-diphenyl-4-penten-1-amine to 3,3-diphenylpyrrolidine was investigated at 100 °C. Even after 48 hours there was no conversion observed as determined by $^{1}$H NMR spectroscopy for either gold catalysts **11** or **12**. Given the lack of reaction, further attempts at any other hydroaminations using alkene containing substrates were not carried out.

### 4.5.3. Intermolecular hydroamination reactions catalysed by complexes 11 and 12

Next, intermolecular hydroamination reactions were examined between phenylacetylene (**19**), pentyne (**20**) and aniline (**19a**) and benzylamine (**21**). These catalysed reactions were conducted in Tol-$d_8$ at 100 °C and monitored by $^{1}$H NMR spectroscopy. No conversion was observed for reactions involving substrates **20** and **21** catalysed by either **11** or **12**. However, hydroamination of phenylacetylene (**19**) and aniline (**19a**) gave 30% conversion to **19b** after 60 minutes using complexes **11** and 26% conversion using complex **12** after 20 minutes. Extended reaction times at 100 °C did not improve the conversions. Though, the initial rate of conversion was certainly faster than expected given the slower nature of intermolecular reactions compared to hydroalkoxylation reactions. Having previously encountered catalyst decomposition with **11** and **12** (observation of Au nanoparticles) at elevated temperatures, the same reaction of aniline (**19a**) with phenylacetylene (**19**) was attempted but at a lower

temperature of 70 °C. Au(I) complex **11** gave 28% conversion after 1 hour, Au(III) complex **12** producing 21% conversion after 1 hour. Upon leaving the reactions for 20 hours the % conversion only increased by a few % indicating the catalyst had decomposed. Given the partial success of reacting phenylacetylene (**19**) with aniline (**19a**), hydroamination of diphenylacetylene with aniline (**19a**) was attempted, however no reaction was observed.



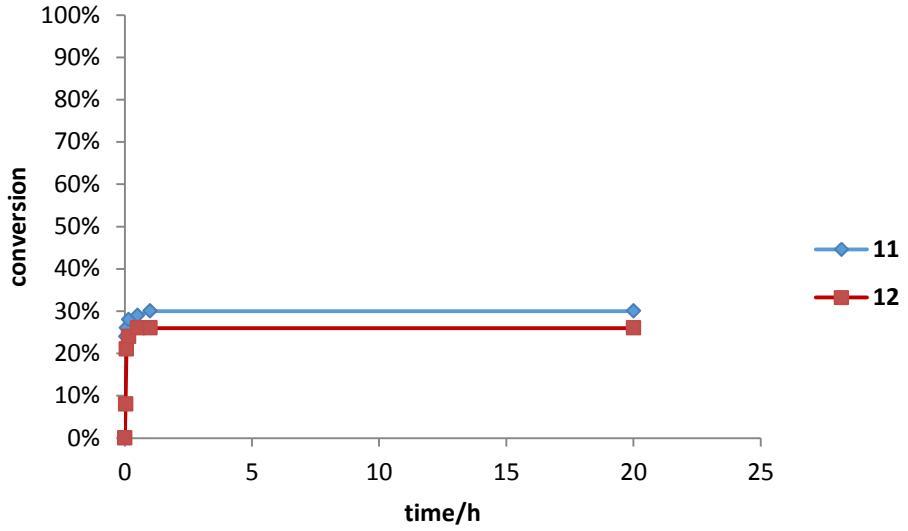




**Chart 4.15** Time course plot for the intermolecular hydroamination reaction of aniline (**19a**) and phenylacetylene (**19**) at 100 °C using complexes **11** and **12**. (equiv. = equivalent relative to catalyst).

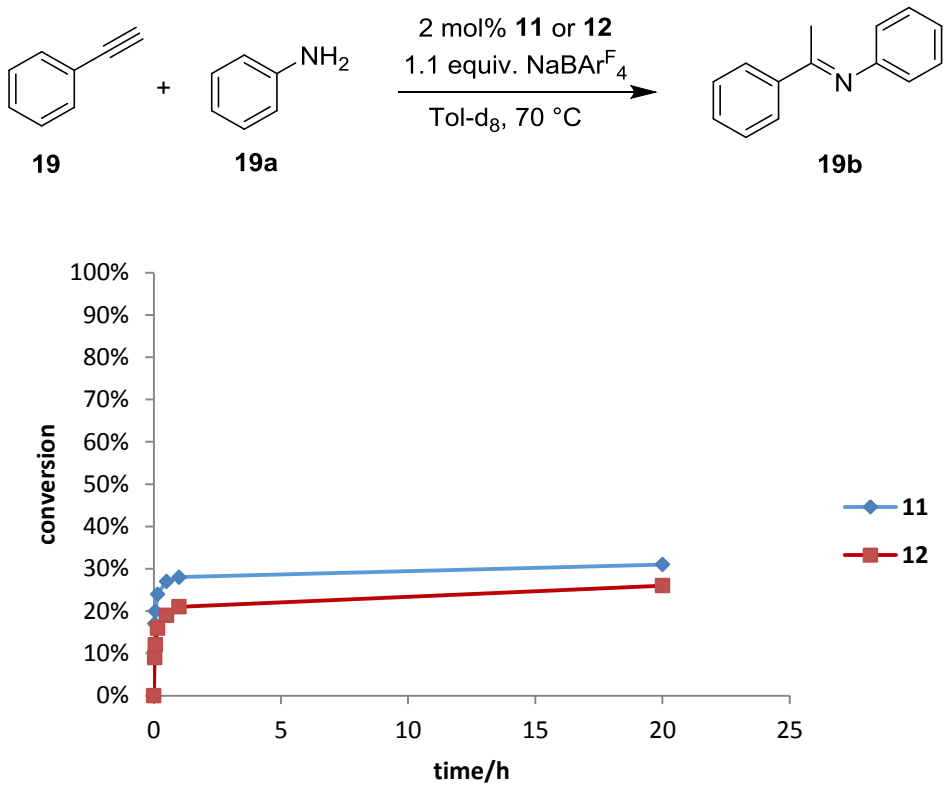



**Chart 4.16** Time course plot for the intermolecular hydroamination reaction of aniline (**19a**) and phenylacetylene (**19**) at 70 °C using complexes **11** and **12**. (equiv. = equivalent relative to catalyst).

## 4.6. Conclusions

Gold complexes consisting of oxidation states I and III were synthesised and characterised.

It was found that a simple NHC-based gold(III) complex **12** was not only significantly faster than its gold(I) analogue, it is the fastest system reported to date at room temperature for the dihydroalkoxylation reaction of alkynyl diols under mild conditions. The next fastest system in literature are Rh(I) complexes containing bidentate imine ligands. [32, 34]

Control experiments proved that the dihydroalkoxylation reactions of alkynyl diols were gold(III)-catalysed processes, with no competing off-ligand reaction or contribution from gold nanoparticles.

Intramolecular hydroamination reactions of alkynes and alkenes were also studied with both catalysts performing well for the reaction with alkynes, achieving excellent conversions in less than 30 min, which places them on par with our previously reported catalysts.

Disappointingly, only one intermolecular hydroamination of aniline with phenylacetylene was found to proceed albeit in low conversion.

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# Chapter 5. Conclusions and Future work

## 5.1. Conclusions

### 5.1.1. Chapter 2

A series of novel Ag(I) and Ru(II) complexes containing pincer imidazolyl-pyrazole ligands were synthesised and characterised. Complexes [Ag($NCN^{Me}$)$_2$]BPh$_4$ (**2**), [Ru($NCN^{Me}$)$_2$](BPh$_4$)$_2$ (**6**), [Ru(H)CO($NCN^{Me}$)(PPh$_3$)$_2$]BPh$_4$ (**5a**), [Ru(H)CO($NCN^{Me}$)(PPh$_3$)$_2$]BPh$_4$ (**5**), [Ru($\eta^6$-C$_6$H$_6$)($NCN^{Me}$)Cl]BPh$_4$ (**3**), [Ru($\eta^6$-C$_{10}$H$_{14}$)($NCN^{Me}$)Cl]BPh$_4$.[B$_5$O$_6$(OH)$_4$] (**4a**), [Ru($\eta^6$-C$_{10}$H$_{14}$)($NCN^{Me}$)Cl]BPh$_4$ (**4**) were prepared in moderate yields.

- The solid state structures of ligands and complexes ($NCN^{Me}$)BPh$_4$ (**1a**), ($NCN^{Et}$)BPh$_4$ (**1c**), [Ag($NCN^{Me}$)$_2$]BPh$_4$ (**2**), [Ru($NCN^{Me}$)$_2$](BPh$_4$)$_2$ (**7**), [Ru(H)CO($NCN^{ME}$)(PPh$_3$)$_2$]BPh$_4$ (**5a**), [Ru($\eta^6$-C$_6$H$_6$)($NCN^{Me}$)Cl]BPh$_4$ (**3**), [Ru($\eta^6$-C$_{10}$H$_{14}$)($NCN^{Me}$)Cl]BPh$_4$[B$_5$O$_6$(OH)$_4$] (**4a**) were obtained using X-ray crystal structure analyses. Complex (**2**) showed the expected linear geometry for a Ag(I) metal centre. The Ru(II) complex (**6**) shows an octahedral geometry with a bis-tridentate coordination of ligand (**1**) about the metal centre, whereas complexes (**5a**), (**3**) and (**4a**) consist of a bidentate coordination of the ligand to the metal centre. Complexes (**3**) and (**5a**) adopt a pseudo-octahedral geometry as expected for Ru(II) complexes containing a $\eta^6$ arene ring.
- X-ray crystal structure analysis of [Ru($\eta^6$-C$_{10}$H$_{14}$)($NCN^{Me}$)Cl]BPh$_4$[B$_5$O$_6$(OH)$_4$] (**4a**) revealed the presence of a rare boronic counterion [B$_5$O$_6$(OH)$_4$]$^-$. Initial attempts in the synthesis of [Ru(H)CO($NCN^{Me}$)(PPh$_3$)$_2$]BPh$_4$ (**5a**) using the silver transmetallation route resulted in the formation of a new Ru(I) cubane complex [RuCl(PPh$_3$)]$_4$ which could only be identified using X-ray crystal structure analysis.

- The Ru(II) complexes $[Ru(NCN^{Me})_2](BPh_4)_2$ (**7**), $[Ru(H)CO(NCN^{Me})(PPh_3)_2]BPh_4$ (**5a**), $[Ru(H)CO(NCN^{Me})(PPh_3)_2]BPh_4$ (**5**), $[Ru(\eta^6\text{-}C_6H_6)(NCN^{Me})Cl]BPh_4$ (**3**), $[Ru(\eta^6\text{-}C_{10}H_{14})(NCN^{Me})Cl]BPh_4[B_5O_6(OH)_4]$ (**4a**), $[Ru(\eta^6\text{-}C_{10}H_{14})(NCN^{Me})Cl]BPh_4$ (**4**) were tested as catalysts for the transfer hydrogenation reaction of acetophenone. Complexes containing arene co-ligands $[Ru(\eta^6\text{-}C_6H_6)(NCN^{Me})Cl]BPh_4$ (**3**), $[Ru(\eta^6\text{-}C_{10}H_{14})(NCN^{Me})Cl]BPh_4[B_5O_6(OH)_4]$ (**4a**), $[Ru(\eta^6\text{-}C_{10}H_{14})(NCN^{Me})Cl]BPh_4$ (**4**) were found to be more active catalysts for the organic transformation with $[Ru(\eta^6\text{-}C_{10}H_{14})(NCN^{Me})Cl]BPh_4[B_5O_6(OH)_4]$ (**4a**) exhibiting the best activity.
- To investigate the scope of the catalyzed transfer hydrogenation, $[Ru(\eta^6\text{-}C_{10}H_{14})(NCN^{Me})Cl]BPh_4[B_5O_6(OH)_4]$ (**4a**) and $[Ru(\eta^6\text{-}C_{10}H_{14})(NCN^{Me})Cl]BPh_4$ (**4**) were used as catalysts for the transfer hydrogenation reaction of a number of substrates. The complexes promoted complete conversions of all substrates in short reaction times (< 1hr). $[Ru(\eta^6\text{-}C_{10}H_{14})(NCN^{Me})Cl]BPh_4[B_5O_6(OH)_4]$ (**4a**) was also found to be active for the organic transformation at room temperature conditions.

A series of coordination motifs were observed for the Ru(II) and Ag(I) complexes in solid state, ranging from a fully saturated tridentate Ru(II) dimer to a mono-dentate Ag(I) dimer. Crystallographic analysis unexpectedly revealed a rare pentaborate anion for complex **4a**. This mixed anion complex was found to be the most active catalyst for the transfer hydrogenation reaction among the Ru(II) catalysts suggesting the petaborate anion enhances catalytic activity. Most probably, the complex catalyses the transfer hydrogenations via a separate mechanism from the organometallic catalyst. The mixture containing the pentaborate anion was also found to be the only active catalyst for the transfer hydrogenation reaction at room temperature conditions.

### 5.1.2. Chapter 3

A series of novel Ni(II) complexes containing pincer imidazolyl-pyrazole ligands were synthesised and characterised. Complexes [Ni(*NCN*$^{Me}$)Cl]$BPh_4$ (**8**), [Ni(*NCN*$^{Me}$)Cl]$PF_6$ (**9**) and [Ni(*NCN*$^{Et}$)$_2$]$(BPh_4)_2$ (**10**) were prepared in moderate yields.

- The solid state structures of complexes [Ni(*NCN*$^{Me}$)Cl]$BPh_4$ (**8**), [Ni(*NCN*$^{Me}$)Cl]$PF_6$ (**9**) and [Ni(*NCN*$^{Me}$)$^{Et}_2$]$(BPh_4)_2$ (**10**) were obtained using X-ray crystal structure analyses. All complexes showed the expected square planar geometry about the metal centre and were symmetrical in structure. Complexes (**8**) and (**9**) consisted of a single pincer ligand **1a** engaged in tridentate coordination to the metal centre, whereas complex (**10**) displayed a bis-bidentate coordination of ligand **1c** to the Ni(II) metal.
- Analysis using UV spectroscopy and variable temperature NMR spectroscopy revealed that the Ni(II) complexes were diamagnetic in nature and that the broad spectra at room temperature conditions resulted from changes in conformation due to the flexible nature of the ligands.
- The Ni(II) complexes [Ni(*NCN*$^{Me}$)Cl]$BPh_4$ (**8**), [Ni(*NCN*$^{Me}$)Cl]$PF_6$ (**9**) and [Ni(*NCN*$^{Et}$)$_2$]$(BPh_4)_2$ (**10**) were tested as catalysts for the Kumada cross coupling reaction of aryl halides.
- Changing the counterion from $BPh_4^-$ to $PF_6^-$ resulted in reduced selectivity for the chlorinated substrate chlorobenzene and different catalytic rates for the Kumada cross coupling reaction of bromobenzene and phenylmagnesium bromide.
- Reduction in catalytic loading resulted in reduced activity of complex **8** for the conversion of chlorobenzene whereas reduction in catalyst loading had an insignificant effect on the final catalytic conversion of bromobenzene.

The choice of ligand used affected the coordination modes observed for the Ni(II) complexes. Use of an *NCN*$^{Me}$ pincer ligand **1c** with longer linker arms between pyrazole and imidazole groups resulted in a bidentate coordination (**10**) whereas a shorter linker arm produced a tridentate coordination mode of the ligand to the Ni(II) metal centre (**8** and **9**). Complex **8** containing the pincer geometry was found to be the most active catalyst for the Kumada cross coupling reaction in comparison to complexes **9** and **10**. The coordinatively saturated complex **10** was found to be nearly inactive for the organic transformation and any conversion attained was attributed to the lability of the pyrazole arms. Complex **8** catalysed the Kumada cross coupling reaction for a wide range of substrates with higher activities achieved for substrates with electronegative substituents. The investigation showed that the catalytic activity was dependent on the type of substituents present on the aryl substrates.

### 5.1.3. Chapter 4

A series of new Au(I) and Au(III) complexes containing pincer imidazolyl-pyrazole (*NCN*$^{Me}$) ligands were synthesised and characterised. Complexes [Au(I)(*NCN*$^{Me}$)Cl] (**11**) and [Au(III)(*NCN*$^{Me}$)$Cl_3$] (**12**) were prepared in moderate yields.

- The solid state structures of complexes [Au(I)(*NCN*$^{Me}$)Cl] (**11**) and [Au(III)(*NCN*$^{Me}$)$Cl_3$] (**12**) were obtained using X-ray crystal structure analyses. Complex (**11**) showed a linear geometry typical of an Au(I) complex with monodentate coordination of ligand **1** to the gold metal centre. Complex (**12**) shows a square planar geometry as expected for an Au(III) complex with monodentate coordination of the ligand to the metal and three Cl co-ligands occupying the remaining coordination sites.

- The oxidation sates and properties of the complexes were further determined using UV spectroscopy
- Complexes [Au(I)($NCN^{Me}$)Cl] (**11**) and [Au(III)($NCN^{Me}$)$Cl_3$] (**12**) were tested as catalysts for the intramolecular dihydroalkoxylation reactions. Both complexes were highly active for the organic transformation with complex (**12**) showing excellent activity at very high TOF values even at room temperature conditions.
- Intramolecular and intermolecular hydroamination reactions were then tested using both complexes. Complexes (**11**) and (**12**) proved to be highly active for the intramolecular hydroamination reactions of pentyn-4-amine and phenylpentynamine and achieved moderate conversions for the intermolecuar hydroamination reactions of aniline with phenylacetylene.

Unlike the Ru(II) and Ni(II) complexes containing weakly coordinating counterions, both the Au(I) and Au(III) complexes **11** and **12** were found to be neutral in nature with terminally bound chlorine atoms balancing the positive charge of the Au metal centres. The Au(III) complex **12** was found to be more active than its Au(I) analogue **11** for the intramolecular dihydroalkoxylation reaction and was attributed to the increased lewis acidity of Au(III). It was found that the simple NHC-based gold(III) complex **12** is the fastest system reported to date at room temperature for the dihydroalkoxylation reaction of alkynyl diols under mild conditions.

## 5.2. Future work

### Chapter 2:

This chapter has shown that Ru(II) complexes bearing the imidazolyl-pyrazolyl *NCN*$^{Me}$ pincer ligands and $\eta^6$ arene co-ligands are highly active catalysts for the transfer hydrogenation reaction of ketones and that the presence of a boronate counterion $[B_5O_6(OH)_4]^-$ can enhance catalytic activity. However, this requires further investigation to understand the systems' effect on catalytic activity as follows:

- Repeating the catalytic reactions using the Ru(II) complexes with addition of catalytic amounts of boronic acids and testing whether all reactions can be performed under room temperature conditions.
- Utilising a simple salt of $[B_5O_6(OH)_4]^-$ to synthesise complexes containing only the boronate counteranion and investigating the catalytic activity of the complexes for different organic transformations.
- Synthesising new pincer ligands containing a boronate pendant arm and investigating the coordination chemistry of the new ligand to Ru(II) metal and examine the catalytic activity of the resulting complexes for the transfer hydrogenation reaction.

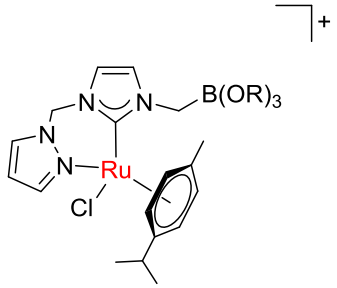



**Figure 5.1** Ru(II) complex bearing a ligand with a boronate pendant arm.

Chapter 3:

Ni(II) complexes bearing the *NCN* pincer ligands were shown to have unusual activity for the Kumada cross coupling reactions. Complex (**8**) showed higher activity for chlorinated substrates in comparison to brominated counterparts. The complex also showed highly selectivity for disubstituted substrates. Further investigation on the catalytic activity of **8** for selected chlorinated, brominated and hetero-disubstituted substrates can reveal important information:

- Perform the catalysed Kumada cross coupling reaction of hetero-halo-disubstituted substrates using complex (**8**) to evaluate the level of selectivity of the Ni(II) complexes for the different halogen functional groups.
- The Ni(II) complexes were found to be air and moisture stable and can therefore be useful in other organic transformations which do not require rigorous air sensitive manipulations.i.e. Initial testing of complex **8** as a catalyst for the Suzuki-Miyura cross coupling reactions in the presence of air and moisture.

Chapter 4:

This chapter has demonstrated that Au(I) and Au(III) complexes containing imidazolyl-pyrazolyl pincer ligands are highly active catalysts for intramolecular dihydrolkoxylation and hydroamination reactions. The Au(III) complex (**12**) achieves extremely high TOF values and remains highly active at room temperature conditions. However, the stability of the complex degrades overtime under catalytic conditions. Achieving bimetallic coordination by the ligand also proved to be difficult. Future work would include:

- Isolation of Au(III) complexes containing a true pincer coordination could be useful for increased stability and elongated catalytic activity. A pincer coordination of the ligand to the metal centre will result in increased thermal and catalytic stability of the complex.
- Investigation of the coordination chemistry of the pincer ligand **1c** containing the longer ethylene linker arms could prove to be useful as the flexible coordination and increased distance between the metal centres may stabilise the bimetallic complex. The bimetallic complexes should be tested as catalysts for tandem reactions where each metal could selectively catalyse a specific organic transformation.

# Chapter 6. Experimental

## General Procedures

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques or in a nitrogen or argon filled glovebox unless otherwise stated. Imidazolium ligand **1** was prepared according to a literature method.[1] $RuHCl(CO)(PPh_3)_3$,[3] $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$[2] and $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$[2] were prepared according to literature procedures.[2, 3] Commercially available reagents were purchased from Sigma-Aldrich or Alfa Aesar Inc. and used as received. $CH_2Cl_2$ and $CH_3CN$ were dried on a solvent purification system and used as dispensed. Propan-2-ol and methanol were freshly distilled from calcium hydride and THF was freshly distilled using a sodium mirror.

$^1H$, $^{13}C$, $^{13}C\{^1H\}$ and $^{31}P$ NMR spectra were recorded on Bruker DPX300, DMX500 and DMX400 spectrometers. Chemical shifts (δ) are quoted in ppm and coupling constants (*J*) are given in Hz (+/- 0.5 Hz). $^1H$, $^{13}C$ and $^{31}P$ NMR chemical shifts were referenced internally to residual solvent resonances. All NMR data was acquired and processed using TopSpin™ version 3.2 from Bruker NMR software.[4]

Mass spectra were acquired using a Thermo Scientific LCQ Fleet (ESI-MS) mass spectrometer, or using a Thermo Scientific LTQ Orbitrap XL instrument at the Bioanalytical Mass Spectrometry Facility at UNSW. 'M' is defined as the molecular weight of the compound or cationic fragment of interest.

IR spectra were recorded as KBr discs using an Avatar 370 FTIR (resolution = 1 $cm^{-1}$) spectrometer at the University of New South Wales. Elemental analyses were carried out at the Campbell Microanalytical Labaoratory, University of Otago, New Zealand,

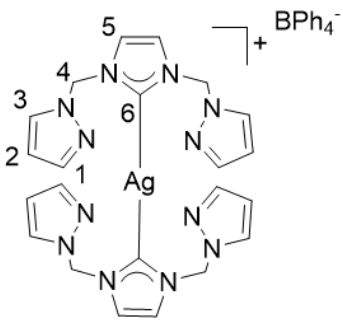
Elemental Analysis Unit, The Research School of Chemistry, Australian National University and the Elemental Microanalysis Service at the Department of Chemistry and Biomolecular Sciences, Macquarie University.

Single crystal X-ray analyses were carried out at the Mark Wainwright Analytical Centre, University of New South Wales, Sydney. X-ray diffraction measurements were recorded on a Bruker Kappa APEXII CCD diffractometer using graphite-monochromated Mo-Kα radiation (λ= 0.710723 Å). All structures were solved by direct methods and the full-matrix least-square refinements were carried out using SHELXL. Absorption correction was performed using Multi-scan SADABS and H-atom parameters were treated as constrained. CCDC 1480997 – 1481002 contains supplementary X-ray crystallographic data for complexes **2**, **3**, **4a**, **5** and **7**. The yields of hydrogenation products were determined using GCMS - QP2010 ULTRA.

## 6.1. Experimental for Chapter 2

### 6.1.1. Synthesis of Ag(I) and Ru(II) complexes

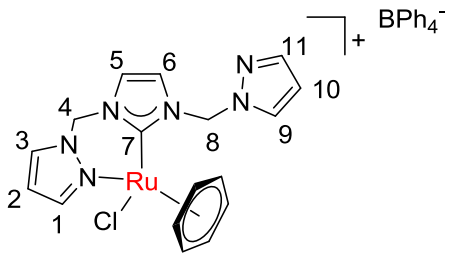
#### Synthesis of $[Ag(NCN^{Me})_2]BPh_4$ (2)




The imidazolium salt $(NCN^{Me})BPh_4$ (**1**) (0.155 g, 0.287 mmol) and $Ag_2O$ (0.090 g, 0.388 mmol) were suspended in 20 mL of dry $CH_2Cl_2$. The suspension was stirred for 16 hours at room temperature. The colourless solution was filtered using glass fibre (GF/C) filter paper and the solvent removed under vacuum yielding a white precipitate.

Yield: 81%. Single crystals were grown by vapour diffusion of pentane into saturated $CH_2Cl_2$ solution of complex **2**. $^1$H NMR (300 MHz, $CD_2Cl_2$): $\delta$ 7.73 (d, $^3J_{H1-H2}$ = 2.4 Hz, 4H, **H**1), 7.58 (d, $^3J_{H3-H2}$ = 1.8 Hz, 4H, **H**3), 7.38 (m, 8H, *o*-$BPh_4$), 7.20 (s, 4H, **H**5), 6.98 (t, $^3J_{H-H}$ = 7.0 Hz, 8H, *m*-$BPh_4$), 6.89 (t, $^3J_{H-H}$ = 7.2 Hz, 4H, *p*-$BPh_4$), 6.38 (dd, $^3J_{H2-H3}$/ $^3J_{H2-H1}$ = 2.1 Hz, 4H, **H**2), 6.36 (s, 8H, **H**4) ppm. $^{13}$C NMR (75 MHz, $CD_2Cl_2$): $\delta$ 183.9 (**C**6, identified through HMBC), 141.9 (**C**1), 136.3 (*o*-**C** of $BPh_4$), 130.5 (**C**3), 126.1 (*m*-**C** of $BPh_4$), 122.3 (*p*-**C** of $BPh_4$), 122.2 (**C**5), 108.1 (**C**2), 65.3 (**C**4) ppm.

#### Synthesis of $[Ru(\eta^6\text{-}C_6H_6)(NCN)Cl]BPh_4$ (3)

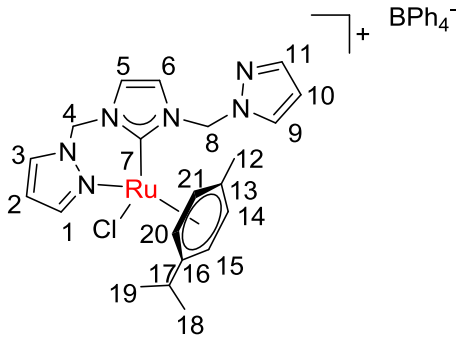



$[Ag(NCN^{Me})_2]BPh_4$ (**2**) (0.060 g, 0.068 mmol) and $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ (0.034 g, 0.068 mmol) were dissolved in 20 mL of $CH_2Cl_2$. The mixture was stirred overnight at room temperature under an atmosphere of argon. The resulting yellow mixture was filtered and pentane (40 mL)

was slowly added to the filtrate resulting in the precipitation of the complex [Ru($\eta^6$-$C_6H_6$)(*NCN*$^{Me}$)Cl]$BPh_4$ (**3**) as a yellow powder.

Yield: 48%. Single crystals were grown by slow evaporation of a saturated methanol solution of **3**. $^1$H NMR (300 MHz, $(CD_3)_2CO$): $\delta$ 8.19 (d, $^3J_{H1-H2}$ = 2.2 Hz, 1H, **H**1), 8.16 (d, $^3J_{H11-H10}$ = 2.4 Hz, 1H, **H**11), 8.14 (d, $^3J_{H3-H2}$ = 2.8 Hz, 1H, **H**3), 7.68 (d, $^3J_{H9-H10}$ = 1.8 Hz, 1H, **H**9), 7.63 (d, $^3J_{H5-H6}$= 2.2 Hz, 1H, **H**5), 7.40 (d, $^3J_{H6-H5}$= 2.2 Hz, 1H, **H**6), 7.37-7.30 (m, 8H, *o*-$BPh_4$), 6.92 (t, $^3J_{H-H}$ = 7.3 Hz, 8H, *m*-$BPh_4$), 6.86 (d, $^2J_{H4-H4}$ = 13.9 Hz, 1H, **H**4), 6.77 (t, $^3J_{H-H}$ = 7.3 Hz, 4H, *p*-$BPh_4$), 6.75 (d, $^2J_{H8-H8}$= 13.9 Hz, 1H, **H**8), 6.55 (dd, $^3J_{H2-H3}$/ $^3J_{H2-H1}$ = 2.4 Hz, 1H, **H**2), 6.49 (d, $^2J_{H8-H8}$ = 13.9 Hz, 1H, **H**8), 6.40 (dd, $^3J_{H10-H9}$/ $^3J_{H10-H11}$ = 2.4 Hz, 1H, **H**10), 6.21 (s, 6H, Ru-$C_6$**H**$_6$), 6.08 (d, $^2J_{H4-H4}$= 13.9 Hz, 1H, **H**4) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $(CD_3)_2CO$): $\delta$ 177.8 (**C**7), 165.9-164.0 (q, $^1J_{C-B}$ = 48.9 Hz, *ipso*-**C** of $BPh_4$), 149.4, (**C**1), 142.1 (**C**9) 137.0 (*o*-**C** of $BPh_4$), 135.4 (**C**3), 132.2 (**C**11), 126.1 (*m*-$BPh_4$), 124.1 (**C**5), 122.3 (p-$BPh_4$& **C**6), 108.8 (**C**2), 107.7 (**C**10), 89.7 (Ru-$C_6H_6$), 64.9 (**C**8), 63.3 (**C**4) ppm. Elemental Analysis found: C, 64.69; H, 5.42; N, 10.85. Calc for $Ru_1C_{41}H_{38}N_6B_1$: C, 64.83; H, 5.44; N, 10.80. ESI MS: (m/z 443.03) [**3**-$BPh_4$]$^+$ amu.

**Synthesis of [Ru($\eta^6$-$C_{10}H_{14}$)(*NCN*$^{Me}$)Cl]$BPh_4$ (4)**

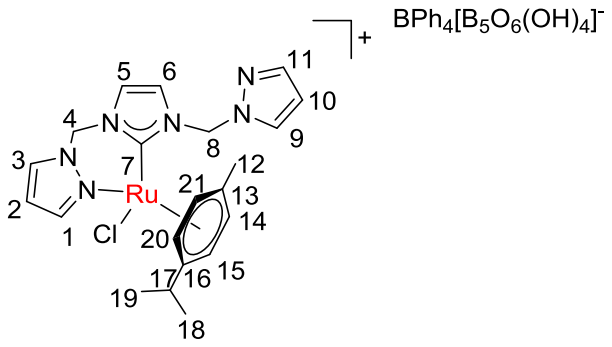



$Ag_2O$ (0.100 g, 0.432 mmol), *NCN*$^{Me}$.$BPh_4$ (**1**) (0.061 g, 0.120 mmol) and [Ru($\eta^6$-$C_{10}H_{14}$)$Cl_2$]$_2$ (0.035 g, 0.056 mmol) were dissolved in 20 mL of dry $CH_2Cl_2$. The mixture was left stirring overnight at room temperature under an $N_2$ atmosphere. The resulting dark suspension was

filtered using glass fibre (GF/C) filter paper producing a yellow filtrate which was reduced to 10 mL. 40 mL of diethyl ether was slowly added to the solution to precipitate [Ru($\eta^6$-$C_{10}H_{14}$)(*NCN*$^{Me}$)Cl]$BPh_4$ as a yellow powder.

Yield: 51%. $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ 7.87 (br d, 1H, **H**1), 7.77 (d, $^3J_{H9\text{-}H10}$ = 2.4 Hz, 1H, **H**9), 7.71 (br d, 1H, **H**3), 7.40 (br t, 8H, *o*-$BPh_4$), 7.09 (d, $^3J_{H11\text{-}H10}$= 2.6 Hz, 1H, H**11**), 7.06 (t, $^3J_{H\text{-}H}$ = 7.5 Hz, 8H, *m*-$BPh_4$), 6.95 (t, $^3J_{H\text{-}H}$ = 7.5 Hz, 5H, *p*-$BPh_4$& **H**5), 6.64 (d, $^3J_{H6\text{-}H5}$ = 2.0 Hz, 1H, **H**6), 6.53 (d, $^2J_{H4\text{-}H4}$ = 13.8 Hz, 1H, **H**4), 6.42 (m, 1H, **H**2), 6.38 (m, 1H, **H**10), 6.09 (d, $^2J_{H4\text{-}H4}$= 13.8 Hz, 1H, **H**4), 5.90 (d, $^3J_{H20\text{-}H21}$ = 6.2 Hz, 1H, **H**20), 5.78 (d, $^3J_{H14\text{-}H15}$ = 6.1 Hz, 1H, **H**14), 5.47 (d, $^3J_{H21\text{-}H20}$ = 6.2 Hz, 1H, **H**21), 5.24 (d, $^3J_{H15\text{-}H14}$= 6.1 Hz, 1H, **H**15), 4.75 (d, $^2J_{H8\text{-}H8}$ = 14.1 Hz, 1H, **H**8), 4.64 (d, $^2J_{H8\text{-}H8}$= 14.1 Hz, 1H, **H**8), 2.64 (sept, $^3J_{H17\text{-}H18}$/ $^3J_{H17\text{-}H19}$ = 7.0 Hz, 1H, **H**17), 2.07 (s, 3H, **H**12), 1.22-1.21 (2 x d, $^3J_{H18\text{-}H17}$/ $^3J_{H19\text{-}H17}$ = 2.1 Hz, 6H, **H**18 & **H**19) ppm. $^{13}$C{$^1$H} NMR (100 MHz, $CD_2Cl_2$): $\delta$ 177.7 (**C**7), 164.8-163.4 (q, $^1J$= 49.3 Hz *ipso*-**C** of $BPh_4$), 148.4 (**C**1), 142.2 (**C**11), 136.4 (*o*-**C** of $BPh_4$), 134.8 (**C**3), 131.2 (**C**9), 126.3 (*m*-**C** of $BPh_4$), 123.4 (**C**5), 122.7 (*p*-**C** of $BPh_4$), 121.2 (**C**6), 112.5 (**C**16), 108.6 (**C**2), 107.8 (**C**10), 102.6 (**C**13), 89.1 (**C**20), 86.9 (**C**21), 86.6 (**C**14), 84.3 (**C**15), 64.5 (**C**8), 61.8 (**C**4), 31.9 (**C**17), 23.7 (**C**19), 21.4 (**C**18), 18.9 (**C**12) ppm. Elemental Analysis found: C, 65.86; H, 5.77; N, 9.83 %. Calcd. for $Ru_1C_{45}H_{46}N_6B_1$: C, 65.97; H, 5.78; N, 10.26. ESI MS: (m/z 499.19) [**4**-$BPh_4$]$^+$ amu.

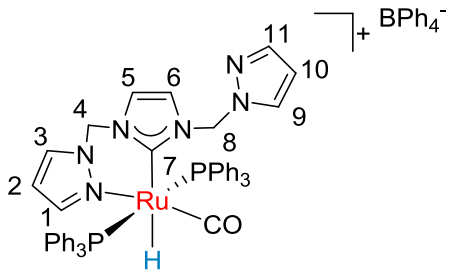
### Synthesis of $[Ru(\eta^6\text{-}C_{10}H_{14})(NCN^{Me})Cl]BPh_4[B_5O_6(OH)_4]$ (4a)




$[Ag(NCN^{Me})_2]BPh_4$ (**2**) (0.050 g, 0.056 mmol) and $[Ru(\eta^6\text{-}C_{10}H_{14})Cl_2]_2$ (0.035 g, 0.056 mmol) were dissolved in 20 mL of dry $CH_2Cl_2$. The mixture was left stirring overnight at room temperature under an $N_2$ atmosphere. The resulting yellow mixture was filtered using glass fibre (GF/C) filter paper and the filtrate reduced to 10 mL. 40 mL of diethylether was slowly added to the solution to precipitate $[Ru(\eta^6\text{- }C_{10}H_{14})(NCN^{Me})Cl]BPh_4[B_5O_6(OH)_4]$ as a yellow powder.

Yield: 51%. Elemental Analysis found: C, 40.05; H, 4.08; N, 11.64. Calc. for $[Ru(\eta^6\text{-}C_{10}H_{14})(NCN^{Me})Cl]14\%BPh_4.86\%[B_5O_6(OH)_4]$: C, 40.01; H, 4.44; N, 11.49. ESI MS: (m/z 499.19) [**4a**-$BPh_4/B_5O_6(OH)_4]^+$ amu.

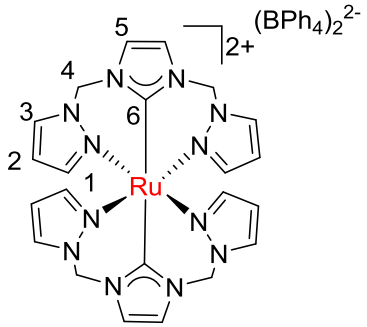
### Synthesis of $[Ru(H)CO(NCN^{Me})(PPh_3)_2]BPh_4$ (5)




$(NCN^{Me})BPh_4$ (**1**) (0.040 g, 0.073 mmol) and $[Ru(H)(CO)Cl(PPh_3)_3]$ (0.070 g, 0.073 mmol) were suspended in 20 mL of dry MeOH and $NEt_3$ (1 mL). The mixture was refluxed for 2 hours. The resulting pale yellow mixture was filtered using glass fibre (GF/B) filter paper. The beige filtrate was dried *in vacuo* to precipitate $[Ru(H)CO(NCN^{Me})(PPh_3)_2]BPh_4$ as a white solid. The crude product was washed with diethyl ether (2 x 20 mL) and dried under vacuum.

Yield: 40%. Single crystals were grown by vapour diffusion of diethyl ether into saturated dichloromethane solution of **5**. $^{1}$H NMR (300 MHz, $(CD_3)_2CO$): $\delta$ 7.60 (d, $^{3}J_{H1-H2}$ = 1.8 Hz, 1H, **H**1), 7.57 (d, $^{3}J_{H5-H6}$ = 2.1 Hz, 1H, **H**5), 7.49 (d, $^{3}J_{H6-H5}$ = 2.1 Hz, 1H, **H**6), 7.48-7.30 (m, 40H, *o*-$BPh_4$,$PPh_3$, **H**3, **H**9), 6.92 (t, $^{3}J_{H-H}$ = 7.2 Hz, 9H, *m*-$BPh_4$, **H**11), 6.77 (br m, $^{3}J_{H-H}$ = 7.2 Hz, 4H, *p*-$BPh_4$), 6.26 (dd, $^{3}J_{H2-H1}$ /$^{3}J_{H2-H3}$ = 1.8 Hz, 1H, **H**2), 5.67 (br s, 2H, **H**8), 5.53 (dd, $^{3}J_{H10-H9}$/ $^{3}J_{H10-H11}$ = 1.8 Hz, 1H, **H**10) 5.30 (br s, 2H, **H**4), -6.03 (t, $^{2}J_{H-P}$ = 22.0 Hz, 1H, Ru-**H**) ppm. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CD_2Cl_2$): $\delta$ 206.7 (Ru-**C**O), 189.3 (**C**7), 149.3 (**C**9), 141.6 (**C**3), 136.3 (**C**1), 134.7-133.7 (4 x **C**, $PPh_3$) 130.7 (3 x **C**, $PPh_3$), 130.2 (**C**11), 129.3-129.0 (3 x **C**, $PPh_3$) 126.2 (*m*-**C** of $BPh_4$) 124.7 (**C**5), 122.4 (*o*-**C** of $BPh_4$), 122.0 (**C**6), 107.5 (**C**2) 107.2 (**C**10), 62.1 (**C**8), 61.8 (**C**4) ppm.$^{31}$P NMR (121 MHz, $(CD_3)_2CO$): $\delta$ 47.7 (**P**-Ru) ppm. Elemental analysis found: C, 70.93; H, 5.51; N, 6.90. Calc. for $Ru_1C_{72}H_{63}N_6B$. 0.25 $CH_2Cl_2$: C, 70.93; H, 5.23; N, 6.87. ESI-MS: (m/z 883.26) [**5**-$BPh_4$]$^{+}$amu. IR (Solid): Ru-H: 1606.2 cm$^{-1}$, Ru-C=O: 1938.3 cm$^{-1}$.

## Synthesis of [Ru(*NCN*$^{Me}$)$_2$](BPh$_4$)$_2$ (7)




(*NCN*$^{Me}$)$BPh_4$ (**1**) (0.050 g, 0.092 mmol) and $RuCl_3.xH_2O$ (0.024 g, 0.092 mmol) and $NEt_3$ (1 mL) were suspended in 15 mL of dry ethanol. The mixture was refluxed for 16 hours. The resulting dark green solid, [Ru(*NCN*$^{Me}$)$_2$](BPh$_4$)$_2$ was separated from a pale yellow solution using glass fibre (GF/C) filter paper.

Yield: 65%. Single crystals were grown by slow evaporation of a saturated acetone solution of **7**. $^{1}$H NMR (400 MHz, $(CD_3)_2CO$): $\delta$ 8.14 (d, $^{3}J_{H1-H2}$ = 2.6 Hz, 4H, **H**1), 7.85 (s, 4H, **H**5), 7.28 (m, 16H, *o*-$BPh_4$), 6.88 (t, $^{3}J_{H-H}$ = 7.3 Hz, 16H, *m*-$BPh_4$), 6.85 (d, $^{3}J_{H4-H4}$= 13.7 Hz, 4H, **H**4), 6.73 (t, $^{3}J_{H-H}$ = 7.2 Hz, 8H, *p*-$BPh_4$), 6.52 (d, $^{3}J_{H3-H2}$ = 1.6 Hz, 4H, **H**3), 6.17 (br m, 4H, **H**2), 5.97 (d, $^{3}J_{H4-H4}$ = 13.7 Hz, 4H, **H**4) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, $(CD_3)_2SO$): $\delta$ 195.4 (**C**6), 164.3-162.3 (q, $^{1}J$= 49.8 Hz, *ipso*-**C** of $BPh_4$), 147.0 (**C**1), 136.1 (**C**3), 135.5 (*o*-$BPh_4$), 125.2 (*m*-$BPh_4$), 121.4, (*p*-$BPh_4$), 120.8 (**C**5), 107.2 (**C**2), 62.4 (**C**4) ppm. Elemental analysis found: C, 70.17; H, 5.50; N, 14.05. Calc. for $Ru_1C_{70}H_{64}N_{12}B_2$: C, 70.18; H, 5.55; N, 14.03. ESI MS: (m/z 279.08) [**7**-2($BPh_4$)]$^{2+}$amu.

## Catalysed Transfer Hydrogenation reactions using Ru(II) complexes 3, 4, 4a, 5, 5a and 7.

### General procedure for Transfer Hydrogenation reactions

The transfer hydrogenation experiments were carried out under standard schlenk conditions. The substrates (0.25 mmol), catalyst (1.5 mol%) and base (KOH, 0.045 mmol) were mixed in 10 mL of 2-propanol. The mixture was heated to reflux (82 $^{\circ}$C) for 24 hours. 1 mL aliquots were taken at regular intervals, which were quenched with cold isopropanol (1 mL) and filtered through a plug of silica. The crude products were diluted in dichloromethane and analysed using GC-MS analysis. Selected aliquots were also analysed using $^{1}$H NMR spectroscopy. Integration of selected resonance signals were compared in quantitative ratio between substrates and products. The GC-MS product yield values were consistently within 2% of the $^{1}$H NMR analysed yield values.

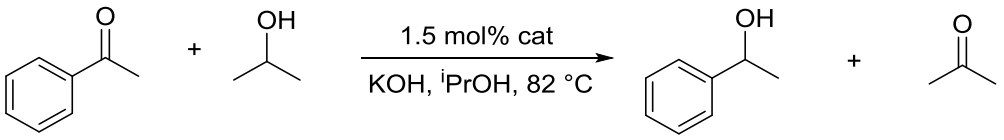
GC-MS analyses were performed on a Shimadzu QP2010 Plus gas chromatograph-mass spectrometer. A BP20 column was used, and the oven temperature was ramped from 50 to 220 °C at a rate of 10 °C min$^{-1}$. Ultra high purity grade helium was used as the carrier gas. The screw-cap autosampler vials used were obtained from Agilent Technologies and were fitted with PTFE/silicone septa and 0.2 mL micro inserts. The identification of products was confirmed using GC-MS spectroscopy and $^{1}$H NMR spectroscopy, and the conversion of substrate to product(s) was monitored by GC-MS by comparing the peak areas of the product(s).

**Catalysed Transfer Hydrogenation of Acetophenone to form Acetophenol using Ru(II) complexes 3, 4, 4a, 5, 5a and 7.**

The catalysed transfer hydrogenation of acetophenone to form acetophenol at 80 $^{o}$C was investigated using complexes; $[Ru(NCN^{Me})_2](BPh_4)_2$ (**7**), $[Ru(H)CO(NCN^{Me})(PPh_3)_2]BPh_4$ (**5a**), $[Ru(CO)H(NCN^{Me})(PPh_3)_2]BPh_4$ (**5**), $[Ru(\eta^6\text{-}C_6H_6)(NCN^{Me})Cl]BPh_4$ (**3**), $[Ru(\eta^6\text{-}C_{10}H_{14})(NCN^{Me})Cl]BPh_4.[B_5O_6(OH)_4]$ (**4a**), $[Ru(\eta^6\text{-}C_{10}H_{14})(NCN^{Me})Cl]BPh_4$ (**4**). A typical reaction was performed as follows:

The catalyst was weighed in air and transferred to a schlenk flask. The flask was then filled with an inert atmosphere, 10 mL of 2-propanol added followed by subsequent addition of acetophenone (0.25 mmol) and base (KOH, 0.045 mmol). The mixture was heated to reflux (82 $^{\circ}$C) for 24 hours. Refer to chapter 2, section 2.5 for final results.

**Table 6.1** Quantities of acetophenone and catalyst used.




| Catalyst | Catalyst loading (mol %) | Mass of catalyst (mg) | Mass of Acetophenone (mg) |
|---|---|---|---|
| $[Ru(\eta^6\text{-}C_6H_6)(NCN^{Me})Cl]BPh_4$ (**3**) | 1.5 | 2.8 | 30 (0.02 mL) |
| $[Ru(\eta^6\text{-}C_{10}H_{14})(NCN^{Me})Cl]BPh_4$ (**4**). | 1.5 | 3.0 | 30 (0.02 mL) |
| $[Ru(\eta^6\text{-}C_{10}H_{14})(NCN^{Me})Cl]BPh_4$ $[B_5O_6(OH)_4]^-$ (**4a**). | 1.5 | 3.2 | 30 (0.02 mL) |

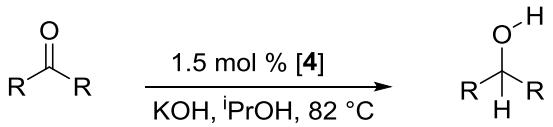
| | | | |
|---|---|---|---|
| [Ru(H)CO($NCN^{Me}$)($PPh_3$)$_2$]$BPh_4$ (**5**) | 1.5 | 4.2 | 30 (0.02 mL) |
| [Ru(CO)H($NCN^{Me}$)($PPh_3$)$_2$]$BPh_4$ (**5a**), | 1.5 | 4.2 | 30 (0.02 mL) |
| [Ru($NCN^{Me}$)$_2$]($BPh_4$)$_2$ (**7**), | 1.5 | 4.0 | 30 (0.02 mL) |

**Catalysed transfer hydrogenation of ketones to form alcohols using Ru(II) complexes 4 and 4a.**

The catalysed transfer hydrogenation reaction of acetophenone, benzophenone, 4-nitro-acetophenone, cyclohexanone and 2-hexanone was investigated at 25 and 82 °C using $[Ru(\eta^6\text{-}C_{10}H_{14})(NCN^{Me})Cl]BPh_4$ (**4**) or $[Ru(\eta^6\text{-}C_{10}H_{14})(NCN^{Me})Cl]BPh_4[B_5O_6(OH)_4]$ (**4a**) A typical reaction was performed as follows:

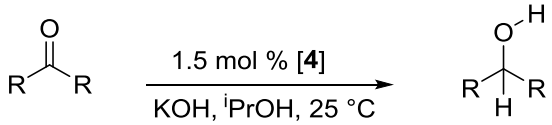
The catalyst was weighed in air and transferred to a schlenk flask. The flask was then filled with an inert atmosphere, 10 mL of 2-propanol added followed by subsequent addition of substrate (0.25 mmol) and base (KOH, 0.045 mmol). The mixture was heated to reflux (82 °C) for 4 hours. or maintained at 25 °C for 24 hours. Refer to chapter 2, section 2.5 for final results.

**Table 6.2** Quantities of catalyst **4** and substrates used at 82 °C.



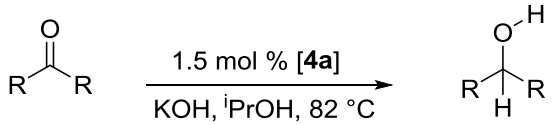

| Substrate | Catalyst loading (mol %) | Mass of catalyst (mg) | Mass of substrate (mg) |
|---|---|---|---|
| Acetophenone | 1.5 | 3.0 | 30 (0.02 mL) |
| Benzophenone | 1.5 | 3.1 | 46 |
| 4-Nitroacetophenone | 1.5 | 3.0 | 42 |
| Cyclohexanone | 1.5 | 3.0 | 24.5 (0.026 mL) |
| 2-Hexanone | 1.5 | 3.1 | 25 (0.031 mL) |

**Table 6.3** Quantities of catalyst **4** and substrates used at RT.



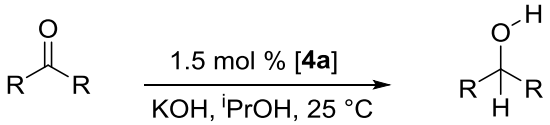

| Substrate | Catalyst loading (mol %) | Mass of catalyst (mg) | Mass of Substrate (mg) |
|---|---|---|---|
| Acetophenone | 1.5 | 3.0 | 30 (0.02 mL) |
| Benzophenone | 1.5 | 3.0 | 46 |
| 4-Nitroacetophenone | 1.5 | 3.2 | 43 |
| Cyclohexanone | 1.5 | 3.1 | 24.5 (0.026 mL) |
| 2-Hexanone | 1.5 | 3.0 | 25 (0.031 mL) |

**Table 6.4** Quantities of catalyst **4a** and substrates used at 82 °C.



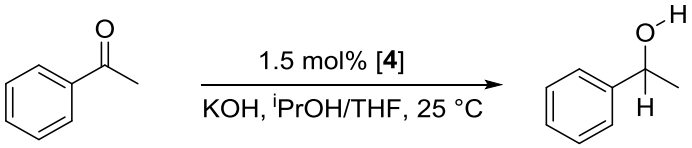

| Substrate | Catalyst loading (mol %) | Mass of catalyst (mg) | Mass of Substrate (mg) |
|---|---|---|---|
| Acetophenone | 1.5 | 3.3 | 30 (0.02 mL) |
| Benzophenone | 1.5 | 3.4 | 45 |
| 4-Nitroacetophenone | 1.5 | 3.4 | 43 |
| Cyclohexanone | 1.5 | 3.2 | 24.5 (0.026 mL) |
| 2-Hexanone | 1.5 | 3.3 | 25 (0.031 mL) |

**Table 6.5** Quantities of catalyst **4a** and substrates used at RT.




| Substrate | Catalyst loading (mol %) | Mass of catalyst (mg) | Mass of Substrate (mg) |
|---|---|---|---|
| Acetophenone | 1.5 | 3.4 | 30 (0.02 mL) |
| Benzophenone | 1.5 | 3.4 | 46 |
| 4-nitroacetophenone | 1.5 | 3.3 | 44 |
| cyclohexanone | 1.5 | 3.2 | 24.5 (0.026 mL) |
| 2-hexanone | 1.5 | 3.3 | 25 (0.031 mL) |

**Table 6.6** Quantities of catalyst **4a** and substrates used for $^{i}$PrOH/THF solvent mix.




| Substrate | Catalyst loading (mol %) | Mass of catalyst (mg) | Mass of Substrate (mg) |
|---|---|---|---|
| Acetophenone | 1.5 | 3.1 | 30 (0.02 mL) |

## 6.1.2. Crystal data for chapter 2

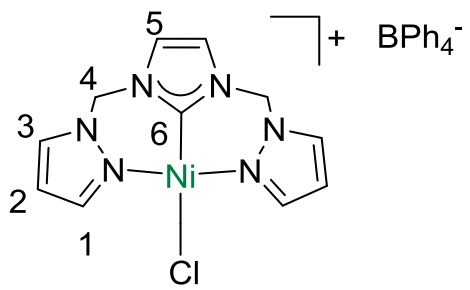
### Crystal data for ligand 1 and complexes 2, 3, 4a, 5, 6 and 7

| | **1** | **2** | **3** | **4a** | **5** | **6** | **7** |
|---|---|---|---|---|---|---|---|
| Chemical formula | $C_{11}H_{13}N_6 \cdot C_{24}H_{20}B$ | $2(C_{22}H_{24}AgN_{12}) \cdot C_{22}H_{23}AgN_{12} \cdot 3(C_{24}H_{20}B)$ | $C_{17}H_{18}ClN_6Ru \cdot 3(C_{16}H_{18}ClN_7Ru) \cdot 4(C_{24}H_{20}B) \cdot 3(CH_4O)$ | $C_{21}H_{26}ClN_6Ru \cdot B_5H_4O_{10}$ | $C_{48}H_{43}N_6OP_2Ru \cdot C_{24}H_{20}B$ | $C_{36}H_{30}Cl_2P_2Ru_2$ | $C_{11}H_{12}N_6Ru_{0.5} \cdot C_{24}H_{20}B$ |
| M (g mol$^{-1}$) | 548.48 | 2649.82 | 3150.53 | 717.08 | 1202.10 | 797.62 | 598.01 |
| Crystal System | Orthorhombic | Triclinic | Triclinic | Monoclinic | Monoclinic | Orthorhombic | Monoclinic |
| Space Group | $P2_12_12_1$ | $P\bar{1}$ | $P\bar{1}$ | $P2_1/n$ | $P2_1/c$ | *Pbcn* | $P2_1/n$ |
| Crystal Habit | | | | | | | |
| Temperature (K) | 150 | 150 | 150 | 150 | 150 | 150 | 150 |
| a (Å) | 8.5977 (3) | 14.4586(6) | 16.8274 (12) | 11.3903 (4) | 37.968 (2) | 17.815 (4) | 9.6717 (8) |
| b (Å) | 17.9211 (6) | 19.1802(7) | 18.3619 (15) | 11.8757 (4) | 11.5676 (7), | 20.572 (4) | 15.4965 (13) |
| c (Å) | 19.1642 (7) | 24.5632(10) | 24.387 (2) | 23.6462 (9) | 28.5760 (18) | 18.093 (4) | 19.8638 (18) |
| α (°) | 90 | 99.448(2) | 74.808 (4) | 90 | 90 | | 90 |
| β (°) | 90 | 99.315(2) | 89.916 (4) | 101.366 (2) | 92.123 (3) | | 91.611 (5) |
| γ (°) | 90 | 106.299(2) | 81.797 (4) | 90 | 90 | | 90 |
| V (Å$^3$) | 2952.82 (18) | 6291.9 (4) | 7192.5 (10) | 3135.84 (19) | 12542.0 (13) | 6631 (2) | 2976.0 (4) |
| Z | 4 | 2 | 2 | 4 | 8 | 8 | 4 |
| Radiation type | Mo *K*a | Mo *K*α | Mo *K*a | Mo *K*α | Mo *K*α | Mo *K*α | Mo *K*α |
| μ (mm$^{-1}$) | 0.07 | 0.53 | 0.55 | 0.65 | 0.35 | 1.19 | 0.32 |
| Crystal size (mm) | 0.46 × 0.20 × 0.15 | 0.26 × 0.24 × 0.08 | 0.12 × 0.11 × 0.05 | 0.21 × 0.17 × 0.06 | 0.23 × 0.06 × 0.04 | -- | 0.15 × 0.08 × 0.05 |
| Tmin, Tmax | 0.538, 0.746 | 0.692, 0.746 | 0.638, 0.746 | 0.660, 0.746 | 0.667, 0.746 | | 0.636, 0.745 |
| Refl. measured | 14308 | 87774 | 112286 | 27698 | 27324 | 134939 | 20709 |
| Unique reflections | 6260 | 21420 | 25301 | 6813 | 27320 | 9474 | 5648 |
| Obsd. Reflections [I > 2σ(I)] | 5658 | 13558 | 16486 | 5717 | 11308 | 9021 | 3092 |
| Rint | 0.051 | 0.082 | 0.122 | 0.033 | 0.0000 | 0.053 | 0.111 |
| R[F$^2$> 2σ(F$^2$)] | 0.042 | 0.047 | 0.091 | 0.034 | 0.068 | 0.042 | 0.055 |
| *wR(F$^2$)* | 0.105 | 0.117 | 0.240 | 0.094 | 0.172 | 0.152 | 0.133 |
| S | 1.04 | 1.00 | 1.03 | 1.06 | 0.88 | 1.43 | 1.00 |
| Reflections used | 6260 | 21420 | 25301 | 3796 | 27320 | 9474 | 5648 |
| Parameters | 379 | 1624 | 1861 | 413 | 1524 | 378 | 385 |
| Restraints | 0 | 482 | H-atom parameters constrained | 6 | 37 | H-atom parameters constrained | 122 |
| Δρmax, Δρmin (e Å$^{-3}$) | 0.24,, -0.21 | 0.70, -0.70 | 4.71, -1.01 | 1.19, -0.77 | 1.36, -0.93 | 1.61, -2.95 | 0.50, -0..91 |

## 6.2. Experimental for chapter 3

### 6.2.1. Synthesis of Ni(II) complexes

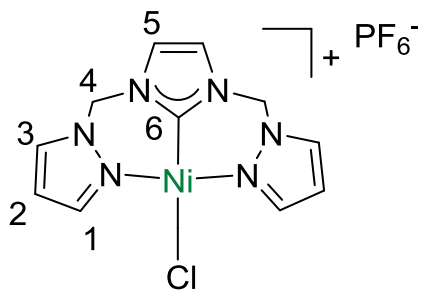
#### Synthesis of [Ni(*NCN*$^{Me}$)Cl]BPh$_4$ (8)




[Ag(*NCN*$^{Me}$)$_2$]BPh$_4$ (**2**) (0.050 g, 0.056 mmol) and Ni(PPh$_3$)$_2$Cl$_2$ (0.077 g, 0.118 mmol) were dissolved in 20 mL of dry THF. The mixture was left stirring overnight at room temperature under an N$_2$ atmosphere. The resulting yellow mixture was filtered using glass fibre (GF/C) filter paper and the filtrate reduced to 10 mL. 40 mL of diethyl ether was slowly added to the solution to precipitate [Ni(*NCN*$^{Me}$)Cl]BPh$_4$ (**8**) as a yellow powder. Crystals suitable for X-ray crystallography were grown by vapour diffusion of diethyl ether into a saturated acetone (2 mL) solution of **8**.

Yield: 40%. $^1$H NMR (600 MHz, (CD$_3$)$_2$CO): $\delta$ 8.29 (br d, 2H, **H**3), 8.18 (br d, 2H, **H**1), 7.70 (br s, 2H, **H**5), 7.37-7.30 (m, 8H, *o*-BPh$_4$), 6.92 (t, $^3J_{H-H}$ = 7.3 Hz, 8H, *m*-BPh$_4$), 6.95 (t, $^3J_{H-H}$ = 7.3 Hz, 4H, *p*-BPh$_4$) 6.81 (br d, 4H, **H**4), 6.58 (m, 2H, **H**2). $^{13}$C{$^1$H} NMR (150 MHz, (CD$_3$)$_2$CO): $\delta$, 164.3-163.3 (**C** ipso of BPh$_4$), 147.6 (**C**3), 143.9 (**C**6), 136.9 (**C**1), 136.0 (*o*-**C** of BPh$_4$), 125.6 (*m*-**C** of BPh$_4$), 121.8 (*p*-**C** of BPh$_4$), 122.0 (**C**5), 107.6 (**C**2), 61.9 (**C**4) ppm. Elemental analysis found: C, 65.54; H, 5.07; N, 13.04.Calc. for NiC$_{35}$H$_{32}$B N$_6$Cl.: C, 65.52; H, 5.03; N, 13.10. ESI MS (m/z= 286.04704) [**8**-Cl]$^+$.

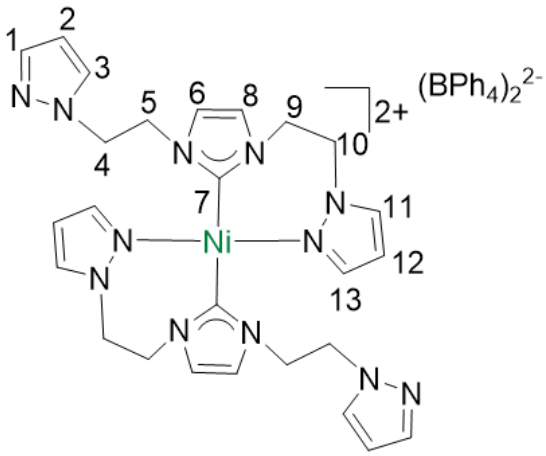
Synthesis of [Ni(*NCN*$^{Me}$)Cl]$PF_6$ (9)




(*NCN*$^{Me}$)$PF_6$ (**1b**) (0.090 g, 0.242 mmol) and $Ag_2O$ (0.150 g, 0.640 mmol) were mixed in 30 mL of dry $CH_2Cl_2$ and the mixture was left stirring overnight at room temperature under an $N_2$ atmosphere. Filtration of the dark mixture using glass fibre (GF/C) filter paper gave a colourless filtrate which was reduced to dryness. The resulting white powder was redissolved in 30 mL of dry THF to which $Ni(PPh_3)_2Cl_2$ (0.158 g, 0.242 mmol) was added. The orange suspension was left stirring overnight at room temperature under an $N_2$ atmosphere. The resulting yellow solution was filtered using glass fibre (GF/C) filter paper and the filtrate reduced to 10 mL. 40 mL of diethyl ether was slowly added to the solution to precipitate [Ni(*NCN*$^{Me}$)Cl].$PF_6$ (**9**) as a yellow powder. Crystals suitable for X-ray crystallography were grown by vapour diffusion of diethyl ether into a saturated acetone (2 mL) solution of **9**.

Yield: 62%. $^1$H NMR (600 MHz, $(CD_3)_2CO$): $\delta$ 8.36 (br d, 2H, **H**3), 8.16 (br d, 2H, **H**1), 7.79 (br s, 2H, **H**5), 6.92 (br d, 4H, **H**4), 6.60 (m, 2H, **H**2). $^{13}C\{^1H\}$ NMR (150 MHz, $(CD_3)_2CO$): $\delta$ 147.6 (**C**3), 143.9 (**C**6), 136.9 (**C**1), 122.0 (**C**5), 107.6 (**C**2), 61.9 (**C**4) ppm. Elemental analysis found: C, 28.24; H, 2.52; N, 17.90.Calc. for $Ni_1C_{11}H_{12}P\ N_6F_6Cl$.: C, 28.27; H, 2.59; N, 17.98. ESI MS (m/z= 303.05) [**9**+OH]$^+$.

Synthesis of [Ni($NCN^{Et}$) $_2$].$(BPh_4)_2$(10)




($NCN^{Et}$)$BPh_4$ (**1c**) (0.100 g, 0.242 mmol) and KHMDS (0.150 g, 0.640 mmol) and $Ni(PPh_3)_2Cl_2$ (0.158 g, 0.242 mmol) were mixed in 30 mL of dry THF and the resulting yellow mixture was left stirring overnight at room temperature under an $N_2$ atmosphere. The resulting yellow solution was filtered using glass fibre (GF/C) filter paper and the filtrate reduced to 10 mL. 40 mL of diethyl ether was slowly added to the solution to precipitate [Ni($NCN^{Et}$) $_2$]$(BPh_4)_2$ (**10**) as a yellow powder. Crystals suitable for X-ray crystallography were grown by vapour diffusion of diethyl ether into a saturated acetone (2 mL) solution of **10**.

Yield: 18%.$^1$H NMR (600 MHz, $(CD_3)_2CO$): $\delta$ 8.11 (d, $^3J_{H13-H12}$ = 2.3 Hz, 2H, **H**13), 7.98 (br t, 2H, **H**9a), 7.84 (br d, 2H, **H**1), 7.60 (d, $^3J_{H11-H12}$ = 2.3 Hz, 2H, **H**11), 7.53 (d, $^3J_{H8-H6}$ = 2.2 Hz, 2H, **H**8), 7.49 (br d, 2H, **H**6), 7.47 (d, $^3J_{H3-H2}$ = 2.2 Hz, 2H, **H**3), 7.35-7.29 (m, 8H, *o*-$BPh_4$), 6.94 (t, $^3J_{H-H}$ = 7.3 Hz, 8H, *m*-$BPh_4$), 6.80 (t, $^3J_{H-H}$ = 7.3 Hz, 4H, *p*-$BPh_4$), 6.42 (dd, $^3J_{H12-H11}$/ $^3J_{H12-H13}$ = 2.2 Hz 4H, **H**12), 6.16 (br m, 2H, **H**2), 5.61 (br d, 2H, **H**10a), 5.58 (br d, 2H, **H**10b), 5.04 (br m, 2H, **H**4a) 4.88 (br m, 2H, **H**9b), 4.63 (br m, 2H, **H**4b), 4.37 (br m, 2H, **H**5a), 4.29 (br m, 2H, **H**5b). $^{13}C\{^1H\}$ NMR (150 MHz, $(CD_3)_2CO$):, 151.7 (**C**7), 147.6 (**C**3), $\delta$142.5 (**C11**), $\delta$141.9 (**C1**), 140.8 (**C**10), 136.0 (*o*-**C** of $BPh_4$), 135.0 (**C**13), 131.1 (**C**3), 127 (**C**8), 125.6 (*m*-**C** of $BPh_4$), 123.5 (**C**6), 121.8 (*p*-**C** of $BPh_4$), 108.9 (**C**12), 105.5 (**C**2), 50.6 (**C**5), 50.0 (**C**4), 49.4 (**C**9), 48.7 (**C**10) ppm. Elemental analysis found: C, 72.07; H, 5.97; N, 13.04.Calc. for

$Ni_1C_{74}H_{72}B_2$ $N_{12}$.: C, 73.47; H, 6.00; N, 13.89. ESI MS: m/z calculated for $Ni_1C_{50}H_{52}BN_{12}$ = 889.38789. ESI MS: (m/Z= 889.38823) [**10**-$BPh_4$]$^+$.

### 6.2.2. Catalysed Kumada cross coupling reactions using complexes 8, 9 and 10.

#### General procedure for Kumada cross coupling reactions

THF used for catalysis reactions was distilled and dried using a sodium mirror and stored under an inert atmosphere. All substrates were purified by distillation and was glassware oven-dried (120- 150°C) prior to use. The nickel complexes were pre-dried under vacuum prior to catalysis reactions. The Kumada cross coupling experiments were carried out under standard schlenk conditions. GC-MS analyses were performed on a Shimadzu QP2010 Plus gas chromatograph-mass spectrometer. A BP20 column was used, and the oven temperature was ramped from 50 to 220 °C at a rate of 10 °C $min^{-1}$. UHP grade helium was used as the carrier gas. The screw-cap autosampler vials used were obtained from Agilent Technologies and were fitted with PTFE/silicone septa and 0.2 mL micro inserts. The identification of products was confirmed using GC-MS spectroscopy and $^1$H NMR spectroscopy and the conversion of substrate to product(s) was monitored by GC-MS by comparing the peak areas of the product(s). All catalytic reactions were carried out in duplicates. A typical catalysed Kumada coupling experiment was performed as follows:

A Schlenk flask was charged with the catalyst (2 mol%) to which 10 mL of THF was cannulated in an inert atmosphere. The organohalide substrate (0.5 mmol) and phenylmagnesium bromide (1.5 mmol) were added subsequently using an air tight

syringe. The mixture was stirred at 25 °C for 4 hours. Aliquots were taken at regular intervals, which were quenched with cold deionised $H_2O$ (1 mL) followed by the addition of $Et_2O$ (1 mL). The organic phase was extracted, dried using anhydrous $MgSO_4$ and filtered using a plug of silica The crude products (2-3 drops of the $Et_2O$ phase) were diluted in 1 mL of dichloromethane and collected for GC-MS analysis.

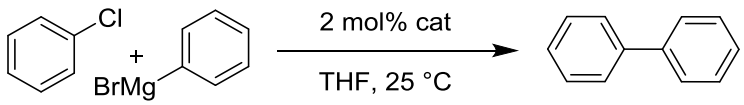
The $Et_2O$ of selected reactions were also reduced to dryness under vacuum, dissolved in $CD_3Cl_3$ and analysed using $^1H$ NMR spectra. Integration of selected resonance signals were compared in quantitative ratio between substrates and respective products.

**Catalysed Kumada cross coupling reactions of aryl halides and phenylmagnesium bromide using complexes 8, 9 and 10.**

The Kumada cross coupling reaction of aryl halides with phenylmagnesium bromide was catalysed by the complex [Ni($NCN^{Me}$)Cl]$BPh_4$ **(8),** [Ni($NCN^{Me}$)Cl]$PF_6$ **(9)** or [Ni($NCN^{Et}$)$_2$]$(BPh_4)_2$ **(10)**. A typical reaction was performed as follows:

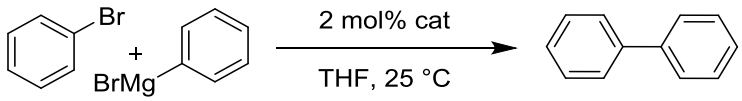
A schlenk flask was charged with the pre-dried catalyst (2 mol%) to which 10 mL of THF was cannulated in an inert atmosphere. The organohalide substrate (0.5 mmol) and phenylmagnesium bromide (1.5 mmol) were added subsequently using an air tight syringe. The mixture was stirred at 25 °C for 4 hours. Refer to chapter 3 section 3.4 for final results.

**Table 6.7** Quantities of catalyst and chlorobenzene and PhMgBr used.



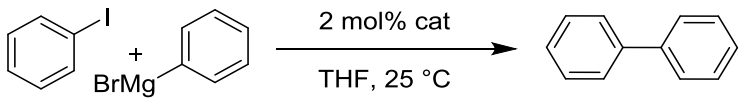

| Catalyst | Catalyst loading (mol %) | Mass of catalyst (mg) | Volume of PhCl (mL) | Volume of PhMgBr (mL) |
|---|---|---|---|---|
| [Ni(*NCN*$^{Me}$)Cl]$BPh_4$ **(8)** | 2.0 | 6.6 | 0.051 | 1.5 |
| [Ni(*NCN*$^{Me}$)Cl]$PF_6$**(9)** | 2.0 | 4.7 | 0.051 | 1.5 |
| [Ni(*NCN*$^{Et}$)$_2$]$(BPh_4)_2$**(10)** | 2.0 | 6.0 | 0.025 | 0.75 |

**Table 6.8** Quantities of catalyst, bromobenzene and PhMgBr used.



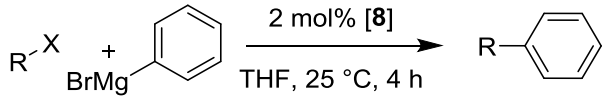

| Catalyst | Catalyst loading (mol %) | Mass of catalyst (mg) | Volume of PhBr (mL) | Volume of PhMgBr (mL) |
|---|---|---|---|---|
| [Ni(*NCN*$^{Me}$)Cl]$BPh_4$ **(8)** | 2.0 | 6.5 | 0.053 | 1.5 |
| [Ni(*NCN*$^{Me}$)Cl]$PF_6$**(9)** | 2.0 | 4.7 | 0.053 | 1.5 |
| [Ni(*NCN*$^{Et}$)$_2$]$(BPh_4)_2$**(10)** | 2.0 | 6.0 | 0.027 | 0.75 |

**Table 6.9** Quantities of catalyst and iodobenzene and PhMgBr used.

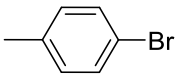
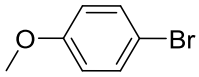
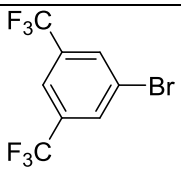
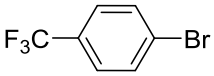
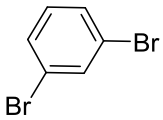


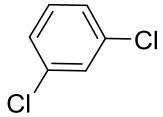
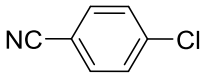

| Catalyst | Catalyst loading (mol %) | Mass of catalyst (mg) | Volume of PhI (mL) | Volume of PhMgBr (mL) |
|---|---|---|---|---|
| [Ni(*NCN*$^{Me}$)Cl]$BPh_4$ **(8)** | 2.0 | 6.5 | 0.056 | 1.5 |
| [Ni(*NCN*$^{Me}$)Cl]$PF_6$**(9)** | 2.0 | 4.6 | 0.056 | 1.5 |

**Table 6.10** Quantities of catalyst and substrates used.



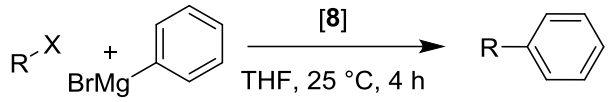

X = Cl, Br

| Substrate | Catalyst loading (mol %) | Mass of catalyst (mg) | Mass of substrate (mg) | Volume of PhMgBr (mL) |
|---|---|---|---|---|
|  | 2.0 | 6.6 | 85.5 | 1.5 |
|  | 2.0 | 3.3 | 46.8 | 0.75 |
|  | 2.0 | 3.3 | 73.1 | 0.75 |
|  | 2.0 | 3.3 | 56.2 | 0.75 |
|  | 2.0 | 3.4 | 83.9 | 0.75 |

| | | | | |
|---|---|---|---|---|
|  | 2.0 | 3.4 | 37.1 | 0.75 |
|  | 2.0 | 3.3 | 34.4 | 0.75 |

Refer to chapter 3 section 3.4 for final results.

**Table 6.11** Quantities of catalyst 8 and substrates used.




X = Cl, Br
R = phenyl, tolyl

| Substrate | Catalyst loading (mol %) | Mass of catalyst (mg) | Volume(mL) or mass(mg) of Substrate | Volume of PhMgBr (mL) |
|---|---|---|---|---|
| Phenyl chloride | 1.0 | 3.3 | 0.051 mL | 1.5 |
| Phenyl Bromide | 1.0 | 3.3 | 0.053 mL | 1.5 |
| Tolyl Bromide | 5.0 | 6.6 | 34.2 mg | 0.6 |

### 6.2.3. Crystal data for chapter 3

#### Crystal data for ligand 1c

| | p21byn_a |
|---|---|
| Crystal data | |
| Chemical formula | $C_{13}H_{17}N_6 \cdot C_{24}H_{20}B$ |
| $M_r$ | 576.53 |
| Crystal system, space group | Monoclinic, $P2_1/n$ |
| Temperature (K) | 150 |
| *a*, *b*, *c* (Å) | 11.3106 (4), 17.5185 (8), 15.8531 (6) |
| b (°) | 100.0240 (16) |
| *V* (Å$^3$) | 3093.3 (2) |
| *Z* | 4 |
| Radiation type | Mo *K*a |
| m (mm$^{-1}$) | 0.07 |
| Crystal size (mm) | 0.27 × 0.17 × 0.07 |
| | |
| Data collection | |
| Diffractometer | Bruker *APEX*-II CCD |
| Absorption correction | Multi-scan<br>*SADABS2012*/1 (Bruker,2012) was used for absorption correction. wR2(int) was 0.0758 before and 0.0528 after correction. The Ratio of minimum to maximum transmission is 0.8924. The l/2 correction factor is 0.0015. |
| $T_{min}$, $T_{max}$ | 0.665, 0.746 |
| No. of measured, independent and observed [$I$ > 2s($I$)] reflections | 27165, 6757, 5114 |
| $R_{int}$ | 0.048 |
| (sin q/l)$_{max}$ (Å$^{-1}$) | 0.640 |
| | |
| Refinement | |
| $R[F^2 > 2s(F^2)]$, $wR(F^2)$, $S$ | 0.044, 0.111, 1.02 |
| No. of reflections | 6757 |
| No. of parameters | 397 |
| H-atom treatment | H-atom parameters constrained |
| Dρ$_{max}$, Dρ$_{min}$ (e Å$^{-3}$) | 0.25, -0.22 |

Computer programs: *SAINT* v8.34A (Bruker, 2013), *SHELXL* (Sheldrick, 2008), Olex2 (Dolomanov *et al.*, 2009).

Crystal data for complex 8

| | |
|---|---|
| | ashwin_31oct13_a |
| Crystal data | |
| Chemical formula | $C_{11}H_{12}ClN_6Ni \cdot C_3H_6O \cdot C_{24}H_{20}B$ |
| $M_r$ | 699.71 |
| Crystal system, space group | Monoclinic, $P2_1/c$ |
| Temperature (K) | 150 |
| $a$, $b$, $c$ (Å) | 16.0883 (12), 12.3222 (8), 18.5299 (15) |
| β (°) | 109.158 (3) |
| $V$ (Å$^3$) | 3470.0 (4) |
| $Z$ | 4 |
| Radiation type | Mo $K\alpha$ |
| μ (mm$^{-1}$) | 0.68 |
| Crystal size (mm) | 0.09 × 0.09 × 0.03 |
| | |
| Data collection | |
| Diffractometer | Bruker *APEX*-II CCD |
| Absorption correction | Multi-scan *SADABS2012*/1 (Bruker,2012) was used for absorption correction. wR2(int) was 0.1184 before and 0.0785 after correction. The Ratio of minimum to maximum transmission is 0.8131. The λ/2 correction factor is 0.0015. |
| $T_{min}$, $T_{max}$ | 0.606, 0.746 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 23797, 6092, 3657 |
| $R_{int}$ | 0.110 |
| $(\sin \theta/\lambda)_{max}$ (Å$^{-1}$) | 0.595 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.055, 0.131, 1.01 |
| No. of reflections | 6092 |
| No. of parameters | 454 |
| No. of restraints | 18 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.38, -0.39 |

Computer programs: *SHELXL* (Sheldrick, 2008), Olex2 (Dolomanov *et al.*, 2009).

Crystal data for complex 9

| | p-1_a |
|---|---|
| Crystal data | |
| Chemical formula | $C_{11}H_{12}ClN_6Ni \cdot F_6P$ |
| $M_r$ | 467.40 |
| Crystal system, space group | Triclinic, $P\bar{1}$ |
| Temperature (K) | 100 |
| *a*, *b*, *c* (Å) | 7.9770 (16), 8.7170 (17), 12.200 (2) |
| a, b, g (°) | 91.69 (3), 104.13 (3), 104.66 (3) |
| *V* (Å$^3$) | 792.1 (3) |
| *Z* | 2 |
| Radiation type | Synchrotron, l = 0.71073 Å |
| m (mm$^{-1}$) | 1.57 |
| Crystal size (mm) | 0.02 × 0.01 × 0.01 |
| | |
| Data collection | |
| Diffractometer | Bruker *APEX*-II CCD |
| Absorption correction | – |
| No. of measured, independent and observed [*I* > 2s(*I*)] reflections | 16062, 4211, 3991 |
| $R_{int}$ | 0.036 |
| (sin q/l)$_{max}$ (Å$^{-1}$) | 0.705 |
| | |
| Refinement | |
| $R[F^2 > 2s(F^2)]$, $wR(F^2)$, *S* | 0.038, 0.100, 1.09 |
| No. of reflections | 4211 |
| No. of parameters | 235 |
| H-atom treatment | H-atom parameters constrained |
| Dρ$_{max}$, Dρ$_{min}$ (e Å$^{-3}$) | 0.66, -0.85 |

Computer programs: BluIce (McPhillips, 2002), XDS (Kabsch, 1993), *SIR2004* (Burla *et al.*, 2007), *SHELXL* (Sheldrick, 2008), Olex2 (Dolomanov *et al.*, 2009).

Crystal data for complex 10

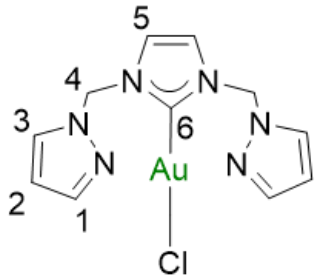
| | |
|---|---|
| | ashwin_26aug14_0m |
| Crystal data | |
| Chemical formula | $C_{12.25}H_{14.25}N_{5.75}Ni_{0.5}\cdot C_8H_8N_4Ni_{0.5}\cdot C_{24}H_{15}B\cdot C_{24}H_{19}B$ |
| $M_r$ | 1171.39 |
| Crystal system, space group | Monoclinic, *P*2/*n* |
| Temperature (K) | 150 |
| *a*, *b*, *c* (Å) | 23.4252 (19), 12.5805 (9), 24.392 (2) |
| b (°) | 118.202 (3) |
| *V* (Å$^3$) | 6334.9 (9) |
| *Z* | 4 |
| Radiation type | Mo *K*a |
| m (mm$^{-1}$) | 0.36 |
| Crystal size (mm) | ×× |
| | |
| Data collection | |
| Diffractometer | Bruker *APEX*-II CCD |
| Absorption correction | Multi-scan<br>*SADABS2014*/5 (Bruker,2014/5) was used for absorption correction. wR2(int) was 0.1903 before and 0.0707 after correction. The Ratio of minimum to maximum transmission is 0.7724. The l/2 correction factor is 0.00150. |
| $T_{min}$, $T_{max}$ | 0.576, 0.746 |
| No. of measured, independent and observed [*I* > 2s(*I*)] reflections | 54182, 14136, 4841 |
| $R_{int}$ | 0.177 |
| (sin q/l)$_{max}$ (Å$^{-1}$) | 0.646 |
| | |
| Refinement | |
| $R[F^2 > 2s(F^2)]$, $wR(F^2)$, *S* | 0.176, 0.481, 1.80 |
| No. of reflections | 14136 |
| No. of parameters | 674 |
| No. of restraints | 705 |
| H-atom treatment | H-atom parameters constrained |
| Dρ$_{max}$, Dρ$_{min}$ (e Å$^{-3}$) | 2.71, -1.22 |

Computer programs: *SAINT* v8.37A (Bruker, 2015), XT (Sheldrick, 2015), *SHELXL* (Sheldrick, 2015), Olex2 (Dolomanov *et al.*, 2009).

## 6.3. Experimental for chapter 4

### 6.3.1. Synthesis of Au(I) and Au(III) complexes

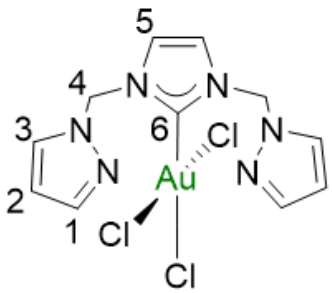
#### Synthesis of Au(I)(*NCN*$^{Me}$)Cl (11)




(*NCN*$^{Me}$)$BPh_4$ (**1**) (0.050 g, 0.092 mmol) and $NEt_3$ (1 mL) were suspended in 20 mL of dry $CH_2Cl_2$ to which [$HAuCl_4.xH_2O$] (0.036 g, 0.092 mmol) dissolved in 5 mL of methanol was added. The resulting grey-white suspension was stirred at room temperature for 16 hours. The mixture was then filtered using a GF/C filter producing a colourless solution. The filtrate was reduced in vacuo to 10 mL and pentane (40 mL) added to precipitate a grey-white solid, the solid was washed with distilled water (25 mL), diethyl ether (25 mL) and dried in vacuo.

Yield: 40%. $^1$H NMR (600 MHz, $(CD_3)_2CO$): $\delta$ 8.07 (d, $^3J_{H3-H2}$ = 2.5 Hz, 2H, **H**3), 7.54 (s, 2H, **H**5), 7.53 (d, $^3J_{H1-H2}$ = 1.5 Hz, 2H, **H**1), 6.55 (s, 4H, **H**4), 6.33 (m, 2H, **H**2) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, $(CD_3)_2CO$): $\delta$ 172.9 (**C**6), 141.9 (**C**1), 131.5 (**C**3), 122.6 (**C**5), 107.6 (**C**2), 65.1 (**C**4) ppm. Elemental analysis found: C, 30.06; H, 2.91; N, 17.62. Calc. for $Au_1C_{11}H_{12}N_6Cl.0.2C_5H_{12}$: C, 30.34; H, 3.06; N, 17.69. ESI MS: (m/z= 425.0778) [**11**-Cl]$^+$.

#### Synthesis of Au(III)(*NCN*$^{Me}$)$Cl_3$ (12)




[Ag(*NCN*$^{Me}$)$_2$]$BPh_4$ (**2**) (0.10 g, 0.11 mmol) was dissolved in 20 mL of dry $CH_2Cl_2$ to which a solution of [$HAuCl_4.xH_2O$] (0.09g, 0.22mmol) in ethanol (5 mL) was added. The resulting yellow suspension was stirred at room temperature in an $N_2$ atmosphere for 16 h. Filtration using GF/C filter paper (cannulation) produced a clear

yellow filtrate solution which was reduced in vacuo to 10 mL in volume. Pentane (40 mL) was added to the solution slowly to precipitate the complex as a yellow solid. The mixture was filtered using GF/B filter and the product dried in vacuo.

Yield: 50 %. $^{1}$H NMR (600 MHz, $(CD_3)_2CO$): $\delta$ 8.08 (d, $^{3}J_{H3-H2}$ = 2.4 Hz, 2H, **H**3), 7.82 (s, 2H, **H**5), 7.60 (d, $^{3}J_{H1-H2}$ = 1.6 Hz, 2H, **H**1), 6.78 (s, 4H, **H**4), 6.37 (m, 2H, **H**2) ppm. $^{13}$C{$^{1}$H} NMR (150 MHz, $(CD_3)_2CO$): $\delta$ 142.9 (**C**6), 142.4 (**C**3), 132.0 (**C**1), 125.4 (**C**5), 108.2 (**C**2), 64.4 (**C**4) ppm. Elemental analysis found: C, 24.86; H, 2.16; N, 15.26. Calc. for $Au_1C_{11}H_{12}N_6Cl_3$: C, 24.85; H, 2.28; N, 15.81. ESI MS: (m/z = 495.0155) [**12**-Cl]$^{+}$.

### 6.3.2. Catalysed dihydroalkoxylation reactions using complexes 11 and 12

#### General method for catalysed dihydroalkoxylation reactions

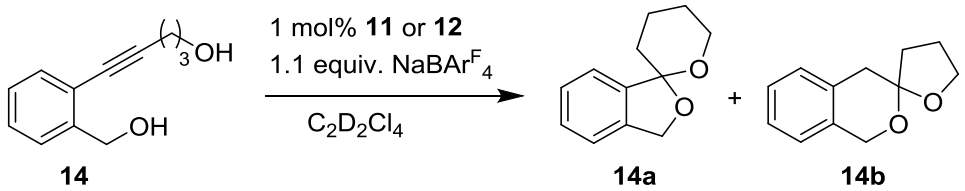
A Young's NMR tube was charged with 1 mol% catalyst and 1.1 equiv. of $NaBAr^{F}_4$, relative to the amount of substrate. In an Argon filled glovebox, the alkyne diol substrate (0.2 mmol) was subsequently added to the Young's NMR tube, followed by 0.6 mL of $C_2D_2Cl_4$. The samples were frozen at -72 $^{\circ}$C in an acetone/liquid $N_2$ slush bath and thawed directly before injecting the sample into the NMR instrument for analysis. The temperature of the NMR spectrometer was calibrated using an Omega Microprocessor Thermometer (HH23) that was fitted with a K-type thermocouple immersed in ethylene glycol or ethanol. The identification of products was confirmed using $^{1}$H NMR spectroscopy with reference to literature.[5] Refer to chapter 4 section 4.4 for final results. All catalytic reactions were carried out in duplicate. TONs were determined by dividing the moles of substrate converted by moles of catalyst used. TOFs (error = +/- 1%) were determined by dividing TON by time at 50% conversion.

**Catalysed dihydroalkoxylation of 14 using Au(I) complex 11 or Au(III) complex 12:**

The catalysed dihydroalkoxylation reaction of **14** was catalysed by the complexes [Au(I)(*NCN*$^{Me}$)Cl] (**11**) and [Au(III)(*NCN*$^{Me}$)$Cl_3$] (**12**). A typical reaction was performed as follows:

The Au(I) catalyst **11** or Au(III) catalyst **12** (1 mol%), $NaBAr^F{}_4$ (1.1 equiv.) and **14** (0.036 g, 0.2 mmol) were weighed in air using a 5 decimal point balance and transferred into an NMR tube fitted with a Youngs™ valve. Substrate **14** was not allowed to come in contact with the catalyst in the weighing process. The sample was brought into a nitrogen filled glovebox where $C_2D_2Cl_4$ (0.6 mL) was added slowly without allowing contact with substrate **14**. The samples were thoroughly mixed upon removal from the glovebox, immediately frozen at -72 °C in an acetone/liquid $N_2$ slush bath and thawed directly before injecting the sample into the NMR instrument for analysis. The reactions were monitored by $^1$H NMR spectroscopy while maintaining a constant temperature of 100, 80, 70, 40 or 25 °C.

**Table 6.12** Quantities of catalyst and substrate **14** used.




| Catalyst (loading) | Temperature(°C) | Mass of catalyst (mg) | Mass of 14 (mg) |
|---|---|---|---|
| **11** (1 mol%) | 100 | 0.98 | 37 |
| **11** (1 mol%) | 80 | 0.94 | 37 |

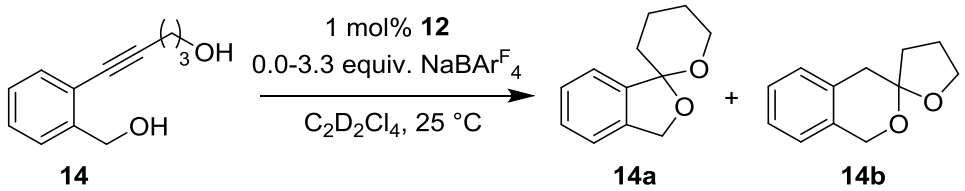
| | | | |
|---|---|---|---|
| **11** (1 mol%) | 70 | 0.96 | 38 |
| **11** (1 mol%) | 25 | 0.96 | 38 |
| **12** (1 mol%) | 70 | 1.06 | 38 |
| **12** (1 mol%) | 25 | 1.06 | 37 |

**Catalysed dihydroalkoxylation of 14 using 12, variation in $NaBAr^F_4$ loading.**

The catalysed dihydroalkoxylation reaction of **14** was catalysed by the complex [Au(III)(*NCN*$^{Me}$)$Cl_3$] (**12**) with varying amounts of $NaBAr^F_4$.

The Au(III) catalyst **12** (1 mol%), $NaBAr^F_4$ (0.0-3.3 equiv.) and **14** (0.036g, 0.2mmol) were weighed in air using a 5 decimal point balance and transferred into an NMR tube fitted with a Youngs™ valve. Substrate **14** was not allowed to come in contact with the catalyst in the weighing process. The sample was brought into a nitrogen filled glovebox where $C_2D_2Cl_4$ (0.6 mL) was added slowly without allowing contact with substrate **14**. The samples were thoroughly mixed upon removal from the glovebox, immediately frozen at -72 °C in an acetone/liquid $N_2$ slush bath and thawed directly before injecting the sample into the NMR instrument for analysis. The reaction was monitored by $^1$H NMR spectroscopy while maintaining a constant temperature of 25 °C.

**Table 6.13** Quantities of catalyst **12**, $NaBAr^F_4$ and substrate **14** used.




| Catalyst (loading) | $NaBAr^F_4$ (loading) | Mass of catalyst (mg) | Mass of $NaBAr^F_4$ (mg) | Mass of 14 (mg) |
|---|---|---|---|---|
| **12 (1 mol%)** | 0.0 equiv. | 1.06 | 0 | 38 |
| **12 (1 mol%)** | 1.1 equiv. | 1.06 | 1.98 | 38 |
| **12 (1 mol%)** | 2.2 equiv. | 1.04 | 3.98 | 37 |

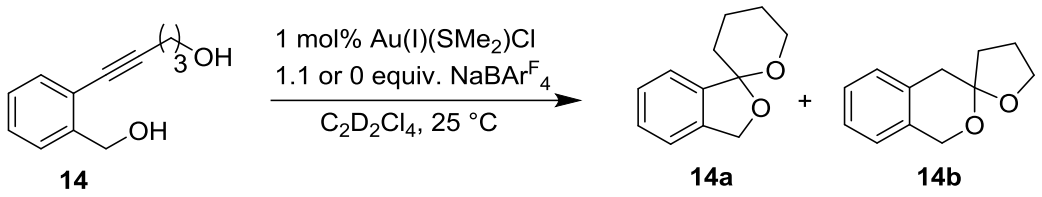
| | | | | |
|---|---|---|---|---|
| **12 (1 mol%)** | 3.3 equiv. | 1.05 | 6.01 | 38 |

**Catalysed dihydroalkoxylation of 14 using Au(I)(SMe$_2$)Cl:**

The catalysed dihydroalkoxylation reaction of **14** was catalysed by the complex [Au(I)(SMe$_2$)Cl] with varying amounts of NaBAr$^F{}_4$. A typical reaction was performed as follows:

The Au(I) catalyst **Au(I)(SMe$_2$)Cl** (1 mol%), NaBAr$^F{}_4$ (0.0 or 1.1 equiv.) and **14** (0.036g, 0.2mmol) were weighed in air using a 5 decimal point balance and transferred into an NMR tube fitted with a Youngs$^{TM}$ valve. Substrate **14** was not allowed to come in contact with the catalyst in the weighing process. The sample was brought into a nitrogen filled glovebox where $C_2D_2Cl_4$ (0.6 mL) was added slowly without allowing contact with substrate **14**. The samples were thoroughly mixed upon removal from the glovebox, immediately frozen at -72 $^{\circ}$C in an acetone/liquid $N_2$ slush bath and thawed directly before injecting the sample into the NMR instrument for analysis. The reaction was monitored by $^1$H NMR spectroscopy while maintaining a constant temperature of 25 °C.

**Table 6.14** Quantities of catalyst, $NaBAr^F_4$ and substrate **14** used.




| Catalyst (loading) | $NaBAr^F_4$ (loading) | Mass of catalyst (mg) | Mass of $NaBAr^F_4$ (mg) | Mass of 14 (mg) |
|---|---|---|---|---|
| [Au(I)($SMe_2$)Cl] (1 mol%) | 0.0 equiv. | 0.70 | 0 | 37 |
| [Au(I)($SMe_2$)Cl] (1 mol%) | 1.1 equiv. | 0.71 | 1.99 | 37 |

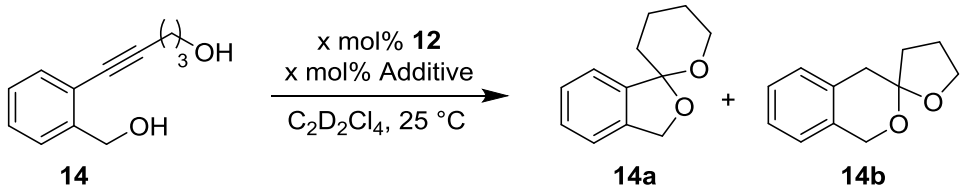
**Catalysed dihydroalkoxylation of 14, kinetic studies using Au(III) complex 12:**

The catalysed dihydroalkoxylation reaction of **14** was catalysed by the complex [Au(III)($NCN^{Me}$)$Cl_3$] (**12**) with varying amounts of $NaBAr^F_4$ or $AgSbF_6$. A typical reaction was performed as follows:

The Au(III) catalyst **12** (1 mol%), $NaBAr^F_4$ or $AgSbF_6$ (1.1 equivalent) and **14** (0.036g, 0.2mmol) were weighed in air, and **14** was transferred into an NMR tube fitted with a Youngs™ valve. Sample vials containing the Au(III) catalyst **12** and $NaBAr^F_4$ or $AgSbF_6$ were introduced separately from the NMR tube containing **14** into a nitrogen filled glove box. The Au(III) catalyst **12** and $NaBAr^F_4$ or $AgSbF_6$ were dissolved in 1 mL of $C_2D_2Cl_4$ from which 0.1 mL (0.1 mol%) and 0.01 mL (0.01 mol%) of the sample were extracted. These 0.1 mL and 0.01 mL of samples were diluted separately to a total volume of 0.6 mL of $C_2D_2Cl_4$ and added to the NMR tubes containing the substrate **14**. The samples were thoroughly mixed upon removal from the glovebox, immediately frozen at -72 °C in an acetone/liquid $N_2$ slush bath and thawed directly before injecting the sample into the NMR instrument for analysis.

The reaction was monitored by $^{1}H$ NMR spectroscopy while maintaining a constant temperature of 40 or 25 °C.

**Table 6.15** Quantities of catalyst, $NaBAr^{F}_{4}$, $AgSbF_6$ and substrate **14** used.




| Catalyst (loading) | Additive (loading) | Mass of catalyst (mg) | Mass of Additive (mg) | Mass of 14 (mg) |
|---|---|---|---|---|
| **12 (1 mol%)** | $NaBAr^{F}_{4}$ (1.1 equivalent) | 1.06 | 1.98 | 38 |
| **12 (0.1 mol%)** | $NaBAr^{F}_{4}$ (0.11 equivaent) | Diluted from 1 mL of 1 mol% stock solution | Diluted from 1 mL of 1 mol% stock solution | Diluted from 1 mL of 1 mol% stock solution |
| **12 (0.01 mol%)** | $NaBAr^{F}_{4}$ (0.011 equivalent) | Diluted from 1 mL of 0.1 mol% stock solution | Diluted from 1 mL of 0.1 mol% stock solution | Diluted from 1 mL of 0.1 mol% stock solution |
| **12 (1 mol%)** | $AgSbF_6$ (1.1 equivalent) | 1.05 | 0.7 | 37 |

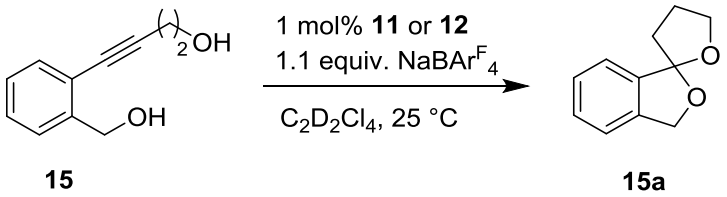
| | | | | |
|---|---|---|---|---|
| **12 (0.1 mol%)** | $AgSbF_6$ (0.11 equivalent) | 0.3 | 0.2 | 11 |

**Catalysed dihydroalkoxylation of 15 using Au(I) complex 11 or Au(III) complex 12:**

The catalysed dihydroalkoxylation reaction of **15** was catalysed by the complexes [Au(I)(*NCN*$^{Me}$)Cl] (**11**) and [Au(III)(*NCN*$^{Me}$)$Cl_3$] (**12**). A typical reaction was performed as follows:

The Au(I) catalyst **11** or Au(III) catalyst **12** (1 mol%), $NaBAr^F{}_4$ (1.1 equiv.)) and **15** (0.034g, 0.2mmol) were weighed in air using a 5 decimal point balance and transferred into an NMR tube fitted with a Youngs™ valve. Substrate **15** was not allowed to come in contact with the catalyst in the weighing process. The sample was brought into a nitrogen filled glovebox where $C_2D_2Cl_4$ (0.6 mL) was added slowly without allowing contact with substrate **15**. The samples were thoroughly mixed upon removal from the glovebox, immediately frozen at -72 °C in an acetone/liquid $N_2$ slush bath and thawed directly before injecting the sample into the NMR instrument for analysis. The reaction was monitored by $^1$H NMR spectroscopy while maintaining a constant temperature of 25 °C.

**Table 6.16** Quantities of catalyst and substrate **15** used.



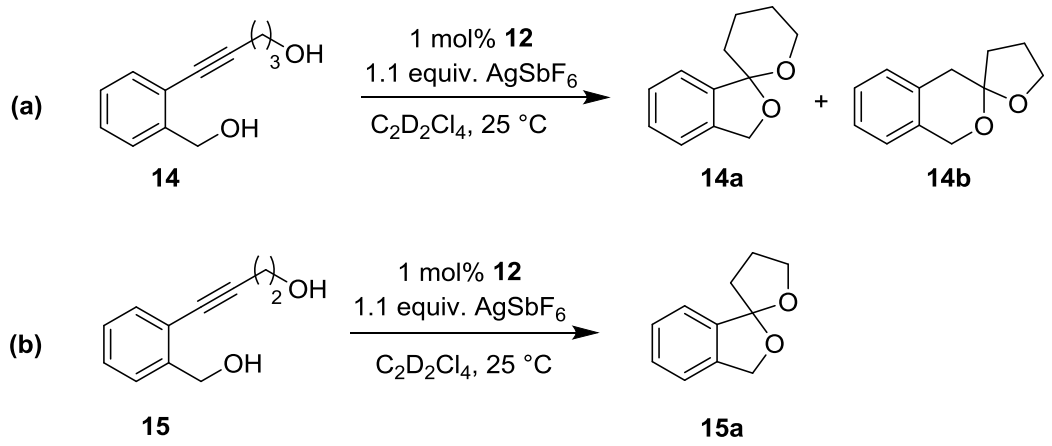

| Catalyst (loading) | Mass of catalyst(mg) | Mass of 15 (mg) |
|---|---|---|
| **11** (1 mol%) | 0.98 | 34 |
| **12** (1 mol%) | 1.05 | 34 |

**Catalysed dihydroalkoxylation of 14 and 15 using Au(III) complex 12 and $AgSbF_6$:**

The catalysed dihydroalkoxylation reaction of **14** and **15** was catalysed by the complex [Au(III)(*NCN*$^{Me}$)$Cl_3$] (**12**). A typical reaction was performed as follows:

The Au(III) catalyst **12** (1 mol%), $AgSbF_6$ (1.1 equiv.) and **14** (0.036g, 0.2mmol) or **15** (0.034g, 0.2mmol) were weighed in air using a 5 decimal point balance and transferred into an NMR tube fitted with a Youngs™ valve. Substrate **14** and **15** were not allowed to come in contact with the catalyst in the weighing process. The samples were brought into a nitrogen filled glovebox where $C_2D_2Cl_4$ (0.6 mL) was added slowly without allowing contact with the substrates. The samples were thoroughly mixed upon removal from the glovebox, immediately frozen at -72 °C in an acetone/liquid $N_2$ slush bath and thawed directly before injecting the sample into the NMR instrument for analysis. The reactions were monitored by $^1$H NMR spectroscopy while maintaining a constant temperature of 25 °C.

**Table 6.17** Quantities of catalyst and substrate **14, 15** used. Refer to Chapter 4 section 4.4 for final results.



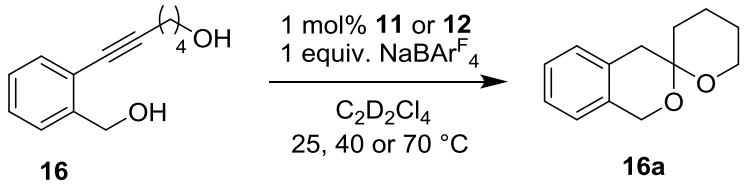
| Catalyst (loading) | Mass of catalyst (mg) | Mass of 14 or 15 (mg) |
|---|---|---|
| **12** (1 mol%) | 0.104 | **14** (37) |
| **12** (1 mol%) | 0.105 | **15** (35) |

Catalysed dihydroalkoxylation of 16 using Au(III) complexes 11 or 12:

The catalysed dihydroalkoxylation reaction of **16** was catalysed by the complex [Au(III)(*NCN*$^{Me}$)$Cl_3$] (**11**) or [Au(III)(*NCN*$^{Me}$)$Cl_3$] (**12**). A typical reaction was performed as follows:

The Au(I) catalyst **11** or Au(III) catalyst **12** (1 mol%), $NaBAr^F{}_4$ (1.1 equiv.)) and **16** (0.038 g, 0.2mmol) were weighed in air using a 5 decimal point balance and transferred into an NMR tube fitted with a Youngs™ valve. Substrate **16** was not allowed to come in contact with the catalyst in the weighing process. The sample was brought into a nitrogen filled glovebox where $C_2D_2Cl_4$ (0.6 mL) was added slowly without allowing contact with substrate **16**. The samples were thoroughly mixed upon removal from the glovebox, immediately frozen at -72 °C in an acetone/liquid $N_2$ slush bath and thawed directly before injecting the sample into the NMR instrument for analysis. The reactions were monitored by $^1$H NMR spectroscopy while maintaining a constant temperature of 40 or 25 °C.

**Table 6.18** Quantities of catalyst and substrate **16** used.




| Catalyst (loading) | Temperature ($^{o}$C) | Mass of catalyst (mg) | Mass of 16 (mg) |
|---|---|---|---|
| **11** (1 mol%) | 70 | 0.99 | 38 |
| **12** (1 mol%) | 25 | 0.105 | 39 |
| **12** (1 mol%) | 40 | 0.105 | 38 |

### 6.3.3. Catalysed hydroamination reactions using complexes 11 and 12

#### General method for hydroamination

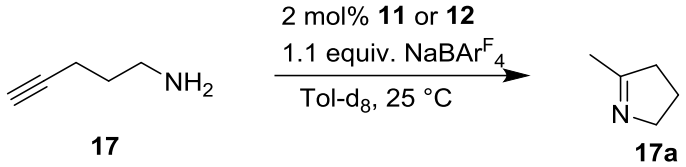
Alkynamines **17** and **18** were synthesised using literature procedures.[6] A Youngs™ NMR tube was charged with 2 mol% catalyst and 1.1 equiv. of $NaBAr^{F}_{4}$ (unless otherwise stated). The substrate (0.2mmol) was subsequently added and 0.6 mL of Tol-$d_8$ was added to the mix in an Ar atmosphere (Ar glovebox). The samples were frozen at -72 °C in an acetone/liquid $N_2$ slush bath and thawed before injecting the sample into the NMR instrument for analysis. Thermometer (HH23) that was fitted with a K-type thermocouple immersed in ethylene glycol or ethanol. The identification of products was confirmed using $^{1}$H NMR spectroscopy with reference to literature.[7] Integration of selected resonance signals were compared in quantitative ratio between substrates and respective products.

**Catalysed hydroamination of 17 using Au(I) complex 11 or Au(III) complex 12:**

The catalysed hydroamination reaction of **17** was catalysed by the complexes [Au(I)(*NCN*$^{Me}$)Cl] (**11**) and [Au(III)(*NCN*$^{Me}$)$Cl_3$] (**12**). A typical reaction was performed as follows:

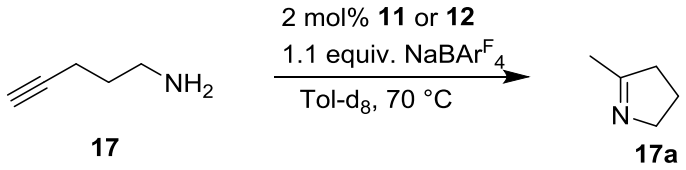
The Au(I) catalyst **11** or Au(III) catalyst **12** (2 mol%), $NaBAr^F{}_4$ (1.1 equiv.) and **17** (0.0174 g, 0.2 mmol) were weighed in air using a 5 decimal point balance. The catalyst and $NaBAr^F{}_4$ were transferred into an NMR tube fitted with a Youngs™ valve and were brought into an Argon filled glovebox where Tol-$d_8$ (0.6 mL) was added. **17** (0.0174 g, 0.2 mmol) was added to the samples upon removal from the glovebox, mixed thoroughly and the NMR tubes were immediately frozen at -72 °C in an acetone/liquid $N_2$ slush bath and thawed directly before injecting the sample into the NMR instrument for analysis. The reaction was monitored by $^1$H NMR spectroscopy while maintaining a constant temperature of 100, 70 or 25 °C.

**Table 6.19** Quantities of catalyst and substrate **17** used at RT. Refer to chapter 4 section 4.5 for final results.



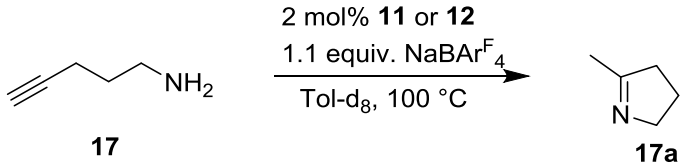

| Catalyst (loading) | Mass of catalyst (mg) | Mass of 17 (mg) |
|---|---|---|
| **11** (1 mol%) | 1.8 | 17.4 |
| **12** (1 mol%) | 2.2 | 17.4 |

**Table 6.20** Quantities of catalyst and substrate **17** used at 70 °C.




| Catalyst (loading) | Mass of catalyst (mg) | Mass of 17 (mg) |
|---|---|---|
| **11** (1 mol%) | 1.8 | 17.2 |
| **12** (1 mol%) | 2.2 | 17.4 |

**Table 6.21** Quantities of catalyst and substrate **17** used at 100 °C.



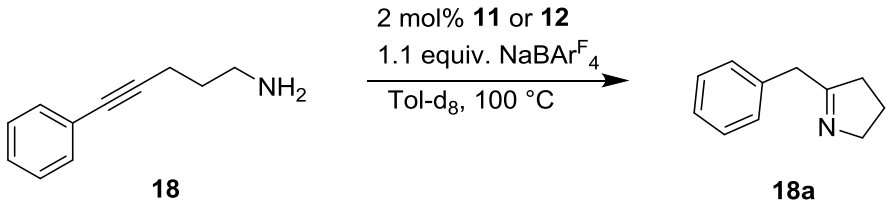

| Catalyst (loading) | Mass of catalyst (mg) | Mass of 17 (mg) |
|---|---|---|
| **11** (1 mol%) | 1.8 | 17.1 |
| **12** (1 mol%) | 2.2 | 17.2 |

**Catalysed hydroamination of 18 using Au(I) complex 11 or Au(III) complex 12:**

The catalysed hydroamination reaction of **18** was catalysed by the complexes [Au(I)($NCN^{Me}$)Cl] (**11**).and [Au(III)($NCN^{Me}$)$Cl_3$] (**12**). A typical reaction was performed as follows:

The Au(I) catalyst **11** or Au(III) catalyst **12** (2 mol%), $NaBAr^F_4$ (1.1 equiv.) and **18** (0.0326 g, 0.2mmol) were weighed in air using a 5 decimal point balance. The catalyst and $NaBAr^F_4$ were transferred into an NMR tube fitted with a Youngs™ valve and were brought into a nitrogen filled glovebox where Tol-$d_8$ (0.6 mL) was added. **18** (0.0326g, 0.2mmol) was added to the samples upon removal from the glovebox, mixed thoroughly and the NMR tubes were immediately frozen at -72 °C in an acetone/liquid $N_2$ slush bath and thawed directly before injecting the sample into the NMR instrument for analysis. The reaction was monitored by $^1$H NMR spectroscopy while maintaining a constant temperature of 100 °C.

**Table 6.22** Quantities of catalyst and substrate **18** used. Refer to chapter 4 section 4.5 for final results.



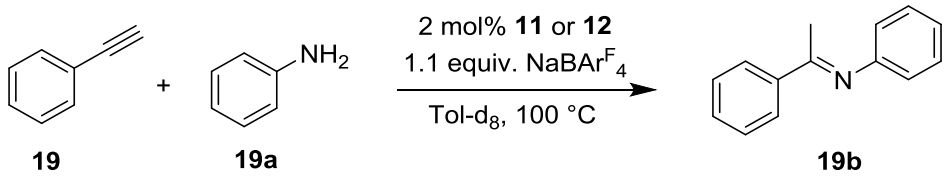

| Catalyst (loading) | Mass of catalyst (mg) | Mass of 18 (mg) |
|---|---|---|
| **11** (1 mol%) | 1.9 | 32.6 |
| **12** (1 mol%) | 2.2 | 32.6 |

**Catalysed hydroamination of 19 + 19a using Au(I) complex 11 or Au(III) complex 12:**

The catalysed hydroamination reaction of **19 + 19a** was catalysed by the complexes [Au(I)($NCN^{Me}$)Cl] (**11**) and [Au(III)($NCN^{Me}$)$Cl_3$] (**12**). A typical reaction was performed as follows:

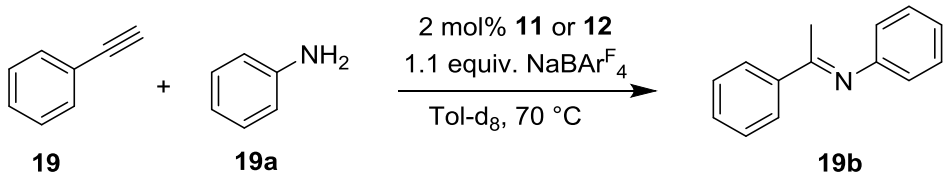
The Au(I) catalyst **11** or Au(III) catalyst **12** (2 mol%), $NaBAr^F_4$ (1.1 equiv.), **19** (0.0337 g, 0.2 mmol) and **19**a (0.0307 g, 0.2 mmol) were weighed in air using a 5 decimal point balance. The catalyst and $NaBAr^F_4$ were transferred into an NMR tube fitted with a Youngs™ valve and were brought into a nitrogen filled glovebox where Tol-$d_8$ (0.6 mL) was added. **19** (0.0337 g, 0.2 mmol) and **19**a (0.0307 g, 0.2 mmol) were added to the samples in the NMR tubes upon removal from the glovebox. This was mixed thoroughly and the NMR tubes were immediately frozen at -72 °C in an acetone/liquid $N_2$ slush bath and thawed directly before injecting the sample into the NMR instrument for analysis. The reaction was monitored by $^1$H NMR spectroscopy while maintaining a constant temperature of 100 or 70 °C.

**Table 6.23** Quantities of catalyst and substrate **19**/**19a** used at 100 °C. Refer to chapter 4 section 4.5 for final results.




| Catalyst (loading) | Mass of catalyst (mg) | Mass of 19 (mg) | Mass of 19a (mg) |
|---|---|---|---|
| **11** (1 mol%) | 3.0 | 33.7 | 30.7 |
| **12** (1 mol%) | 3.5 | 33.8 | 30.7 |

**Table 6.24** Quantities of catalyst and substrate **19**/**19a** used at 70 °C. Refer to chapter 4 section 4.5 for final results.




| Catalyst (loading) | Mass of catalyst (mg) | Mass of 189 (mg) | Mass of 19a (mg) |
|---|---|---|---|
| **11** (1 mol%) | 3.0 | 33.7 | 30.6 |
| **12** (1 mol%) | 3.5 | 33.8 | 30.7 |

### 6.3.4. Crystal data for chapter 4

#### [Au(I)(*NCN*$^{Me}$)Cl] complex 11 crystal data

| | |
|---|---|
| Crystal data | CCDC (1495705) |
| Chemical formula | $C_{22}H_{24}Au_2Cl_2N_{12}$ |
| $M_r$ | 921.35 |
| Crystal system, space group | Monoclinic, $P2_1/n$ |
| Temperature (K) | 150 |
| *a*, *b*, *c* (Å) | 10.5781 (5), 10.8458 (5), 12.0025 (5) |
| β (°) | 101.132 (2) |
| *V* (Å$^3$) | 1351.11 (11) |
| *Z* | 2 |
| Radiation type | Mo *K*α |
| μ (mm$^{-1}$) | 11.08 |
| Crystal size (mm) | 0.40 × 0.40 × 0.40 |
| Data collection | |
| Diffractometer | Bruker Kappa Apex2 |
| Absorption correction | Multi-scan<br>*SADABS* (Siemens, 1996) |
| $T_{min}$, $T_{max}$ | 0.01, 0.01 |
| No. of measured, independent and observed [$I > 2.0\sigma(I)$] reflections | 16358, 2945, 2696 |
| $R_{int}$ | 0.064 |
| $(\sin \theta/\lambda)_{max}$ (Å$^{-1}$) | 0.639 |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.029, 0.075, 0.98 |
| No. of reflections | 2937 |
| No. of parameters | 173 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 2.68, −2.67 |

Computer programs: Apex2 (Bruker AXS, 2006), *SHELXS* 86 (Sheldrick, 1986), *CRYSTALS* (Betteridge *et al.*, 2003), *CAMERON* (Watkin *et al.*, 1996).

[Au(III)(*NCN*$^{Me}$)Cl] complex 12 crystal data

| | |
|---|---|
| Crystal data | CCDC (1495706) |
| Chemical formula | $C_{11}H_{12}AuCl_3N_6$ |
| $M_r$ | 531.58 |
| Crystal system, space group | Triclinic, *P*1 |
| Temperature (K) | 150 |
| *a*, *b*, *c* (Å) | 8.3986 (18), 9.666 (2), 10.058 (2) |
| α, β, γ (°) | 93.034 (9), 101.256 (8), 99.441 (9) |
| *V* (Å$^3$) | 786.9 (3) |
| *Z* | 2 |
| Radiation type | Mo *K*α |
| μ (mm$^{-1}$) | 9.86 |
| Crystal size (mm) | 0.20 × 0.20 × 0.06 |
| Data collection | |
| Diffractometer | Bruker Kappa Apex2 |
| Absorption correction | Multi-scan<br>*SADABS* (Siemens, 1996) |
| $T_{min}$, $T_{max}$ | 0.55, 0.55 |
| No. of measured, independent and observed [$I > 2.0\sigma(I)$] reflections | 16689, 3371, 3283 |
| $R_{int}$ | 0.035 |
| $(\sin \theta/\lambda)_{max}$ (Å$^{-1}$) | 0.637 |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.014, 0.034, 1.01 |
| No. of reflections | 3360 |
| No. of parameters | 190 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 1.09, −0.85 |

Computer programs: Apex2 (Bruker AXS, 2006), *SHELXS* 86 (Sheldrick, 1986), *CRYSTALS* (Betteridge *et al.*, 2003), *CAMERON* (Watkin *et al.*, 1996).

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# Chapter 7. Appendices

## 7.1. X-ray crystallographic data

The X-ray diffraction measurements were carried out on a Bruker APEX II diffractometer (Graphite monochromator (ϕ and ω scans)) at 150 K Symmetry related absorption corrections using the program SADABS2 were applied and the data were corrected for Lorentz and polarisation effects using Bruker APEX2 software.[1] All structures were solved by direct methods and the full-matrix least-square refinements were carried out using SHELXL.[2] The molecular graphics were generated using Mercury or ORTEP.[3]

### 7.1.1. Crystal data for ligand 1

Selected geometric parameters (Å)

| | | | |
|---|---|---|---|
| N1A—N2A | 1.355 (3) | C14—C15 | 1.369 (4) |
| N1A—C1 | 1.431 (3) | C15—H15 | 0.9500 |
| N1A—C3A | 1.340 (4) | C15—C16 | 1.397 (3) |
| N1B—C1 | 1.471 (3) | C16—H16 | 0.9500 |
| N1B—C1B | 1.322 (3) | C21—C22 | 1.416 (3) |
| N1B—C3B | 1.374 (3) | C21—C26 | 1.400 (3) |
| N1C—N2C | 1.351 (3) | C21—B1 | 1.633 (3) |
| N1C—C2 | 1.436 (3) | C22—H22 | 0.9500 |
| N1C—C3C | 1.348 (3) | C22—C23 | 1.375 (4) |
| N2A—C1A | 1.328 (4) | C23—H23 | 0.9500 |
| N2B—C1B | 1.325 (3) | C23—C24 | 1.386 (3) |
| N2B—C2 | 1.468 (3) | C24—H24 | 0.9500 |
| N2B—C2B | 1.374 (3) | C24—C25 | 1.382 (3) |
| N2C—C1C | 1.322 (4) | C25—H25 | 0.9500 |
| C1—H1A | 0.9900 | C25—C26 | 1.387 (3) |
| C1—H1B | 0.9900 | C26—H26 | 0.9500 |
| C1A—H1AA | 0.9500 | C31—C32 | 1.395 (3) |
| C1A—C2A | 1.383 (5) | C31—C36 | 1.404 (3) |
| C1B—H1BA | 0.9500 | C31—B1 | 1.649 (3) |
| C1C—H1C | 0.9500 | C32—H32 | 0.9500 |
| C1C—C2C | 1.390 (4) | C32—C33 | 1.390 (3) |
| C2—H2A | 0.9900 | C33—H33 | 0.9500 |
| C2—H2B | 0.9900 | C33—C34 | 1.376 (3) |
| C2A—H2AA | 0.9500 | C34—H34 | 0.9500 |

| | | | |
|---|---|---|---|
| C2A—C3A | 1.356 (4) | C34—C35 | 1.390 (3) |
| C2B—H2BA | 0.9500 | C35—H35 | 0.9500 |
| C2B—C3B | 1.343 (3) | C35—C36 | 1.382 (3) |
| C2C—H2C | 0.9500 | C36—H36 | 0.9500 |
| C2C—C3C | 1.354 (4) | C41—C42 | 1.393 (3) |
| C3A—H3A | 0.9500 | C41—C46 | 1.406 (3) |
| C3B—H3B | 0.9500 | C41—B1 | 1.648 (3) |
| C3C—H3C | 0.9500 | C42—H42 | 0.9500 |
| C11—C12 | 1.399 (4) | C42—C43 | 1.392 (3) |
| C11—C16 | 1.396 (3) | C43—H43 | 0.9500 |
| C11—B1 | 1.648 (3) | C43—C44 | 1.377 (3) |
| C12—H12 | 0.9500 | C44—H44 | 0.9500 |
| C12—C13 | 1.389 (3) | C44—C45 | 1.376 (4) |
| C13—H13 | 0.9500 | C45—H45 | 0.9500 |
| C13—C14 | 1.379 (4) | C45—C46 | 1.391 (3) |
| C14—H14 | 0.9500 | C46—H46 | 0.9500 |

Selected geometric parameters (º)

| | | | |
|---|---|---|---|
| N2A—N1A—C1 | 118.4 (2) | C14—C15—C16 | 120.3 (2) |
| C3A—N1A—N2A | 112.5 (2) | C16—C15—H15 | 119.9 |
| C3A—N1A—C1 | 128.6 (2) | C11—C16—C15 | 122.6 (2) |
| C1B—N1B—C1 | 125.5 (2) | C11—C16—H16 | 118.7 |
| C1B—N1B—C3B | 109.52 (19) | C15—C16—H16 | 118.7 |
| C3B—N1B—C1 | 124.8 (2) | C22—C21—B1 | 120.69 (19) |
| N2C—N1C—C2 | 118.7 (2) | C26—C21—C22 | 114.4 (2) |
| C3C—N1C—N2C | 112.3 (2) | C26—C21—B1 | 124.71 (19) |
| C3C—N1C—C2 | 128.7 (2) | C21—C22—H22 | 118.5 |
| C1A—N2A—N1A | 103.5 (2) | C23—C22—C21 | 123.0 (2) |
| C1B—N2B—C2 | 123.7 (2) | C23—C22—H22 | 118.5 |
| C1B—N2B—C2B | 109.3 (2) | C22—C23—H23 | 119.8 |
| C2B—N2B—C2 | 126.1 (2) | C22—C23—C24 | 120.3 (2) |
| C1C—N2C—N1C | 103.7 (2) | C24—C23—H23 | 119.8 |
| N1A—C1—N1B | 111.31 (18) | C23—C24—H24 | 120.6 |
| N1A—C1—H1A | 109.4 | C25—C24—C23 | 118.8 (2) |
| N1A—C1—H1B | 109.4 | C25—C24—H24 | 120.6 |
| N1B—C1—H1A | 109.4 | C24—C25—H25 | 119.9 |
| N1B—C1—H1B | 109.4 | C24—C25—C26 | 120.2 (2) |
| H1A—C1—H1B | 108.0 | C26—C25—H25 | 119.9 |
| N2A—C1A—H1AA | 124.0 | C21—C26—H26 | 118.4 |
| N2A—C1A—C2A | 112.0 (3) | C25—C26—C21 | 123.1 (2) |

| | | | |
|---|---|---|---|
| C2A—C1A—H1AA | 124.0 | C25—C26—H26 | 118.4 |
| N1B—C1B—N2B | 107.6 (2) | C32—C31—C36 | 115.27 (18) |
| N1B—C1B—H1BA | 126.2 | C32—C31—B1 | 124.00 (18) |
| N2B—C1B—H1BA | 126.2 | C36—C31—B1 | 120.64 (19) |
| N2C—C1C—H1C | 123.8 | C31—C32—H32 | 118.7 |
| N2C—C1C—C2C | 112.3 (3) | C33—C32—C31 | 122.5 (2) |
| C2C—C1C—H1C | 123.8 | C33—C32—H32 | 118.7 |
| N1C—C2—N2B | 108.9 (2) | C32—C33—H33 | 119.7 |
| N1C—C2—H2A | 109.9 | C34—C33—C32 | 120.6 (2) |
| N1C—C2—H2B | 109.9 | C34—C33—H33 | 119.7 |
| N2B—C2—H2A | 109.9 | C33—C34—H34 | 120.7 |
| N2B—C2—H2B | 109.9 | C33—C34—C35 | 118.6 (2) |
| H2A—C2—H2B | 108.3 | C35—C34—H34 | 120.7 |
| C1A—C2A—H2AA | 127.3 | C34—C35—H35 | 119.9 |
| C3A—C2A—C1A | 105.4 (3) | C36—C35—C34 | 120.2 (2) |
| C3A—C2A—H2AA | 127.3 | C36—C35—H35 | 119.9 |
| N2B—C2B—H2BA | 126.6 | C31—C36—H36 | 118.6 |
| C3B—C2B—N2B | 106.9 (2) | C35—C36—C31 | 122.8 (2) |
| C3B—C2B—H2BA | 126.6 | C35—C36—H36 | 118.6 |
| C1C—C2C—H2C | 127.6 | C42—C41—C46 | 115.15 (19) |
| C3C—C2C—C1C | 104.9 (2) | C42—C41—B1 | 125.10 (18) |
| C3C—C2C—H2C | 127.6 | C46—C41—B1 | 119.74 (19) |
| N1A—C3A—C2A | 106.6 (3) | C41—C42—H42 | 118.5 |
| N1A—C3A—H3A | 126.7 | C43—C42—C41 | 123.0 (2) |
| C2A—C3A—H3A | 126.7 | C43—C42—H42 | 118.5 |
| N1B—C3B—H3B | 126.7 | C42—C43—H43 | 120.0 |
| C2B—C3B—N1B | 106.7 (2) | C44—C43—C42 | 119.9 (2) |
| C2B—C3B—H3B | 126.7 | C44—C43—H43 | 120.0 |
| N1C—C3C—C2C | 106.9 (2) | C43—C44—H44 | 120.4 |
| N1C—C3C—H3C | 126.6 | C45—C44—C43 | 119.3 (2) |
| C2C—C3C—H3C | 126.6 | C45—C44—H44 | 120.4 |
| C12—C11—B1 | 119.6 (2) | C44—C45—H45 | 119.9 |
| C16—C11—C12 | 115.0 (2) | C44—C45—C46 | 120.3 (2) |
| C16—C11—B1 | 125.4 (2) | C46—C45—H45 | 119.9 |
| C11—C12—H12 | 118.6 | C41—C46—H46 | 118.8 |
| C13—C12—C11 | 122.8 (2) | C45—C46—C41 | 122.4 (2) |
| C13—C12—H12 | 118.6 | C45—C46—H46 | 118.8 |
| C12—C13—H13 | 119.9 | C11—B1—C31 | 109.86 (17) |
| C14—C13—C12 | 120.1 (3) | C11—B1—C41 | 108.07 (16) |
| C14—C13—H13 | 119.9 | C21—B1—C11 | 113.13 (18) |
| C13—C14—H14 | 120.4 | C21—B1—C31 | 103.43 (16) |

| | | | |
|---|---|---|---|
| C15—C14—C13 | 119.1 (2) | C21—B1—C41 | 110.39 (18) |
| C15—C14—H14 | 120.4 | C41—B1—C31 | 111.99 (17) |
| C14—C15—H15 | 119.9 | | |

Selected geometric parameters, torsion angles (º)

| | | | |
|---|---|---|---|
| N1A—N2A—C1A—C2A | -0.2 (3) | C22—C21—C26—C25 | -0.9 (3) |
| N1C—N2C—C1C—C2C | 0.0 (3) | C22—C21—B1—C11 | 57.0 (2) |
| N2A—N1A—C1—N1B | -81.2 (3) | C22—C21—B1—C31 | -61.8 (2) |
| N2A—N1A—C3A—C2A | -0.9 (3) | C22—C21—B1—C41 | 178.21 (18) |
| N2A—C1A—C2A—C3A | -0.3 (3) | C22—C23—C24—C25 | -1.0 (3) |
| N2B—C2B—C3B—N1B | -0.2 (3) | C23—C24—C25—C26 | 1.8 (3) |
| N2C—N1C—C2—N2B | 62.2 (3) | C24—C25—C26—C21 | -0.9 (3) |
| N2C—N1C—C3C—C2C | 0.9 (3) | C26—C21—C22—C23 | 1.7 (3) |
| N2C—C1C—C2C—C3C | 0.5 (4) | C26—C21—B1—C11 | -127.8 (2) |
| C1—N1A—N2A—C1A | 173.3 (2) | C26—C21—B1—C31 | 113.4 (2) |
| C1—N1A—C3A—C2A | -172.5 (2) | C26—C21—B1—C41 | -6.6 (3) |
| C1—N1B—C1B—N2B | -176.9 (2) | C31—C32—C33—C34 | 0.0 (4) |
| C1—N1B—C3B—C2B | 177.0 (2) | C32—C31—C36—C35 | 1.6 (3) |
| C1A—C2A—C3A—N1A | 0.7 (3) | C32—C31—B1—C11 | -9.9 (3) |
| C1B—N1B—C1—N1A | -124.7 (3) | C32—C31—B1—C21 | 111.1 (2) |
| C1B—N1B—C3B—C2B | 0.4 (3) | C32—C31—B1—C41 | -130.0 (2) |
| C1B—N2B—C2—N1C | -93.2 (3) | C32—C33—C34—C35 | -0.5 (4) |
| C1B—N2B—C2B—C3B | 0.0 (3) | C33—C34—C35—C36 | 1.6 (4) |
| C1C—C2C—C3C—N1C | -0.8 (3) | C34—C35—C36—C31 | -2.2 (4) |
| C2—N1C—N2C—C1C | -174.5 (2) | C36—C31—C32—C33 | -0.5 (3) |
| C2—N1C—C3C—C2C | 174.0 (2) | C36—C31—B1—C11 | 173.8 (2) |

| | | | |
|---|---|---|---|
| C2—N2B—C1B—N1B | 170.2 (2) | C36—C31—B1—C21 | -65.2 (2) |
| C2—N2B—C2B—C3B | -169.7 (2) | C36—C31—B1—C41 | 53.7 (3) |
| C2B—N2B—C1B—N1B | 0.2 (3) | C41—C42—C43—C44 | 0.3 (3) |
| C2B—N2B—C2—N1C | 75.1 (3) | C42—C41—C46—C45 | -1.6 (3) |
| C3A—N1A—N2A—C1A | 0.7 (3) | C42—C41—B1—C11 | -118.2 (2) |
| C3A—N1A—C1—N1B | 90.0 (3) | C42—C41—B1—C21 | 117.6 (2) |
| C3B—N1B—C1—N1A | 59.3 (3) | C42—C41—B1—C31 | 3.0 (3) |
| C3B—N1B—C1B—N2B | -0.4 (3) | C42—C43—C44—C45 | -0.9 (3) |
| C3C—N1C—N2C—C1C | -0.6 (3) | C43—C44—C45—C46 | 0.2 (4) |
| C3C—N1C—C2—N2B | -110.6 (3) | C44—C45—C46—C41 | 1.1 (4) |
| C11—C12—C13—C14 | 0.8 (4) | C46—C41—C42—C43 | 0.9 (3) |
| C12—C11—C16—C15 | 1.1 (3) | C46—C41—B1—C11 | 62.1 (3) |
| C12—C11—B1—C21 | 176.16 (18) | C46—C41—B1—C21 | -62.1 (2) |
| C12—C11—B1—C31 | -68.8 (2) | C46—C41—B1—C31 | -176.73 (19) |
| C12—C11—B1—C41 | 53.6 (2) | B1—C11—C12—C13 | 176.6 (2) |
| C12—C13—C14—C15 | 0.6 (4) | B1—C11—C16—C15 | -177.0 (2) |
| C13—C14—C15—C16 | -1.1 (4) | B1—C21—C22—C23 | 177.4 (2) |
| C14—C15—C16—C11 | 0.3 (4) | B1—C21—C26—C25 | -176.35 (19) |
| C16—C11—C12—C13 | -1.6 (3) | B1—C31—C32—C33 | -177.0 (2) |
| C16—C11—B1—C21 | -5.9 (3) | B1—C31—C36—C35 | 178.2 (2) |
| C16—C11—B1—C31 | 109.1 (2) | B1—C41—C42—C43 | -178.8 (2) |
| C16—C11—B1—C41 | -128.4 (2) | B1—C41—C46—C45 | 178.1 (2) |
| C21—C22—C23—C24 | -0.8 (3) | | |

### 7.1.2. Crystal data for ligand 1c

#### Selected geometric parameters (Å)

| | | | |
|---|---|---|---|
| N1A—N2A | 1.3534 (18) | C13—H13 | 0.9500 |

| | | | |
|---|---|---|---|
| N1A—C1 | 1.4502 (19) | C13—C14 | 1.387 (2) |
| N1A—C3A | 1.3495 (19) | C14—H14 | 0.9500 |
| N1B—C1B | 1.3280 (18) | C14—C15 | 1.379 (2) |
| N1B—C2 | 1.4690 (19) | C15—H15 | 0.9500 |
| N1B—C3B | 1.3814 (18) | C15—C16 | 1.391 (2) |
| N1C—N2C | 1.3556 (19) | C16—H16 | 0.9500 |
| N1C—C3C | 1.348 (2) | C21—C22 | 1.404 (2) |
| N1C—C4 | 1.453 (2) | C21—C26 | 1.400 (2) |
| N2A—C1A | 1.331 (2) | C21—B1 | 1.646 (2) |
| N2B—C1B | 1.3235 (19) | C22—H22 | 0.9500 |
| N2B—C2B | 1.3777 (19) | C22—C23 | 1.389 (2) |
| N2B—C3 | 1.4603 (19) | C23—H23 | 0.9500 |
| N2C—C1C | 1.329 (2) | C23—C24 | 1.376 (2) |
| C1—H1A | 0.9900 | C24—H24 | 0.9500 |
| C1—H1B | 0.9900 | C24—C25 | 1.383 (2) |
| C1—C2 | 1.510 (2) | C25—H25 | 0.9500 |
| C1A—H1AA | 0.9500 | C25—C26 | 1.393 (2) |
| C1A—C2A | 1.387 (2) | C26—H26 | 0.9500 |
| C1B—H1BA | 0.9500 | C31—C32 | 1.400 (2) |
| C1C—H1C | 0.9500 | C31—C36 | 1.405 (2) |
| C1C—C2C | 1.392 (3) | C31—B1 | 1.643 (2) |
| C2—H2A | 0.9900 | C32—H32 | 0.9500 |
| C2—H2B | 0.9900 | C32—C33 | 1.393 (2) |
| C2A—H2AA | 0.9500 | C33—H33 | 0.9500 |
| C2A—C3A | 1.366 (2) | C33—C34 | 1.381 (2) |
| C2B—H2BA | 0.9500 | C34—H34 | 0.9500 |
| C2B—C3B | 1.341 (2) | C34—C35 | 1.383 (2) |
| C2C—H2C | 0.9500 | C35—H35 | 0.9500 |
| C2C—C3C | 1.370 (3) | C35—C36 | 1.389 (2) |
| C3—H3A | 0.9900 | C36—H36 | 0.9500 |
| C3—H3B | 0.9900 | C41—C42 | 1.398 (2) |
| C3—C4 | 1.516 (2) | C41—C46 | 1.400 (2) |
| C3A—H3AA | 0.9500 | C41—B1 | 1.642 (2) |
| C3B—H3BA | 0.9500 | C42—H42 | 0.9500 |
| C3C—H3C | 0.9500 | C42—C43 | 1.393 (2) |
| C4—H4A | 0.9900 | C43—H43 | 0.9500 |
| C4—H4B | 0.9900 | C43—C44 | 1.379 (2) |
| C11—C12 | 1.402 (2) | C44—H44 | 0.9500 |
| C11—C16 | 1.403 (2) | C44—C45 | 1.383 (2) |
| C11—B1 | 1.644 (2) | C45—H45 | 0.9500 |
| C12—H12 | 0.9500 | C45—C46 | 1.385 (2) |

| | | | |
|---|---|---|---|
| C12—C13 | 1.391 (2) | C46—H46 | 0.9500 |

Selected geometric parameters (º)

| | | | |
|---|---|---|---|
| N2A—N1A—C1 | 119.50 (12) | C14—C13—C12 | 120.12 (15) |
| C3A—N1A—N2A | 112.19 (13) | C14—C13—H13 | 119.9 |
| C3A—N1A—C1 | 127.94 (13) | C13—C14—H14 | 120.6 |
| C1B—N1B—C2 | 124.65 (12) | C15—C14—C13 | 118.88 (15) |
| C1B—N1B—C3B | 108.28 (13) | C15—C14—H14 | 120.6 |
| C3B—N1B—C2 | 126.82 (12) | C14—C15—H15 | 119.8 |
| N2C—N1C—C4 | 119.49 (13) | C14—C15—C16 | 120.41 (15) |
| C3C—N1C—N2C | 111.85 (14) | C16—C15—H15 | 119.8 |
| C3C—N1C—C4 | 127.90 (15) | C11—C16—H16 | 118.7 |
| C1A—N2A—N1A | 103.98 (13) | C15—C16—C11 | 122.61 (15) |
| C1B—N2B—C2B | 108.50 (13) | C15—C16—H16 | 118.7 |
| C1B—N2B—C3 | 125.58 (13) | C22—C21—B1 | 121.60 (13) |
| C2B—N2B—C3 | 125.81 (13) | C26—C21—C22 | 114.85 (13) |
| C1C—N2C—N1C | 104.38 (14) | C26—C21—B1 | 123.16 (13) |
| N1A—C1—H1A | 109.1 | C21—C22—H22 | 118.5 |
| N1A—C1—H1B | 109.1 | C23—C22—C21 | 122.99 (15) |
| N1A—C1—C2 | 112.46 (13) | C23—C22—H22 | 118.5 |
| H1A—C1—H1B | 107.8 | C22—C23—H23 | 119.8 |
| C2—C1—H1A | 109.1 | C24—C23—C22 | 120.31 (15) |
| C2—C1—H1B | 109.1 | C24—C23—H23 | 119.8 |
| N2A—C1A—H1AA | 124.0 | C23—C24—H24 | 120.6 |
| N2A—C1A—C2A | 112.06 (15) | C23—C24—C25 | 118.83 (15) |
| C2A—C1A—H1AA | 124.0 | C25—C24—H24 | 120.6 |
| N1B—C1B—H1BA | 125.6 | C24—C25—H25 | 119.8 |
| N2B—C1B—N1B | 108.84 (13) | C24—C25—C26 | 120.36 (16) |
| N2B—C1B—H1BA | 125.6 | C26—C25—H25 | 119.8 |
| N2C—C1C—H1C | 124.0 | C21—C26—H26 | 118.7 |
| N2C—C1C—C2C | 111.90 (16) | C25—C26—C21 | 122.65 (15) |
| C2C—C1C—H1C | 124.0 | C25—C26—H26 | 118.7 |
| N1B—C2—C1 | 113.24 (12) | C32—C31—C36 | 114.91 (13) |
| N1B—C2—H2A | 108.9 | C32—C31—B1 | 122.76 (13) |
| N1B—C2—H2B | 108.9 | C36—C31—B1 | 122.11 (13) |
| C1—C2—H2A | 108.9 | C31—C32—H32 | 118.5 |
| C1—C2—H2B | 108.9 | C33—C32—C31 | 123.04 (15) |
| H2A—C2—H2B | 107.7 | C33—C32—H32 | 118.5 |
| C1A—C2A—H2AA | 127.5 | C32—C33—H33 | 120.0 |
| C3A—C2A—C1A | 105.05 (14) | C34—C33—C32 | 120.08 (16) |

| | | | |
|---|---|---|---|
| C3A—C2A—H2AA | 127.5 | C34—C33—H33 | 120.0 |
| N2B—C2B—H2BA | 126.4 | C33—C34—H34 | 120.6 |
| C3B—C2B—N2B | 107.28 (13) | C33—C34—C35 | 118.82 (15) |
| C3B—C2B—H2BA | 126.4 | C35—C34—H34 | 120.6 |
| C1C—C2C—H2C | 127.6 | C34—C35—H35 | 119.8 |
| C3C—C2C—C1C | 104.79 (16) | C34—C35—C36 | 120.47 (15) |
| C3C—C2C—H2C | 127.6 | C36—C35—H35 | 119.8 |
| N2B—C3—H3A | 109.2 | C31—C36—H36 | 118.7 |
| N2B—C3—H3B | 109.2 | C35—C36—C31 | 122.66 (15) |
| N2B—C3—C4 | 111.88 (13) | C35—C36—H36 | 118.7 |
| H3A—C3—H3B | 107.9 | C42—C41—C46 | 115.17 (13) |
| C4—C3—H3A | 109.2 | C42—C41—B1 | 125.96 (13) |
| C4—C3—H3B | 109.2 | C46—C41—B1 | 118.73 (12) |
| N1A—C3A—C2A | 106.72 (15) | C41—C42—H42 | 118.9 |
| N1A—C3A—H3AA | 126.6 | C43—C42—C41 | 122.22 (14) |
| C2A—C3A—H3AA | 126.6 | C43—C42—H42 | 118.9 |
| N1B—C3B—H3BA | 126.5 | C42—C43—H43 | 119.7 |
| C2B—C3B—N1B | 107.10 (13) | C44—C43—C42 | 120.67 (14) |
| C2B—C3B—H3BA | 126.5 | C44—C43—H43 | 119.7 |
| N1C—C3C—C2C | 107.07 (16) | C43—C44—H44 | 120.6 |
| N1C—C3C—H3C | 126.5 | C43—C44—C45 | 118.72 (14) |
| C2C—C3C—H3C | 126.5 | C45—C44—H44 | 120.6 |
| N1C—C4—C3 | 109.05 (13) | C44—C45—H45 | 120.0 |
| N1C—C4—H4A | 109.9 | C44—C45—C46 | 120.03 (14) |
| N1C—C4—H4B | 109.9 | C46—C45—H45 | 120.0 |
| C3—C4—H4A | 109.9 | C41—C46—H46 | 118.4 |
| C3—C4—H4B | 109.9 | C45—C46—C41 | 123.16 (14) |
| H4A—C4—H4B | 108.3 | C45—C46—H46 | 118.4 |
| C12—C11—C16 | 115.18 (13) | C11—B1—C21 | 112.20 (11) |
| C12—C11—B1 | 120.17 (13) | C31—B1—C11 | 110.81 (12) |
| C16—C11—B1 | 124.58 (13) | C31—B1—C21 | 103.41 (11) |
| C11—C12—H12 | 118.6 | C41—B1—C11 | 105.56 (11) |
| C13—C12—C11 | 122.74 (15) | C41—B1—C21 | 111.57 (12) |
| C13—C12—H12 | 118.6 | C41—B1—C31 | 113.48 (11) |
| C12—C13—H13 | 119.9 | | |

Selected geometric parameters, torsion angles (º)

| | | | |
|---|---|---|---|
| N1A—N2A—C1A—C2A | 0.07 (18) | C21—C22—C23—C24 | -1.2 (2) |
| N1A—C1—C2—N1B | 65.58 (17) | C22—C21—C26—C25 | 0.3 (2) |

| | | | |
|---|---|---|---|
| N1C—N2C—C1C—C2C | 0.42 (18) | C22—C21—B1—C11 | 43.49 (18) |
| N2A—N1A—C1—C2 | -101.96 (15) | C22—C21—B1—C31 | -75.97 (16) |
| N2A—N1A—C3A—C2A | -0.48 (18) | C22—C21—B1—C41 | 161.71 (13) |
| N2A—C1A—C2A—C3A | -0.3 (2) | C22—C23—C24—C25 | 0.4 (2) |
| N2B—C2B—C3B—N1B | 0.44 (17) | C23—C24—C25—C26 | 0.7 (3) |
| N2B—C3—C4—N1C | -177.50 (12) | C24—C25—C26—C21 | -1.1 (3) |
| N2C—N1C—C3C—C2C | 1.00 (19) | C26—C21—C22—C23 | 0.9 (2) |
| N2C—N1C—C4—C3 | 93.56 (16) | C26—C21—B1—C11 | -144.01 (14) |
| N2C—C1C—C2C—C3C | 0.2 (2) | C26—C21—B1—C31 | 96.53 (16) |
| C1—N1A—N2A—C1A | 173.85 (13) | C26—C21—B1—C41 | -25.79 (19) |
| C1—N1A—C3A—C2A | -173.40 (15) | C31—C32—C33—C34 | -0.7 (2) |
| C1A—C2A—C3A—N1A | 0.48 (19) | C32—C31—C36—C35 | 2.1 (2) |
| C1B—N1B—C2—C1 | 118.84 (16) | C32—C31—B1—C11 | -21.50 (18) |
| C1B—N1B—C3B—C2B | -0.41 (17) | C32—C31—B1—C21 | 98.91 (15) |
| C1B—N2B—C2B—C3B | -0.32 (17) | C32—C31—B1—C41 | -140.05 (13) |
| C1B—N2B—C3—C4 | -101.15 (17) | C32—C33—C34—C35 | 1.1 (2) |
| C1C—C2C—C3C—N1C | -0.68 (19) | C33—C34—C35—C36 | 0.1 (2) |
| C2—N1B—C1B—N2B | 174.85 (13) | C34—C35—C36—C31 | -1.7 (2) |
| C2—N1B—C3B—C2B | -174.90 (14) | C36—C31—C32—C33 | -0.8 (2) |
| C2B—N2B—C1B—N1B | 0.06 (17) | C36—C31—B1—C11 | 164.24 (12) |
| C2B—N2B—C3—C4 | 83.07 (18) | C36—C31—B1—C21 | -75.35 (15) |
| C3—N2B—C1B—N1B | -176.33 (13) | C36—C31—B1—C41 | 45.69 (18) |
| C3—N2B—C2B—C3B | 176.06 (14) | C41—C42—C43—C44 | -1.6 (2) |
| C3A—N1A—N2A—C1A | 0.25 (17) | C42—C41—C46—C45 | -0.6 (2) |
| C3A—N1A—C1—C2 | 70.5 (2) | C42—C41—B1—C11 | -108.34 (15) |
| C3B—N1B—C1B—N2B | 0.21 (17) | C42—C41—B1—C21 | 129.53 (15) |

| | | | |
|---|---|---|---|
| C3B—N1B—C2—C1 | -67.52 (19) | C42—C41—B1—C31 | 13.2 (2) |
| C3C—N1C—N2C—C1C | -0.87 (17) | C42—C43—C44—C45 | 0.0 (2) |
| C3C—N1C—C4—C3 | -75.6 (2) | C43—C44—C45—C46 | 1.3 (2) |
| C4—N1C—N2C—C1C | -171.68 (13) | C44—C45—C46—C41 | -1.0 (2) |
| C4—N1C—C3C—C2C | 170.84 (15) | C46—C41—C42—C43 | 1.9 (2) |
| C11—C12—C13—C14 | 0.6 (2) | C46—C41—B1—C11 | 67.03 (16) |
| C12—C11—C16—C15 | 2.6 (2) | C46—C41—B1—C21 | -55.11 (17) |
| C12—C11—B1—C21 | -164.95 (12) | C46—C41—B1—C31 | -171.44 (12) |
| C12—C11—B1—C31 | -49.92 (17) | B1—C11—C12—C13 | -179.52 (13) |
| C12—C11—B1—C41 | 73.32 (16) | B1—C11—C16—C15 | 179.58 (14) |
| C12—C13—C14—C15 | 1.2 (2) | B1—C21—C22—C23 | 173.95 (14) |
| C13—C14—C15—C16 | -1.0 (2) | B1—C21—C26—C25 | -172.66 (15) |
| C14—C15—C16—C11 | -1.0 (2) | B1—C31—C32—C33 | -175.48 (13) |
| C16—C11—C12—C13 | -2.4 (2) | B1—C31—C36—C35 | 176.73 (13) |
| C16—C11—B1—C21 | 18.23 (19) | B1—C41—C42—C43 | 177.39 (14) |
| C16—C11—B1—C31 | 133.26 (14) | B1—C41—C46—C45 | -176.44 (14) |
| C16—C11—B1—C41 | -103.50 (15) | | |

### 7.1.3. Crystal data for complex 2

#### Selected geometric parameters (Å)

| | | | |
|---|---|---|---|
| Ag1A—C1B1 | 2.080 (4) | N1C6—C2S | 1.430 (5) |
| Ag1A—C1B2 | 2.078 (4) | N1C6—C3C6 | 1.359 (5) |
| N1A1—N2A1 | 1.361 (4) | N2A6—C1A6 | 1.317 (5) |
| N1A1—C1P | 1.434 (5) | N2B6—C1B6 | 1.355 (5) |
| N1A1—C3A1 | 1.349 (5) | N2B6—C2S | 1.462 (5) |
| N1A2—N2A2 | 1.348 (4) | N2B6—C3B6 | 1.378 (4) |
| N1A2—C1P' | 1.438 (5) | N2C6—C1C6 | 1.314 (5) |
| N1A2—C3A2 | 1.336 (5) | C1A6—H1A6 | 0.9500 |
| N1B1—C1B1 | 1.363 (4) | C1A6—C2A6 | 1.375 (5) |
| N1B1—C1P | 1.467 (5) | C1C6—H1C6 | 0.9500 |
| N1B1—C2B1 | 1.380 (4) | C1C6—C2C6 | 1.379 (6) |
| N1B2—C1B2 | 1.360 (5) | C1S—H1SA | 0.9900 |

| | | | |
|---|---|---|---|
| N1B2—C1P' | 1.461 (5) | C1S—H1SB | 0.9900 |
| N1B2—C2B2 | 1.379 (4) | C2A6—H2A6 | 0.9500 |
| N1C1—N2C1 | 1.366 (4) | C2A6—C3A6 | 1.360 (5) |
| N1C1—C2P | 1.444 (5) | C2B6—H2B6 | 0.9500 |
| N1C1—C3C1 | 1.344 (5) | C2B6—C3B6 | 1.332 (5) |
| N1C2—N2C2 | 1.359 (4) | C2C6—H2C6 | 0.9500 |
| N1C2—C2P' | 1.433 (5) | C2C6—C3C6 | 1.349 (6) |
| N1C2—C3C2 | 1.364 (5) | C2S—H2SA | 0.9900 |
| N2A1—C1A1 | 1.317 (5) | C2S—H2SB | 0.9900 |
| N2A2—C1A2 | 1.328 (5) | C3A6—H3A6 | 0.9500 |
| N2B1—C1B1 | 1.357 (5) | C3B6—H3B6 | 0.9500 |
| N2B1—C2P | 1.458 (5) | C3C6—H3C6 | 0.9500 |
| N2B1—C3B1 | 1.381 (4) | C11M—C12M | 1.407 (5) |
| N2B2—C1B2 | 1.351 (4) | C11M—C16M | 1.403 (5) |
| N2B2—C2P' | 1.461 (5) | C11M—B1M | 1.661 (5) |
| N2B2—C3B2 | 1.383 (4) | C12M—H12M | 0.9500 |
| N2C1—C1C1 | 1.309 (6) | C12M—C13M | 1.396 (5) |
| N2C2—C1C2 | 1.320 (5) | C13M—H13M | 0.9500 |
| C1A1—H1A1 | 0.9500 | C13M—C14M | 1.388 (5) |
| C1A1—C2A1 | 1.392 (6) | C14M—H14M | 0.9500 |
| C1A2—H1A2 | 0.9500 | C14M—C15M | 1.381 (5) |
| C1A2—C2A2 | 1.377 (7) | C15M—H15M | 0.9500 |
| C1C1—H1C1 | 0.9500 | C15M—C16M | 1.381 (5) |
| C1C1—C2C1 | 1.356 (7) | C16M—H16M | 0.9500 |
| C1C2—H1C2 | 0.9500 | C21M—C22M | 1.398 (5) |
| C1C2—C2C2 | 1.390 (6) | C21M—C26M | 1.407 (5) |
| C1P—H1PA | 0.9900 | C21M—B1M | 1.641 (6) |
| C1P—H1PB | 0.9900 | C22M—H22M | 0.9500 |
| C1P'—H1PC | 0.9900 | C22M—C23M | 1.396 (5) |
| C1P'—H1PD | 0.9900 | C23M—H23M | 0.9500 |
| C2A1—H2A1 | 0.9500 | C23M—C24M | 1.379 (7) |
| C2A1—C3A1 | 1.355 (5) | C24M—H24M | 0.9500 |
| C2A2—H2A2 | 0.9500 | C24M—C25M | 1.376 (7) |
| C2A2—C3A2 | 1.340 (6) | C25M—H25M | 0.9500 |
| C2B1—H2B1 | 0.9500 | C25M—C26M | 1.387 (6) |
| C2B1—C3B1 | 1.327 (5) | C26M—H26M | 0.9500 |
| C2B2—H2B2 | 0.9500 | C31M—C32M | 1.406 (5) |
| C2B2—C3B2 | 1.337 (5) | C31M—C36M | 1.397 (5) |
| C2C1—H2C1 | 0.9500 | C31M—B1M | 1.634 (6) |
| C2C1—C3C1 | 1.366 (6) | C32M—H32M | 0.9500 |
| C2C2—H2C2 | 0.9500 | C32M—C33M | 1.386 (5) |

| | | | |
|---|---|---|---|
| C2C2—C3C2 | 1.347 (6) | C33M—H33M | 0.9500 |
| C2P—H2PA | 0.9900 | C33M—C34M | 1.377 (5) |
| C2P—H2PB | 0.9900 | C34M—H34M | 0.9500 |
| C2P'—H2PC | 0.9900 | C34M—C35M | 1.378 (5) |
| C2P'—H2PD | 0.9900 | C35M—H35M | 0.9500 |
| C3A1—H3A1 | 0.9500 | C35M—C36M | 1.393 (5) |
| C3A2—H3A2 | 0.9500 | C36M—H36M | 0.9500 |
| C3B1—H3B1 | 0.9500 | C41M—C42M | 1.407 (5) |
| C3B2—H3B2 | 0.9500 | C41M—C46M | 1.397 (5) |
| C3C1—H3C1 | 0.9500 | C41M—B1M | 1.655 (5) |
| C3C2—H3C2 | 0.9500 | C42M—H42M | 0.9500 |
| Ag1C—C1B5$^{i}$ | 2.074 (4) | C42M—C43M | 1.384 (5) |
| Ag1C—C1B5 | 2.074 (4) | C43M—H43M | 0.9500 |
| N1A5—N2A5 | 1.342 (4) | C43M—C44M | 1.376 (5) |
| N1A5—C1R | 1.442 (5) | C44M—H44M | 0.9500 |
| N1A5—C3A5 | 1.350 (5) | C44M—C45M | 1.386 (5) |
| N1B5—C1B5 | 1.352 (5) | C45M—H45M | 0.9500 |
| N1B5—C1R | 1.462 (5) | C45M—C46M | 1.383 (5) |
| N1B5—C2B5 | 1.363 (5) | C46M—H46M | 0.9500 |
| N1C5—N2C5 | 1.361 (5) | C11O—C12O | 1.407 (5) |
| N1C5—C2R | 1.438 (6) | C11O—C16O | 1.397 (5) |
| N1C5—C3C5 | 1.332 (7) | C11O—B11O | 1.643 (5) |
| N2A5—C1A5 | 1.331 (5) | C12O—H12O | 0.9500 |
| N2B5—C1B5 | 1.351 (5) | C12O—C13O | 1.390 (5) |
| N2B5—C2R | 1.461 (5) | C13O—H13O | 0.9500 |
| N2B5—C3B5 | 1.370 (5) | C13O—C14O | 1.361 (6) |
| N2C5—C1C5 | 1.324 (7) | C14O—H14O | 0.9500 |
| C1A5—H1A5 | 0.9500 | C14O—C15O | 1.379 (6) |
| C1A5—C2A5 | 1.398 (6) | C15O—H15O | 0.9500 |
| C1C5—H1C5 | 0.9500 | C15O—C16O | 1.379 (5) |
| C1C5—C2C5 | 1.391 (9) | C16O—H16O | 0.9500 |
| C1R—H1RA | 0.9900 | C21O—C22O | 1.400 (5) |
| C1R—H1RB | 0.9900 | C21O—C26O | 1.407 (5) |
| C2A5—H2A5 | 0.9500 | C21O—B11O | 1.636 (5) |
| C2A5—C3A5 | 1.357 (6) | C22O—H22O | 0.9500 |
| C2B5—H2B5 | 0.9500 | C22O—C23O | 1.386 (5) |
| C2B5—C3B5 | 1.343 (6) | C23O—H23O | 0.9500 |
| C2C5—H2C5 | 0.9500 | C23O—C24O | 1.382 (5) |
| C2C5—C3C5 | 1.368 (7) | C24O—H24O | 0.9500 |
| C2R—H2RA | 0.9900 | C24O—C25O | 1.381 (5) |
| C2R—H2RB | 0.9900 | C25O—H25O | 0.9500 |

| | | | |
|---|---|---|---|
| C3A5—H3A5 | 0.9500 | C25O—C26O | 1.385 (5) |
| C3B5—H3B5 | 0.9500 | C26O—H26O | 0.9500 |
| C3C5—H3C5 | 0.9500 | C31O—C32O | 1.412 (5) |
| Ag1B—C1B3 | 2.078 (4) | C31O—C36O | 1.409 (5) |
| Ag1B—C1B4 | 2.070 (4) | C31O—B11O | 1.647 (5) |
| N1A3—N2A3 | 1.353 (4) | C32O—H32O | 0.9500 |
| N1A3—C1Q | 1.426 (5) | C32O—C33O | 1.387 (5) |
| N1A3—C3A3 | 1.359 (5) | C33O—H33O | 0.9500 |
| N1A4—N2A4 | 1.350 (4) | C33O—C34O | 1.383 (5) |
| N1A4—C1Q' | 1.435 (5) | C34O—H34O | 0.9500 |
| N1A4—C3A4 | 1.350 (5) | C34O—C35O | 1.376 (5) |
| N1B3—C1B3 | 1.356 (4) | C35O—H35O | 0.9500 |
| N1B3—C1Q | 1.462 (5) | C35O—C36O | 1.387 (5) |
| N1B3—C2B3 | 1.378 (5) | C36O—H36O | 0.9500 |
| N1B4—C1B4 | 1.347 (4) | C41O—C42O | 1.403 (5) |
| N1B4—C1Q' | 1.462 (5) | C41O—C46O | 1.395 (5) |
| N1B4—C2B4 | 1.383 (5) | C41O—B11O | 1.649 (6) |
| N1C3—N2C3 | 1.356 (5) | C42O—H42O | 0.9500 |
| N1C3—C2Q | 1.428 (5) | C42O—C43O | 1.383 (5) |
| N1C3—C3C3 | 1.342 (5) | C43O—H43O | 0.9500 |
| N1C4—N2C4 | 1.356 (5) | C43O—C44O | 1.385 (5) |
| N1C4—C2Q' | 1.436 (5) | C44O—H44O | 0.9500 |
| N1C4—C3C4 | 1.334 (6) | C44O—C45O | 1.376 (5) |
| N2A3—C1A3 | 1.319 (5) | C45O—H45O | 0.9500 |
| N2A4—C1A4 | 1.314 (5) | C45O—C46O | 1.392 (5) |
| N2B3—C1B3 | 1.353 (4) | C46O—H46O | 0.9500 |
| N2B3—C2Q | 1.455 (4) | C11N—C12N | 1.397 (5) |
| N2B3—C3B3 | 1.372 (5) | C11N—C16N | 1.411 (5) |
| N2B4—C1B4 | 1.348 (5) | C11N—B1N | 1.644 (5) |
| N2B4—C2Q' | 1.460 (5) | C12N—H12N | 0.9500 |
| N2B4—C3B4 | 1.378 (5) | C12N—C13N | 1.395 (5) |
| N2C3—C1C3 | 1.315 (6) | C13N—H13N | 0.9500 |
| N2C4—C1C4 | 1.325 (7) | C13N—C14N | 1.372 (5) |
| C1A3—H1A3 | 0.9500 | C14N—H14N | 0.9500 |
| C1A3—C2A3 | 1.394 (5) | C14N—C15N | 1.385 (5) |
| C1A4—H1A4 | 0.9500 | C15N—H15N | 0.9500 |
| C1A4—C2A4 | 1.387 (6) | C15N—C16N | 1.379 (5) |
| C1C3—H1C3 | 0.9500 | C16N—H16N | 0.9500 |
| C1C3—C2C3 | 1.373 (8) | C21N—C22N | 1.406 (5) |
| C1C4—H1C4 | 0.9500 | C21N—C26N | 1.394 (5) |
| C1C4—C2C4 | 1.373 (8) | C21N—B1N | 1.630 (5) |

| | | | |
|---|---|---|---|
| C1Q—H1Q | 0.9500 | C22N—H22N | 0.9500 |
| C1Q'—H1QA | 0.9900 | C22N—C23N | 1.392 (5) |
| C1Q'—H1QB | 0.9900 | C23N—H23N | 0.9500 |
| C2A3—H2A3 | 0.9500 | C23N—C24N | 1.363 (6) |
| C2A3—C3A3 | 1.352 (6) | C24N—H24N | 0.9500 |
| C2A4—H2A4 | 0.9500 | C24N—C25N | 1.371 (6) |
| C2A4—C3A4 | 1.344 (6) | C25N—H25N | 0.9500 |
| C2B3—H2B3 | 0.9500 | C25N—C26N | 1.386 (5) |
| C2B3—C3B3 | 1.346 (6) | C26N—H26N | 0.9500 |
| C2B4—H2B4 | 0.9500 | C31N—C32N | 1.391 (5) |
| C2B4—C3B4 | 1.332 (5) | C31N—C36N | 1.405 (5) |
| C2C3—H2C3 | 0.9500 | C31N—B1N | 1.645 (5) |
| C2C3—C3C3 | 1.367 (6) | C32N—H32N | 0.9500 |
| C2C4—H2C4 | 0.9500 | C32N—C33N | 1.391 (5) |
| C2C4—C3C4 | 1.370 (7) | C33N—H33N | 0.9500 |
| C2Q—H2QA | 0.9900 | C33N—C34N | 1.380 (5) |
| C2Q—H2QB | 0.9900 | C34N—H34N | 0.9500 |
| C2Q'—H2QC | 0.9900 | C34N—C35N | 1.392 (5) |
| C2Q'—H2QD | 0.9900 | C35N—H35N | 0.9500 |
| C3A3—H3A3 | 0.9500 | C35N—C36N | 1.387 (5) |
| C3A4—H3A4 | 0.9500 | C36N—H36N | 0.9500 |
| C3B3—H3B3 | 0.9500 | C41N—C42N | 1.397 (5) |
| C3B4—H3B4 | 0.9500 | C41N—C46N | 1.400 (5) |
| C3C3—H3C3 | 0.9500 | C41N—B1N | 1.648 (6) |
| C3C4—H3C4 | 0.9500 | C42N—H42N | 0.9500 |
| Ag1D—C1B6$^{ii}$ | 2.081 (4) | C42N—C43N | 1.384 (5) |
| Ag1D—C1B6 | 2.081 (4) | C43N—H43N | 0.9500 |
| N1A6—N2A6 | 1.362 (4) | C43N—C44N | 1.382 (5) |
| N1A6—C1S | 1.438 (5) | C44N—H44N | 0.9500 |
| N1A6—C3A6 | 1.355 (5) | C44N—C45N | 1.386 (5) |
| N1B6—C1B6 | 1.360 (5) | C45N—H45N | 0.9500 |
| N1B6—C1S | 1.458 (5) | C45N—C46N | 1.380 (5) |
| N1B6—C2B6 | 1.381 (4) | C46N—H46N | 0.9500 |
| N1C6—N2C6 | 1.359 (4) | | |

Symmetry code(s): (i) -*x*, -*y*+1, -*z*+2; (ii) -*x*+1, -*y*+1, -*z*+3.

## Selected geometric parameters (º)

| | | | |
|---|---|---|---|
| C1B2—Ag1A—C1B1 | 174.32 (15) | C1B6—N2B6—C3B6 | 111.2 (3) |
| N2A1—N1A1—C1P | 119.0 (3) | C3B6—N2B6—C2S | 124.8 (3) |
| C3A1—N1A1—N2A1 | 111.8 (3) | C1C6—N2C6—N1C6 | 104.6 (4) |

| | | |
|---|---|---|
| C3A1—N1A1—C1P | 129.2 | (4) |
| N2A2—N1A2—C1P' | 119.1 | (3) |
| C3A2—N1A2—N2A2 | 112.5 | (4) |
| C3A2—N1A2—C1P' | 128.4 | (4) |
| C1B1—N1B1—C1P | 124.2 | (3) |
| C1B1—N1B1—C2B1 | 111.3 | (3) |
| C2B1—N1B1—C1P | 124.3 | (3) |
| C1B2—N1B2—C1P' | 123.6 | (3) |
| C1B2—N1B2—C2B2 | 111.6 | (3) |
| C2B2—N1B2—C1P' | 124.8 | (3) |
| N2C1—N1C1—C2P | 119.1 | (3) |
| C3C1—N1C1—N2C1 | 111.9 | (4) |
| C3C1—N1C1—C2P | 128.3 | (4) |
| N2C2—N1C2—C2P' | 119.8 | (3) |
| N2C2—N1C2—C3C2 | 110.9 | (4) |
| C3C2—N1C2—C2P' | 129.1 | (3) |
| C1A1—N2A1—N1A1 | 103.7 | (3) |
| C1A2—N2A2—N1A2 | 102.4 | (4) |
| C1B1—N2B1—C2P | 124.5 | (3) |
| C1B1—N2B1—C3B1 | 111.3 | (3) |
| C3B1—N2B1—C2P | 124.1 | (3) |
| C1B2—N2B2—C2P' | 123.5 | (3) |
| C1B2—N2B2—C3B2 | 111.5 | (3) |
| C3B2—N2B2—C2P' | 124.9 | (3) |
| C1C1—N2C1—N1C1 | 103.4 | (4) |
| C1C2—N2C2—N1C2 | 104.0 | (3) |
| N2A1—C1A1—H1A1 | 123.7 | |
| N2A1—C1A1—C2A1 | 112.7 | (4) |
| C2A1—C1A1—H1A1 | 123.7 | |
| N2A2—C1A2—H1A2 | 123.5 | |
| N2A2—C1A2—C2A2 | 113.1 | (4) |
| C2A2—C1A2—H1A2 | 123.5 | |
| N1B1—C1B1—Ag1A | 128.2 | (3) |
| N2B1—C1B1—Ag1A | 128.3 | (3) |
| N2B1—C1B1—N1B1 | 103.4 | (3) |
| N1B2—C1B2—Ag1A | 127.0 | (3) |
| N2B2—C1B2—Ag1A | 128.3 | (3) |
| N2B2—C1B2—N1B2 | 103.5 | (3) |
| N2C1—C1C1—H1C1 | 123.4 | |
| N2C1—C1C1—C2C1 | 113.1 | (5) |
| C2C1—C1C1—H1C1 | 123.4 | |

| | | |
|---|---|---|
| N2A6—C1A6—H1A6 | 123.6 | |
| N2A6—C1A6—C2A6 | 112.9 | (4) |
| C2A6—C1A6—H1A6 | 123.6 | |
| N1B6—C1B6—Ag1D | 126.0 | (3) |
| N2B6—C1B6—Ag1D | 130.5 | (3) |
| N2B6—C1B6—N1B6 | 103.4 | (3) |
| N2C6—C1C6—H1C6 | 124.0 | |
| N2C6—C1C6—C2C6 | 112.0 | (4) |
| C2C6—C1C6—H1C6 | 124.0 | |
| N1A6—C1S—N1B6 | 113.2 | (3) |
| N1A6—C1S—H1SA | 108.9 | |
| N1A6—C1S—H1SB | 108.9 | |
| N1B6—C1S—H1SA | 108.9 | |
| N1B6—C1S—H1SB | 108.9 | |
| H1SA—C1S—H1SB | 107.7 | |
| C1A6—C2A6—H2A6 | 127.4 | |
| C3A6—C2A6—C1A6 | 105.1 | (4) |
| C3A6—C2A6—H2A6 | 127.4 | |
| N1B6—C2B6—H2B6 | 126.9 | |
| C3B6—C2B6—N1B6 | 106.1 | (3) |
| C3B6—C2B6—H2B6 | 126.9 | |
| C1C6—C2C6—H2C6 | 127.1 | |
| C3C6—C2C6—C1C6 | 105.7 | (4) |
| C3C6—C2C6—H2C6 | 127.1 | |
| N1C6—C2S—N2B6 | 112.3 | (3) |
| N1C6—C2S—H2SA | 109.1 | |
| N1C6—C2S—H2SB | 109.1 | |
| N2B6—C2S—H2SA | 109.1 | |
| N2B6—C2S—H2SB | 109.1 | |
| H2SA—C2S—H2SB | 107.9 | |
| N1A6—C3A6—C2A6 | 106.7 | (4) |
| N1A6—C3A6—H3A6 | 126.6 | |
| C2A6—C3A6—H3A6 | 126.6 | |
| N2B6—C3B6—H3B6 | 126.2 | |
| C2B6—C3B6—N2B6 | 107.5 | (3) |
| C2B6—C3B6—H3B6 | 126.2 | |
| N1C6—C3C6—H3C6 | 126.6 | |
| C2C6—C3C6—N1C6 | 106.8 | (4) |
| C2C6—C3C6—H3C6 | 126.6 | |
| C12M—C11M—B1M | 121.7 | (3) |
| C16M—C11M— | 114.6 | (3) |

| | | | |
|---|---|---|---|
| | | C12M | |
| N2C2—C1C2—H1C2 | 123.6 | C16M—C11M—B1M | 123.7 (3) |
| N2C2—C1C2—C2C2 | 112.7 (4) | C11M—C12M—H12M | 118.5 |
| C2C2—C1C2—H1C2 | 123.6 | C13M—C12M—C11M | 122.9 (4) |
| N1A1—C1P—N1B1 | 112.0 (3) | C13M—C12M—H12M | 118.5 |
| N1A1—C1P—H1PA | 109.2 | C12M—C13M—H13M | 120.0 |
| N1A1—C1P—H1PB | 109.2 | C14M—C13M—C12M | 120.0 (4) |
| N1B1—C1P—H1PA | 109.2 | C14M—C13M—H13M | 120.0 |
| N1B1—C1P—H1PB | 109.2 | C13M—C14M—H14M | 120.7 |
| H1PA—C1P—H1PB | 107.9 | C15M—C14M—C13M | 118.7 (4) |
| N1A2—C1P'—N1B2 | 113.1 (3) | C15M—C14M—H14M | 120.7 |
| N1A2—C1P'—H1PC | 108.9 | C14M—C15M—H15M | 119.7 |
| N1A2—C1P'—H1PD | 108.9 | C14M—C15M—C16M | 120.6 (4) |
| N1B2—C1P'—H1PC | 108.9 | C16M—C15M—H15M | 119.7 |
| N1B2—C1P'—H1PD | 108.9 | C11M—C16M—H16M | 118.4 |
| H1PC—C1P'—H1PD | 107.8 | C15M—C16M—C11M | 123.2 (4) |
| C1A1—C2A1—H2A1 | 127.7 | C15M—C16M—H16M | 118.4 |
| C3A1—C2A1—C1A1 | 104.6 (4) | C22M—C21M—C26M | 115.3 (4) |
| C3A1—C2A1—H2A1 | 127.7 | C22M—C21M—B1M | 120.4 (4) |
| C1A2—C2A2—H2A2 | 127.8 | C26M—C21M—B1M | 124.3 (4) |
| C3A2—C2A2—C1A2 | 104.4 (5) | C21M—C22M—H22M | 118.5 |
| C3A2—C2A2—H2A2 | 127.8 | C23M—C22M—C21M | 123.1 (4) |
| N1B1—C2B1—H2B1 | 126.6 | C23M—C22M—H22M | 118.5 |
| C3B1—C2B1—N1B1 | 106.9 (3) | C22M—C23M—H23M | 120.4 |
| C3B1—C2B1—H2B1 | 126.6 | C24M—C23M—C22M | 119.1 (5) |
| N1B2—C2B2—H2B2 | 126.7 | C24M—C23M—H23M | 120.4 |

| | | | |
|---|---|---|---|
| C3B2—C2B2—N1B2 | 106.6 (3) | C23M—C24M—H24M | 120.0 |
| C3B2—C2B2—H2B2 | 126.7 | C25M—C24M—C23M | 120.0 (5) |
| C1C1—C2C1—H2C1 | 127.1 | C25M—C24M—H24M | 120.0 |
| C1C1—C2C1—C3C1 | 105.9 (5) | C24M—C25M—H25M | 119.9 |
| C3C1—C2C1—H2C1 | 127.1 | C24M—C25M—C26M | 120.2 (5) |
| C1C2—C2C2—H2C2 | 127.7 | C26M—C25M—H25M | 119.9 |
| C3C2—C2C2—C1C2 | 104.7 (4) | C21M—C26M—H26M | 118.9 |
| C3C2—C2C2—H2C2 | 127.7 | C25M—C26M—C21M | 122.2 (5) |
| N1C1—C2P—N2B1 | 111.8 (3) | C25M—C26M—H26M | 118.9 |
| N1C1—C2P—H2PA | 109.3 | C32M—C31M—B1M | 121.1 (3) |
| N1C1—C2P—H2PB | 109.3 | C36M—C31M—C32M | 114.3 (4) |
| N2B1—C2P—H2PA | 109.3 | C36M—C31M—B1M | 124.5 (3) |
| N2B1—C2P—H2PB | 109.3 | C31M—C32M—H32M | 118.5 |
| H2PA—C2P—H2PB | 107.9 | C33M—C32M—C31M | 123.1 (4) |
| N1C2—C2P'—N2B2 | 112.0 (3) | C33M—C32M—H32M | 118.5 |
| N1C2—C2P'—H2PC | 109.2 | C32M—C33M—H33M | 119.7 |
| N1C2—C2P'—H2PD | 109.2 | C34M—C33M—C32M | 120.6 (4) |
| N2B2—C2P'—H2PC | 109.2 | C34M—C33M—H33M | 119.7 |
| N2B2—C2P'—H2PD | 109.2 | C33M—C34M—H34M | 120.8 |
| H2PC—C2P'—H2PD | 107.9 | C33M—C34M—C35M | 118.5 (4) |
| N1A1—C3A1—C2A1 | 107.2 (4) | C35M—C34M—H34M | 120.8 |
| N1A1—C3A1—H3A1 | 126.4 | C34M—C35M—H35M | 119.8 |
| C2A1—C3A1—H3A1 | 126.4 | C34M—C35M—C36M | 120.4 (4) |
| N1A2—C3A2—C2A2 | 107.6 (4) | C36M—C35M—H35M | 119.8 |
| N1A2—C3A2—H3A2 | 126.2 | C31M—C36M—H36M | 118.4 |

| | | | |
|---|---|---|---|
| C2A2—C3A2—H3A2 | 126.2 | C35M—C36M—C31M | 123.1 (4) |
| N2B1—C3B1—H3B1 | 126.4 | C35M—C36M—H36M | 118.4 |
| C2B1—C3B1—N2B1 | 107.1 (3) | C42M—C41M—B1M | 124.7 (3) |
| C2B1—C3B1—H3B1 | 126.4 | C46M—C41M—C42M | 114.2 (3) |
| N2B2—C3B2—H3B2 | 126.6 | C46M—C41M—B1M | 121.1 (3) |
| C2B2—C3B2—N2B2 | 106.8 (3) | C41M—C42M—H42M | 118.4 |
| C2B2—C3B2—H3B2 | 126.6 | C43M—C42M—C41M | 123.3 (4) |
| N1C1—C3C1—C2C1 | 105.6 (5) | C43M—C42M—H42M | 118.4 |
| N1C1—C3C1—H3C1 | 127.2 | C42M—C43M—H43M | 119.9 |
| C2C1—C3C1—H3C1 | 127.2 | C44M—C43M—C42M | 120.2 (4) |
| N1C2—C3C2—H3C2 | 126.2 | C44M—C43M—H43M | 119.9 |
| C2C2—C3C2—N1C2 | 107.6 (4) | C43M—C44M—H44M | 120.6 |
| C2C2—C3C2—H3C2 | 126.2 | C43M—C44M—C45M | 118.7 (4) |
| C1B5$^{i}$—Ag1C—C1B5 | 180.00 (8) | C45M—C44M—H44M | 120.6 |
| N2A5—N1A5—C1R | 119.2 (3) | C44M—C45M—H45M | 119.9 |
| N2A5—N1A5—C3A5 | 113.1 (4) | C46M—C45M—C44M | 120.2 (4) |
| C3A5—N1A5—C1R | 127.6 (4) | C46M—C45M—H45M | 119.9 |
| C1B5—N1B5—C1R | 124.3 (3) | C41M—C46M—H46M | 118.3 |
| C1B5—N1B5—C2B5 | 112.0 (4) | C45M—C46M—C41M | 123.4 (4) |
| C2B5—N1B5—C1R | 123.7 (4) | C45M—C46M—H46M | 118.3 |
| N2C5—N1C5—C2R | 119.0 (5) | C21M—B1M—C11M | 109.1 (3) |
| C3C5—N1C5—N2C5 | 112.4 (5) | C21M—B1M—C41M | 110.3 (3) |
| C3C5—N1C5—C2R | 128.6 (5) | C31M—B1M—C11M | 107.8 (3) |
| C1A5—N2A5—N1A5 | 103.4 (3) | C31M—B1M—C21M | 110.6 (3) |
| C1B5—N2B5—C2R | 124.5 (3) | C31M—B1M—C41M | 110.1 (3) |
| C1B5—N2B5—C3B5 | 111.7 (4) | C41M—B1M—C11M | 108.9 (3) |
| C3B5—N2B5—C2R | 123.7 (4) | C12O—C11O—B11O | 122.4 (3) |
| C1C5—N2C5—N1C5 | 104.0 (5) | C16O—C11O—C12O | 115.4 (3) |
| N2A5—C1A5—H1A5 | 123.9 | C16O—C11O—B11O | 121.5 (3) |

| | | |
|---|---|---|
| N2A5—C1A5—C2A5 | 112.2 | (4) |
| C2A5—C1A5—H1A5 | 123.9 | |
| N1B5—C1B5—Ag1C | 127.8 | (3) |
| N2B5—C1B5—Ag1C | 128.6 | (3) |
| N2B5—C1B5—N1B5 | 103.3 | (3) |
| N2C5—C1C5—H1C5 | 124.2 | |
| N2C5—C1C5—C2C5 | 111.6 | (6) |
| C2C5—C1C5—H1C5 | 124.2 | |
| N1A5—C1R—N1B5 | 112.6 | (3) |
| N1A5—C1R—H1RA | 109.1 | |
| N1A5—C1R—H1RB | 109.1 | |
| N1B5—C1R—H1RA | 109.1 | |
| N1B5—C1R—H1RB | 109.1 | |
| H1RA—C1R—H1RB | 107.8 | |
| C1A5—C2A5—H2A5 | 127.7 | |
| C3A5—C2A5—C1A5 | 104.7 | (4) |
| C3A5—C2A5—H2A5 | 127.7 | |
| N1B5—C2B5—H2B5 | 126.7 | |
| C3B5—C2B5—N1B5 | 106.5 | (4) |
| C3B5—C2B5—H2B5 | 126.7 | |
| C1C5—C2C5—H2C5 | 127.4 | |
| C3C5—C2C5—C1C5 | 105.1 | (6) |
| C3C5—C2C5—H2C5 | 127.4 | |
| N1C5—C2R—N2B5 | 111.3 | (3) |
| N1C5—C2R—H2RA | 109.4 | |
| N1C5—C2R—H2RB | 109.4 | |
| N2B5—C2R—H2RA | 109.4 | |
| N2B5—C2R—H2RB | 109.4 | |
| H2RA—C2R—H2RB | 108.0 | |
| N1A5—C3A5—C2A5 | 106.6 | (4) |
| N1A5—C3A5—H3A5 | 126.7 | |
| C2A5—C3A5—H3A5 | 126.7 | |
| N2B5—C3B5—H3B5 | 126.8 | |
| C2B5—C3B5—N2B5 | 106.5 | (4) |
| C2B5—C3B5—H3B5 | 126.8 | |
| N1C5—C3C5—C2C5 | 106.8 | (6) |
| N1C5—C3C5—H3C5 | 126.6 | |
| C2C5—C3C5—H3C5 | 126.6 | |
| C1B4—Ag1B—C1B3 | 175.61 | (15) |
| N2A3—N1A3—C1Q | 120.0 | (3) |
| N2A3—N1A3—C3A3 | 111.8 | (3) |

| | | |
|---|---|---|
| C11O—C12O—H12O | 119.2 | |
| C13O—C12O—C11O | 121.6 | (4) |
| C13O—C12O—H12O | 119.2 | |
| C12O—C13O—H13O | 119.6 | |
| C14O—C13O—C12O | 120.8 | (4) |
| C14O—C13O—H13O | 119.6 | |
| C13O—C14O—H14O | 120.2 | |
| C13O—C14O—C15O | 119.5 | (4) |
| C15O—C14O—H14O | 120.2 | |
| C14O—C15O—H15O | 120.2 | |
| C16O—C15O—C14O | 119.7 | (4) |
| C16O—C15O—H15O | 120.2 | |
| C11O—C16O—H16O | 118.5 | |
| C15O—C16O—C11O | 123.0 | (4) |
| C15O—C16O—H16O | 118.5 | |
| C22O—C21O—C26O | 114.3 | (3) |
| C22O—C21O—B11O | 123.9 | (3) |
| C26O—C21O—B11O | 121.8 | (3) |
| C21O—C22O—H22O | 118.5 | |
| C23O—C22O—C21O | 123.1 | (4) |
| C23O—C22O—H22O | 118.5 | |
| C22O—C23O—H23O | 119.8 | |
| C24O—C23O—C22O | 120.3 | (4) |
| C24O—C23O—H23O | 119.8 | |
| C23O—C24O—H24O | 120.6 | |
| C25O—C24O—C23O | 118.8 | (4) |
| C25O—C24O—H24O | 120.6 | |
| C24O—C25O—H25O | 120.0 | |
| C24O—C25O—C26O | 120.0 | (4) |
| C26O—C25O—H25O | 120.0 | |
| C21O—C26O—H26O | 118.4 | |
| C25O—C26O—C21O | 123.3 | (4) |
| C25O—C26O—H26O | 118.4 | |
| C32O—C31O—B11O | 121.8 | (3) |
| C36O—C31O—C32O | 115.0 | (3) |
| C36O—C31O—B11O | 123.2 | (3) |
| C31O—C32O—H32O | 118.6 | |
| C33O—C32O—C31O | 122.8 | (4) |
| C33O—C32O—H32O | 118.6 | |
| C32O—C33O—H33O | 120.0 | |
| C34O—C33O—C32O | 120.0 | (4) |

| | | |
|---|---|---|
| C3A3—N1A3—C1Q | 127.9 | (4) |
| N2A4—N1A4—C1Q' | 120.2 | (3) |
| N2A4—N1A4—C3A4 | 111.8 | (4) |
| C3A4—N1A4—C1Q' | 127.9 | (4) |
| C1B3—N1B3—C1Q | 124.0 | (3) |
| C1B3—N1B3—C2B3 | 111.3 | (4) |
| C2B3—N1B3—C1Q | 124.7 | (3) |
| C1B4—N1B4—C1Q' | 125.3 | (3) |
| C1B4—N1B4—C2B4 | 111.9 | (3) |
| C2B4—N1B4—C1Q' | 122.8 | (3) |
| N2C3—N1C3—C2Q | 119.2 | (4) |
| C3C3—N1C3—N2C3 | 111.9 | (4) |
| C3C3—N1C3—C2Q | 128.8 | (4) |
| N2C4—N1C4—C2Q' | 118.8 | (4) |
| C3C4—N1C4—N2C4 | 112.4 | (4) |
| C3C4—N1C4—C2Q' | 128.6 | (4) |
| C1A3—N2A3—N1A3 | 104.2 | (3) |
| C1A4—N2A4—N1A4 | 103.5 | (3) |
| C1B3—N2B3—C2Q | 124.7 | (3) |
| C1B3—N2B3—C3B3 | 111.4 | (3) |
| C3B3—N2B3—C2Q | 123.7 | (3) |
| C1B4—N2B4—C2Q' | 124.2 | (3) |
| C1B4—N2B4—C3B4 | 112.0 | (3) |
| C3B4—N2B4—C2Q' | 123.8 | (3) |
| C1C3—N2C3—N1C3 | 104.3 | (5) |
| C1C4—N2C4—N1C4 | 103.2 | (5) |
| N2A3—C1A3—H1A3 | 124.0 | |
| N2A3—C1A3—C2A3 | 112.0 | (4) |
| C2A3—C1A3—H1A3 | 124.0 | |
| N2A4—C1A4—H1A4 | 123.5 | |
| N2A4—C1A4—C2A4 | 112.9 | (4) |
| C2A4—C1A4—H1A4 | 123.5 | |
| N1B3—C1B3—Ag1B | 128.0 | (3) |
| N2B3—C1B3—Ag1B | 127.9 | (3) |
| N2B3—C1B3—N1B3 | 104.0 | (3) |
| N1B4—C1B4—Ag1B | 126.0 | (3) |
| N1B4—C1B4—N2B4 | 103.3 | (3) |
| N2B4—C1B4—Ag1B | 130.6 | (3) |
| N2C3—C1C3—H1C3 | 124.0 | |
| N2C3—C1C3—C2C3 | 112.1 | (5) |
| C2C3—C1C3—H1C3 | 124.0 | |

| | | |
|---|---|---|
| C34O—C33O—H33O | 120.0 | |
| C33O—C34O—H34O | 120.5 | |
| C35O—C34O—C33O | 119.0 | (4) |
| C35O—C34O—H34O | 120.5 | |
| C34O—C35O—H35O | 119.5 | |
| C34O—C35O—C36O | 121.0 | (4) |
| C36O—C35O—H35O | 119.5 | |
| C31O—C36O—H36O | 119.0 | |
| C35O—C36O—C31O | 122.1 | (4) |
| C35O—C36O—H36O | 119.0 | |
| C42O—C41O—B11O | 118.5 | (3) |
| C46O—C41O—C42O | 114.5 | (3) |
| C46O—C41O—B11O | 126.5 | (3) |
| C41O—C42O—H42O | 118.1 | |
| C43O—C42O—C41O | 123.8 | (4) |
| C43O—C42O—H42O | 118.1 | |
| C42O—C43O—H43O | 120.2 | |
| C42O—C43O—C44O | 119.6 | (4) |
| C44O—C43O—H43O | 120.2 | |
| C43O—C44O—H44O | 120.6 | |
| C45O—C44O—C43O | 118.8 | (4) |
| C45O—C44O—H44O | 120.6 | |
| C44O—C45O—H45O | 119.7 | |
| C44O—C45O—C46O | 120.7 | (4) |
| C46O—C45O—H45O | 119.7 | |
| C41O—C46O—H46O | 118.7 | |
| C45O—C46O—C41O | 122.7 | (4) |
| C45O—C46O—H46O | 118.7 | |
| C11O—B11O—C31O | 112.2 | (3) |
| C11O—B11O—C41O | 102.2 | (3) |
| C21O—B11O—C11O | 112.9 | (3) |
| C21O—B11O—C31O | 106.7 | (3) |
| C21O—B11O—C41O | 113.6 | (3) |
| C31O—B11O—C41O | 109.3 | (3) |
| C12N—C11N—C16N | 114.5 | (3) |
| C12N—C11N—B1N | 123.9 | (3) |
| C16N—C11N—B1N | 121.7 | (3) |
| C11N—C12N—H12N | 118.2 | |
| C13N—C12N—C11N | 123.6 | (4) |
| C13N—C12N—H12N | 118.2 | |
| C12N—C13N—H13N | 120.2 | |

| | | |
|---|---|---|
| N2C4—C1C4—H1C4 | 123.5 | |
| N2C4—C1C4—C2C4 | 113.0 | (6) |
| C2C4—C1C4—H1C4 | 123.5 | |
| N1A3—C1Q—N1B3 | 112.2 | (3) |
| N1A3—C1Q—H1Q | 123.9 | |
| N1B3—C1Q—H1Q | 123.9 | |
| N1A4—C1Q'—N1B4 | 112.2 | (3) |
| N1A4—C1Q'—H1QA | 109.2 | |
| N1A4—C1Q'—H1QB | 109.2 | |
| N1B4—C1Q'—H1QA | 109.2 | |
| N1B4—C1Q'—H1QB | 109.2 | |
| H1QA—C1Q'—H1QB | 107.9 | |
| C1A3—C2A3—H2A3 | 127.4 | |
| C3A3—C2A3—C1A3 | 105.3 | (4) |
| C3A3—C2A3—H2A3 | 127.4 | |
| C1A4—C2A4—H2A4 | 127.8 | |
| C3A4—C2A4—C1A4 | 104.4 | (4) |
| C3A4—C2A4—H2A4 | 127.8 | |
| N1B3—C2B3—H2B3 | 126.8 | |
| C3B3—C2B3—N1B3 | 106.4 | (4) |
| C3B3—C2B3—H2B3 | 126.8 | |
| N1B4—C2B4—H2B4 | 126.8 | |
| C3B4—C2B4—N1B4 | 106.4 | (4) |
| C3B4—C2B4—H2B4 | 126.8 | |
| C1C3—C2C3—H2C3 | 127.3 | |
| C3C3—C2C3—C1C3 | 105.5 | (5) |
| C3C3—C2C3—H2C3 | 127.3 | |
| C1C4—C2C4—H2C4 | 127.8 | |
| C3C4—C2C4—C1C4 | 104.4 | (6) |
| C3C4—C2C4—H2C4 | 127.8 | |
| N1C3—C2Q—N2B3 | 111.3 | (3) |
| N1C3—C2Q—H2QA | 109.4 | |
| N1C3—C2Q—H2QB | 109.4 | |
| N2B3—C2Q—H2QA | 109.4 | |
| N2B3—C2Q—H2QB | 109.4 | |
| H2QA—C2Q—H2QB | 108.0 | |
| N1C4—C2Q'—N2B4 | 111.4 | (3) |
| N1C4—C2Q'—H2QC | 109.3 | |
| N1C4—C2Q'—H2QD | 109.3 | |
| N2B4—C2Q'—H2QC | 109.3 | |
| N2B4—C2Q'—H2QD | 109.3 | |

| | | |
|---|---|---|
| C14N—C13N—C12N | 119.6 | (4) |
| C14N—C13N—H13N | 120.2 | |
| C13N—C14N—H14N | 120.5 | |
| C13N—C14N—C15N | 119.1 | (4) |
| C15N—C14N—H14N | 120.5 | |
| C14N—C15N—H15N | 119.7 | |
| C16N—C15N—C14N | 120.7 | (4) |
| C16N—C15N—H15N | 119.7 | |
| C11N—C16N—H16N | 118.7 | |
| C15N—C16N—C11N | 122.6 | (4) |
| C15N—C16N—H16N | 118.7 | |
| C22N—C21N—B1N | 123.5 | (3) |
| C26N—C21N—C22N | 114.8 | (3) |
| C26N—C21N—B1N | 121.4 | (3) |
| C21N—C22N—H22N | 118.8 | |
| C23N—C22N—C21N | 122.4 | (4) |
| C23N—C22N—H22N | 118.8 | |
| C22N—C23N—H23N | 119.9 | |
| C24N—C23N—C22N | 120.2 | (4) |
| C24N—C23N—H23N | 119.9 | |
| C23N—C24N—H24N | 120.2 | |
| C23N—C24N—C25N | 119.6 | (4) |
| C25N—C24N—H24N | 120.2 | |
| C24N—C25N—H25N | 120.0 | |
| C24N—C25N—C26N | 120.0 | (4) |
| C26N—C25N—H25N | 120.0 | |
| C21N—C26N—H26N | 118.5 | |
| C25N—C26N—C21N | 123.0 | (4) |
| C25N—C26N—H26N | 118.5 | |
| C32N—C31N—C36N | 114.6 | (3) |
| C32N—C31N—B1N | 125.5 | (4) |
| C36N—C31N—B1N | 119.9 | (3) |
| C31N—C32N—H32N | 118.3 | |
| C33N—C32N—C31N | 123.3 | (4) |
| C33N—C32N—H32N | 118.3 | |
| C32N—C33N—H33N | 119.9 | |
| C34N—C33N—C32N | 120.2 | (4) |
| C34N—C33N—H33N | 119.9 | |
| C33N—C34N—H34N | 120.6 | |
| C33N—C34N—C35N | 118.8 | (4) |
| C35N—C34N—H34N | 120.6 | |

| | | | |
|---|---|---|---|
| H2QC—C2Q'—H2QD | 108.0 | C34N—C35N—H35N | 120.2 |
| N1A3—C3A3—H3A3 | 126.7 | C36N—C35N—C34N | 119.7 (4) |
| C2A3—C3A3—N1A3 | 106.6 (4) | C36N—C35N—H35N | 120.2 |
| C2A3—C3A3—H3A3 | 126.7 | C31N—C36N—H36N | 118.3 |
| N1A4—C3A4—H3A4 | 126.3 | C35N—C36N—C31N | 123.4 (4) |
| C2A4—C3A4—N1A4 | 107.4 (4) | C35N—C36N—H36N | 118.3 |
| C2A4—C3A4—H3A4 | 126.3 | C42N—C41N—C46N | 114.6 (3) |
| N2B3—C3B3—H3B3 | 126.5 | C42N—C41N—B1N | 127.0 (3) |
| C2B3—C3B3—N2B3 | 107.0 (4) | C46N—C41N—B1N | 118.3 (3) |
| C2B3—C3B3—H3B3 | 126.5 | C41N—C42N—H42N | 118.4 |
| N2B4—C3B4—H3B4 | 126.8 | C43N—C42N—C41N | 123.2 (4) |
| C2B4—C3B4—N2B4 | 106.5 (4) | C43N—C42N—H42N | 118.4 |
| C2B4—C3B4—H3B4 | 126.8 | C42N—C43N—H43N | 119.8 |
| N1C3—C3C3—C2C3 | 106.2 (5) | C44N—C43N—C42N | 120.4 (4) |
| N1C3—C3C3—H3C3 | 126.9 | C44N—C43N—H43N | 119.8 |
| C2C3—C3C3—H3C3 | 126.9 | C43N—C44N—H44N | 120.9 |
| N1C4—C3C4—C2C4 | 107.0 (6) | C43N—C44N—C45N | 118.2 (4) |
| N1C4—C3C4—H3C4 | 126.5 | C45N—C44N—H44N | 120.9 |
| C2C4—C3C4—H3C4 | 126.5 | C44N—C45N—H45N | 119.8 |
| C1B6—Ag1D—C1B6$^{ii}$ | 180.0 | C46N—C45N—C44N | 120.5 (4) |
| N2A6—N1A6—C1S | 119.7 (3) | C46N—C45N—H45N | 119.8 |
| C3A6—N1A6—N2A6 | 111.4 (3) | C41N—C46N—H46N | 118.4 |
| C3A6—N1A6—C1S | 128.9 (3) | C45N—C46N—C41N | 123.1 (4) |
| C1B6—N1B6—C1S | 124.4 (3) | C45N—C46N—H46N | 118.4 |
| C1B6—N1B6—C2B6 | 111.8 (3) | C11N—B1N—C31N | 106.6 (3) |
| C2B6—N1B6—C1S | 123.8 (3) | C11N—B1N—C41N | 109.2 (3) |
| N2C6—N1C6—C2S | 120.4 (3) | C21N—B1N—C11N | 112.4 (3) |
| N2C6—N1C6—C3C6 | 110.9 (4) | C21N—B1N—C31N | 112.9 (3) |
| C3C6—N1C6—C2S | 128.7 (3) | C21N—B1N—C41N | 103.7 (3) |
| C1A6—N2A6—N1A6 | 103.9 (3) | C31N—B1N—C41N | 112.1 (3) |
| C1B6—N2B6—C2S | 124.0 (3) | | |

Symmetry code(s): (i) -*x*, -*y*+1, -*z*+2; (ii) -*x*+1, -*y*+1, -*z*+3.

## Selected geometric parameters, torsion angles (º)

| | | | |
|---|---|---|---|
| N1A1—N2A1—C1A1—C2A1 | 0.2 (5) | C1C6—C2C6—C3C6—N1C6 | -0.2 (5) |
| N1A2—N2A2—C1A2—C2A2 | -0.5 (5) | C1S—N1A6—N2A6—C1A6 | -179.1 (3) |
| N1B1—C2B1—C3B1—N2B1 | -0.2 (4) | C1S—N1A6—C3A6—C2A6 | 178.8 (4) |
| N1B2—C2B2— | 0.4 (4) | C1S—N1B6—C1B6— | -6.7 (5) |

| | | | |
|---|---|---|---|
| C3B2—N2B2 | | Ag1D | |
| N1C1—N2C1—C1C1—C2C1 | -0.2 (6) | C1S—N1B6—C1B6—N2B6 | 177.4 (3) |
| N1C2—N2C2—C1C2—C2C2 | 0.6 (5) | C1S—N1B6—C2B6—C3B6 | -177.9 (3) |
| N2A1—N1A1—C1P—N1B1 | -96.4 (4) | C2B6—N1B6—C1B6—Ag1D | 175.1 (3) |
| N2A1—N1A1—C3A1—C2A1 | 0.0 (5) | C2B6—N1B6—C1B6—N2B6 | -0.8 (4) |
| N2A1—C1A1—C2A1—C3A1 | -0.2 (5) | C2B6—N1B6—C1S—N1A6 | -104.8 (4) |
| N2A2—N1A2—C1P'—N1B2 | 86.0 (4) | C2S—N1C6—N2C6—C1C6 | 176.6 (4) |
| N2A2—N1A2—C3A2—C2A2 | -0.5 (5) | C2S—N1C6—C3C6—C2C6 | -176.2 (4) |
| N2A2—C1A2—C2A2—C3A2 | 0.3 (6) | C2S—N2B6—C1B6—Ag1D | 3.7 (5) |
| N2C1—N1C1—C2P—N2B1 | -80.6 (4) | C2S—N2B6—C1B6—N1B6 | 179.3 (3) |
| N2C1—N1C1—C3C1—C2C1 | -2.0 (5) | C2S—N2B6—C3B6—C2B6 | -179.2 (3) |
| N2C1—C1C1—C2C1—C3C1 | -1.0 (7) | C3A6—N1A6—N2A6—C1A6 | -0.7 (4) |
| N2C2—N1C2—C2P'—N2B2 | 78.9 (4) | C3A6—N1A6—C1S—N1B6 | 96.1 (5) |
| N2C2—N1C2—C3C2—C2C2 | -0.1 (5) | C3B6—N2B6—C1B6—Ag1D | -174.6 (3) |
| N2C2—C1C2—C2C2—C3C2 | -0.7 (6) | C3B6—N2B6—C1B6—N1B6 | 1.0 (4) |
| C1A1—C2A1—C3A1—N1A1 | 0.1 (5) | C3B6—N2B6—C2S—N1C6 | 70.0 (5) |
| C1A2—C2A2—C3A2—N1A2 | 0.1 (6) | C3C6—N1C6—N2C6—C1C6 | -0.3 (5) |
| C1B1—N1B1—C1P—N1A1 | 71.1 (5) | C3C6—N1C6—C2S—N2B6 | 92.2 (5) |
| C1B1—N1B1—C2B1—C3B1 | 0.4 (4) | C11M—C12M—C13M—C14M | 0.0 (5) |
| C1B1—N2B1—C2P—N1C1 | -96.2 (4) | C12M—C11M—C16M—C15M | -0.8 (5) |
| C1B1—N2B1—C3B1—C2B1 | -0.1 (4) | C12M—C11M—B1M—C21M | -156.6 (3) |
| C1B2—N1B2—C1P'—N1A2 | -97.0 (4) | C12M—C11M—B1M—C31M | -36.5 (4) |
| C1B2—N1B2—C2B2—C3B2 | -0.8 (4) | C12M—C11M—B1M—C41M | 83.0 (4) |
| C1B2—N2B2—C2P'—N1C2 | 104.7 (4) | C12M—C13M—C14M—C15M | -1.8 (5) |
| C1B2—N2B2— | 0.2 (4) | C13M—C14M— | 2.2 (6) |

| | | | |
|---|---|---|---|
| C3B2—C2B2 | | C15M—C16M | |
| C1C1—C2C1—C3C1—N1C1 | 1.8 (6) | C14M—C15M—C16M—C11M | -0.9 (6) |
| C1C2—C2C2—C3C2—N1C2 | 0.4 (5) | C16M—C11M—C12M—C13M | 1.3 (5) |
| C1P—N1A1—N2A1—C1A1 | -179.1 (4) | C16M—C11M—B1M—C21M | 25.1 (5) |
| C1P—N1A1—C3A1—C2A1 | 178.8 (4) | C16M—C11M—B1M—C31M | 145.2 (3) |
| C1P—N1B1—C1B1—Ag1A | -9.1 (5) | C16M—C11M—B1M—C41M | -95.3 (4) |
| C1P—N1B1—C1B1—N2B1 | 174.1 (3) | C21M—C22M—C23M—C24M | -2.1 (6) |
| C1P—N1B1—C2B1—C3B1 | -174.1 (3) | C22M—C21M—C26M—C25M | -0.2 (6) |
| C1P'—N1A2—N2A2—C1A2 | 179.2 (3) | C22M—C21M—B1M—C11M | -76.7 (4) |
| C1P'—N1A2—C3A2—C2A2 | -179.0 (4) | C22M—C21M—B1M—C31M | 164.8 (3) |
| C1P'—N1B2—C1B2—Ag1A | 15.6 (5) | C22M—C21M—B1M—C41M | 42.9 (5) |
| C1P'—N1B2—C1B2—N2B2 | -176.2 (3) | C22M—C23M—C24M—C25M | 1.2 (7) |
| C1P'—N1B2—C2B2—C3B2 | 176.2 (3) | C23M—C24M—C25M—C26M | 0.1 (7) |
| C2B1—N1B1—C1B1—Ag1A | 176.3 (3) | C24M—C25M—C26M—C21M | -0.6 (7) |
| C2B1—N1B1—C1B1—N2B1 | -0.5 (4) | C26M—C21M—C22M—C23M | 1.6 (6) |
| C2B1—N1B1—C1P—N1A1 | -115.0 (4) | C26M—C21M—B1M—C11M | 102.1 (4) |
| C2B2—N1B2—C1B2—Ag1A | -167.3 (3) | C26M—C21M—B1M—C31M | -16.3 (5) |
| C2B2—N1B2—C1B2—N2B2 | 0.9 (4) | C26M—C21M—B1M—C41M | -138.3 (4) |
| C2B2—N1B2—C1P'—N1A2 | 86.3 (4) | C31M—C32M—C33M—C34M | -0.6 (6) |
| C2P—N1C1—N2C1—C1C1 | 172.7 (4) | C32M—C31M—C36M—C35M | -0.8 (5) |
| C2P—N1C1—C3C1—C2C1 | -172.4 (4) | C32M—C31M—B1M—C11M | -51.1 (4) |
| C2P—N2B1—C1B1—Ag1A | -0.1 (5) | C32M—C31M—B1M—C21M | 68.1 (4) |
| C2P—N2B1—C1B1—N1B1 | 176.7 (3) | C32M—C31M—B1M—C41M | -169.8 (3) |
| C2P—N2B1—C3B1—C2B1 | -176.5 (3) | C32M—C33M—C34M—C35M | -0.3 (6) |
| C2P'—N1C2— | -176.8 (4) | C33M—C34M— | 0.7 (6) |

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| N2C2—C1C2 | | C35M—C36M | |
| C2P'—N1C2—C3C2—C2C2 | 176.0 (4) | C34M—C35M—C36M—C31M | -0.1 (6) |
| C2P'—N2B2—C1B2—Ag1A | -15.3 (5) | C36M—C31M—C32M—C33M | 1.1 (6) |
| C2P'—N2B2—C1B2—N1B2 | 176.8 (3) | C36M—C31M—B1M—C11M | 131.3 (4) |
| C2P'—N2B2—C3B2—C2B2 | -177.2 (3) | C36M—C31M—B1M—C21M | -109.5 (4) |
| C3A1—N1A1—N2A1—C1A1 | -0.1 (4) | C36M—C31M—B1M—C41M | 12.6 (5) |
| C3A1—N1A1—C1P—N1B1 | 84.9 (5) | C41M—C42M—C43M—C44M | -2.1 (6) |
| C3A2—N1A2—N2A2—C1A2 | 0.6 (5) | C42M—C41M—C46M—C45M | -0.8 (6) |
| C3A2—N1A2—C1P'—N1B2 | -95.6 (5) | C42M—C41M—B1M—C11M | 139.4 (4) |
| C3B1—N2B1—C1B1—Ag1A | -176.4 (3) | C42M—C41M—B1M—C21M | 19.7 (5) |
| C3B1—N2B1—C1B1—N1B1 | 0.4 (4) | C42M—C41M—B1M—C31M | -102.5 (4) |
| C3B1—N2B1—C2P—N1C1 | 79.7 (4) | C42M—C43M—C44M—C45M | 1.3 (6) |
| C3B2—N2B2—C1B2—Ag1A | 167.3 (3) | C43M—C44M—C45M—C46M | -0.4 (6) |
| C3B2—N2B2—C1B2—N1B2 | -0.7 (4) | C44M—C45M—C46M—C41M | 0.2 (6) |
| C3B2—N2B2—C2P'—N1C2 | -78.3 (4) | C46M—C41M—C42M—C43M | 1.7 (5) |
| C3C1—N1C1—N2C1—C1C1 | 1.3 (5) | C46M—C41M—B1M—C11M | -42.3 (5) |
| C3C1—N1C1—C2P—N2B1 | 89.2 (5) | C46M—C41M—B1M—C21M | -162.0 (3) |
| C3C2—N1C2—N2C2—C1C2 | -0.3 (5) | C46M—C41M—B1M—C31M | 75.7 (4) |
| C3C2—N1C2—C2P'—N2B2 | -96.8 (5) | B1M—C11M—C12M—C13M | -177.2 (3) |
| N1A5—N2A5—C1A5—C2A5 | 0.0 (5) | B1M—C11M—C16M—C15M | 177.6 (3) |
| N1B5—C2B5—C3B5—N2B5 | -0.9 (6) | B1M—C21M—C22M—C23M | -179.5 (4) |
| N1C5—N2C5—C1C5—C2C5 | -1.2 (7) | B1M—C21M—C26M—C25M | -179.1 (4) |
| N2A5—N1A5—C1R—N1B5 | -95.7 (4) | B1M—C31M—C32M—C33M | -176.7 (4) |
| N2A5—N1A5—C3A5—C2A5 | -0.2 (5) | B1M—C31M—C36M—C35M | 177.0 (3) |
| N2A5—C1A5— | -0.1 (5) | B1M—C41M— | -179.9 (4) |

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|---|---|---|---|
| C2A5—C3A5 | | C42M—C43M | |
| N2C5—N1C5—C2R—N2B5 | -89.1 (5) | B1M—C41M—C46M—C45M | -179.2 (4) |
| N2C5—N1C5—C3C5—C2C5 | 0.0 (6) | C11O—C12O—C13O—C14O | -2.6 (7) |
| N2C5—C1C5—C2C5—C3C5 | 1.2 (7) | C12O—C11O—C16O—C15O | 1.1 (6) |
| C1A5—C2A5—C3A5—N1A5 | 0.2 (5) | C12O—C11O—B11O—C21O | -148.8 (3) |
| C1B5—N1B5—C1R—N1A5 | 74.5 (5) | C12O—C11O—B11O—C31O | -28.2 (5) |
| C1B5—N1B5—C2B5—C3B5 | 0.7 (6) | C12O—C11O—B11O—C41O | 88.8 (4) |
| C1B5—N2B5—C2R—N1C5 | -115.5 (4) | C12O—C13O—C14O—C15O | 2.7 (8) |
| C1B5—N2B5—C3B5—C2B5 | 0.8 (6) | C13O—C14O—C15O—C16O | -1.0 (7) |
| C1C5—C2C5—C3C5—N1C5 | -0.7 (6) | C14O—C15O—C16O—C11O | -0.9 (7) |
| C1R—N1A5—N2A5—C1A5 | 178.4 (4) | C16O—C11O—C12O—C13O | 0.6 (6) |
| C1R—N1A5—C3A5—C2A5 | -178.3 (4) | C16O—C11O—B11O—C21O | 41.3 (5) |
| C1R—N1B5—C1B5—Ag1C | -6.5 (6) | C16O—C11O—B11O—C31O | 162.0 (3) |
| C1R—N1B5—C1B5—N2B5 | 179.3 (3) | C16O—C11O—B11O—C41O | -81.1 (4) |
| C1R—N1B5—C2B5—C3B5 | -178.8 (4) | C21O—C22O—C23O—C24O | -1.0 (6) |
| C2B5—N1B5—C1B5—Ag1C | 174.0 (3) | C22O—C21O—C26O—C25O | -3.7 (5) |
| C2B5—N1B5—C1B5—N2B5 | -0.2 (5) | C22O—C21O—B11O—C11O | 18.9 (5) |
| C2B5—N1B5—C1R—N1A5 | -106.0 (5) | C22O—C21O—B11O—C31O | -104.8 (4) |
| C2R—N1C5—N2C5—C1C5 | 178.5 (4) | C22O—C21O—B11O—C41O | 134.7 (4) |
| C2R—N1C5—C3C5—C2C5 | -177.5 (4) | C22O—C23O—C24O—C25O | -1.6 (6) |
| C2R—N2B5—C1B5—Ag1C | 8.7 (6) | C23O—C24O—C25O—C26O | 1.4 (6) |
| C2R—N2B5—C1B5—N1B5 | -177.1 (4) | C24O—C25O—C26O—C21O | 1.3 (6) |
| C2R—N2B5—C3B5—C2B5 | 177.6 (4) | C26O—C21O—C22O—C23O | 3.5 (5) |
| C3A5—N1A5—N2A5—C1A5 | 0.1 (5) | C26O—C21O—B11O—C11O | -162.3 (3) |
| C3A5—N1A5— | 82.3 (5) | C26O—C21O— | 74.0 (4) |

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|---|---|---|---|
| C1R—N1B5 | | B11O—C31O | |
| C3B5—N2B5—C1B5—Ag1C | -174.5 (3) | C26O—C21O—B11O—C41O | -46.5 (5) |
| C3B5—N2B5—C1B5—N1B5 | -0.3 (5) | C31O—C32O—C33O—C34O | 1.8 (5) |
| C3B5—N2B5—C2R—N1C5 | 68.1 (6) | C32O—C31O—C36O—C35O | 1.6 (5) |
| C3C5—N1C5—N2C5—C1C5 | 0.7 (6) | C32O—C31O—B11O—C11O | -39.3 (5) |
| C3C5—N1C5—C2R—N2B5 | 88.3 (6) | C32O—C31O—B11O—C21O | 84.9 (4) |
| N1A3—N2A3—C1A3—C2A3 | -0.4 (5) | C32O—C31O—B11O—C41O | -151.9 (3) |
| N1A4—N2A4—C1A4—C2A4 | -0.4 (5) | C32O—C33O—C34O—C35O | -0.3 (5) |
| N1B3—C2B3—C3B3—N2B3 | 0.1 (5) | C33O—C34O—C35O—C36O | -0.5 (5) |
| N1B4—C2B4—C3B4—N2B4 | -0.4 (5) | C34O—C35O—C36O—C31O | -0.2 (5) |
| N1C3—N2C3—C1C3—C2C3 | 0.5 (7) | C36O—C31O—C32O—C33O | -2.3 (5) |
| N1C4—N2C4—C1C4—C2C4 | -1.4 (6) | C36O—C31O—B11O—C11O | 142.2 (3) |
| N2A3—N1A3—C1Q—N1B3 | 93.0 (4) | C36O—C31O—B11O—C21O | -93.6 (4) |
| N2A3—N1A3—C3A3—C2A3 | 1.1 (5) | C36O—C31O—B11O—C41O | 29.6 (5) |
| N2A3—C1A3—C2A3—C3A3 | 1.0 (5) | C41O—C42O—C43O—C44O | 0.9 (6) |
| N2A4—N1A4—C1Q'—N1B4 | -97.3 (4) | C42O—C41O—C46O—C45O | 1.1 (5) |
| N2A4—N1A4—C3A4—C2A4 | -0.8 (5) | C42O—C41O—B11O—C11O | -62.3 (4) |
| N2A4—C1A4—C2A4—C3A4 | 0.0 (6) | C42O—C41O—B11O—C21O | 175.8 (3) |
| N2C3—N1C3—C2Q—N2B3 | 86.5 (4) | C42O—C41O—B11O—C31O | 56.8 (4) |
| N2C3—N1C3—C3C3—C2C3 | 0.2 (5) | C42O—C43O—C44O—C45O | 1.2 (6) |
| N2C3—C1C3—C2C3—C3C3 | -0.4 (7) | C43O—C44O—C45O—C46O | -2.0 (6) |
| N2C4—N1C4—C2Q'—N2B4 | -95.1 (4) | C44O—C45O—C46O—C41O | 0.8 (6) |
| N2C4—N1C4—C3C4—C2C4 | -0.3 (6) | C46O—C41O—C42O—C43O | -2.0 (5) |
| N2C4—C1C4—C2C4—C3C4 | 1.2 (7) | C46O—C41O—B11O—C11O | 108.9 (4) |
| C1A3—C2A3— | -1.2 (5) | C46O—C41O— | -13.0 (5) |

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| C3A3—N1A3 | | B11O—C21O | |
| C1A4—C2A4—C3A4—N1A4 | 0.5 (5) | C46O—C41O—B11O—C31O | -132.1 (4) |
| C1B3—N1B3—C1Q—N1A3 | -72.2 (5) | B11O—C11O—C12O—C13O | -169.8 (4) |
| C1B3—N1B3—C2B3—C3B3 | -0.2 (5) | B11O—C11O—C16O—C15O | 171.6 (4) |
| C1B3—N2B3—C2Q—N1C3 | 118.5 (4) | B11O—C21O—C22O—C23O | -177.6 (4) |
| C1B3—N2B3—C3B3—C2B3 | 0.1 (5) | B11O—C21O—C26O—C25O | 177.4 (3) |
| C1B4—N1B4—C1Q'—N1A4 | 82.4 (5) | B11O—C31O—C32O—C33O | 179.1 (3) |
| C1B4—N1B4—C2B4—C3B4 | 0.2 (5) | B11O—C31O—C36O—C35O | -179.8 (3) |
| C1B4—N2B4—C2Q'—N1C4 | -113.6 (4) | B11O—C41O—C42O—C43O | 170.2 (3) |
| C1B4—N2B4—C3B4—C2B4 | 0.4 (5) | B11O—C41O—C46O—C45O | -170.3 (3) |
| C1C3—C2C3—C3C3—N1C3 | 0.1 (6) | C11N—C12N—C13N—C14N | -0.6 (6) |
| C1C4—C2C4—C3C4—N1C4 | -0.5 (6) | C12N—C11N—C16N—C15N | 2.3 (5) |
| C1Q—N1A3—N2A3—C1A3 | -175.5 (3) | C12N—C11N—B1N—C21N | -138.3 (4) |
| C1Q—N1A3—C3A3—C2A3 | 175.7 (4) | C12N—C11N—B1N—C31N | 97.4 (4) |
| C1Q—N1B3—C1B3—Ag1B | 4.9 (5) | C12N—C11N—B1N—C41N | -23.9 (5) |
| C1Q—N1B3—C1B3—N2B3 | -179.3 (3) | C12N—C13N—C14N—C15N | 1.4 (6) |
| C1Q—N1B3—C2B3—C3B3 | 179.3 (3) | C13N—C14N—C15N—C16N | -0.3 (6) |
| C1Q'—N1A4—N2A4—C1A4 | 175.8 (3) | C14N—C15N—C16N—C11N | -1.7 (6) |
| C1Q'—N1A4—C3A4—C2A4 | -175.4 (4) | C16N—C11N—C12N—C13N | -1.2 (5) |
| C1Q'—N1B4—C1B4—Ag1B | -4.4 (6) | C16N—C11N—B1N—C21N | 43.7 (5) |
| C1Q'—N1B4—C1B4—N2B4 | 179.4 (3) | C16N—C11N—B1N—C31N | -80.6 (4) |
| C1Q'—N1B4—C2B4—C3B4 | -179.2 (4) | C16N—C11N—B1N—C41N | 158.1 (3) |
| C2B3—N1B3—C1B3—Ag1B | -175.5 (3) | C21N—C22N—C23N—C24N | 0.9 (7) |
| C2B3—N1B3—C1B3—N2B3 | 0.3 (4) | C22N—C21N—C26N—C25N | 0.8 (6) |
| C2B3—N1B3— | 108.2 (4) | C22N—C21N— | 19.2 (5) |

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|---|---|---|---|
| C1Q—N1A3 | | B1N—C11N | |
| C2B4—N1B4—C1B4—Ag1B | 176.2 (3) | C22N—C21N—B1N—C31N | 139.8 (4) |
| C2B4—N1B4—C1B4—N2B4 | 0.0 (4) | C22N—C21N—B1N—C41N | -98.6 (4) |
| C2B4—N1B4—C1Q'—N1A4 | -98.3 (4) | C22N—C23N—C24N—C25N | -0.3 (7) |
| C2Q—N1C3—N2C3—C1C3 | -176.5 (4) | C23N—C24N—C25N—C26N | 0.0 (7) |
| C2Q—N1C3—C3C3—C2C3 | 175.8 (4) | C24N—C25N—C26N—C21N | -0.3 (7) |
| C2Q—N2B3—C1B3—Ag1B | -9.0 (5) | C26N—C21N—C22N—C23N | -1.1 (6) |
| C2Q—N2B3—C1B3—N1B3 | 175.1 (3) | C26N—C21N—B1N—C11N | -168.3 (3) |
| C2Q—N2B3—C3B3—C2B3 | -175.3 (3) | C26N—C21N—B1N—C31N | -47.7 (5) |
| C2Q'—N1C4—N2C4—C1C4 | 176.4 (4) | C26N—C21N—B1N—C41N | 73.9 (4) |
| C2Q'—N1C4—C3C4—C2C4 | -175.1 (4) | C31N—C32N—C33N—C34N | 1.5 (6) |
| C2Q'—N2B4—C1B4—Ag1B | 3.7 (6) | C32N—C31N—C36N—C35N | 2.6 (5) |
| C2Q'—N2B4—C1B4—N1B4 | 179.7 (3) | C32N—C31N—B1N—C11N | 112.3 (4) |
| C2Q'—N2B4—C3B4—C2B4 | -179.6 (4) | C32N—C31N—B1N—C21N | -11.6 (5) |
| C3A3—N1A3—N2A3—C1A3 | -0.4 (4) | C32N—C31N—B1N—C41N | -128.2 (4) |
| C3A3—N1A3—C1Q—N1B3 | -81.3 (5) | C32N—C33N—C34N—C35N | 0.8 (6) |
| C3A4—N1A4—N2A4—C1A4 | 0.7 (5) | C33N—C34N—C35N—C36N | -1.2 (6) |
| C3A4—N1A4—C1Q'—N1B4 | 76.9 (5) | C34N—C35N—C36N—C31N | -0.6 (6) |
| C3B3—N2B3—C1B3—Ag1B | 175.6 (3) | C36N—C31N—C32N—C33N | -3.1 (6) |
| C3B3—N2B3—C1B3—N1B3 | -0.3 (4) | C36N—C31N—B1N—C11N | -65.2 (4) |
| C3B3—N2B3—C2Q—N1C3 | -66.7 (5) | C36N—C31N—B1N—C21N | 170.9 (3) |
| C3B4—N2B4—C1B4—Ag1B | -176.2 (3) | C36N—C31N—B1N—C41N | 54.2 (4) |
| C3B4—N2B4—C1B4—N1B4 | -0.2 (4) | C41N—C42N—C43N—C44N | 0.2 (6) |
| C3B4—N2B4—C2Q'—N1C4 | 66.3 (5) | C42N—C41N—C46N—C45N | 0.1 (5) |
| C3C3—N1C3— | -0.4 (6) | C42N—C41N— | 123.1 (4) |

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|---|---|---|---|
| N2C3—C1C3 | | B1N—C11N | |
| C3C3—N1C3—C2Q—N2B3 | -88.8 (5) | C42N—C41N—B1N—C21N | -116.9 (4) |
| C3C4—N1C4—N2C4—C1C4 | 1.0 (5) | C42N—C41N—B1N—C31N | 5.2 (5) |
| C3C4—N1C4—C2Q'—N2B4 | 79.4 (5) | C42N—C43N—C44N—C45N | 0.4 (6) |
| N1A6—N2A6—C1A6—C2A6 | 0.6 (5) | C43N—C44N—C45N—C46N | -0.8 (6) |
| N1B6—C2B6—C3B6—N2B6 | 0.4 (4) | C44N—C45N—C46N—C41N | 0.5 (6) |
| N1C6—N2C6—C1C6—C2C6 | 0.1 (5) | C46N—C41N—C42N—C43N | -0.5 (5) |
| N2A6—N1A6—C1S—N1B6 | -85.7 (4) | C46N—C41N—B1N—C11N | -60.7 (4) |
| N2A6—N1A6—C3A6—C2A6 | 0.6 (5) | C46N—C41N—B1N—C21N | 59.3 (4) |
| N2A6—C1A6—C2A6—C3A6 | -0.2 (5) | C46N—C41N—B1N—C31N | -178.6 (3) |
| N2C6—N1C6—C2S—N2B6 | -84.0 (4) | B1N—C11N—C12N—C13N | -179.3 (3) |
| N2C6—N1C6—C3C6—C2C6 | 0.3 (5) | B1N—C11N—C16N—C15N | -179.5 (3) |
| N2C6—C1C6—C2C6—C3C6 | 0.1 (6) | B1N—C21N—C22N—C23N | 171.9 (4) |
| C1A6—C2A6—C3A6—N1A6 | -0.2 (5) | B1N—C21N—C26N—C25N | -172.3 (4) |
| C1B6—N1B6—C1S—N1A6 | 77.2 (5) | B1N—C31N—C32N—C33N | 179.2 (4) |
| C1B6—N1B6—C2B6—C3B6 | 0.3 (4) | B1N—C31N—C36N—C35N | -179.5 (3) |
| C1B6—N2B6—C2S—N1C6 | -108.0 (4) | B1N—C41N—C42N—C43N | 175.8 (3) |
| C1B6—N2B6—C3B6—C2B6 | -0.9 (4) | B1N—C41N—C46N—C45N | -176.5 (3) |

### 7.1.4. Crystal data for complex 3

#### Selected geometric parameters (Å)

| | | | |
|---|---|---|---|
| Ru1—C1AA | 2.179 (11) | C79—H79 | 0.9500 |
| Ru1—Cl7 | 2.397 (2) | C79—C137 | 1.387 (11) |
| Ru1—N26 | 2.091 (8) | C79—C146 | 1.392 (12) |
| Ru1—C102 | 2.185 (9) | C80—H80 | 0.9500 |
| Ru1—C114 | 2.040 (9) | C80—C92 | 1.371 (15) |

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|---|---|---|---|
| Ru1—C150 | 2.236 (9) | C80—C131 | 1.370 (14) |
| Ru1—C184 | 2.233 (9) | C81—H81 | 0.9500 |
| Ru1—C0AA | 2.171 (10) | C81—C155 | 1.365 (13) |
| Ru1—C2AA | 2.201 (11) | C81—C161 | 1.413 (12) |
| Ru3—Cl8 | 2.392 (2) | C82—C139 | 1.402 (12) |
| Ru3—N7 | 2.016 (8) | C82—C152 | 1.392 (12) |
| Ru3—C10 | 2.169 (9) | C82—B191 | 1.649 (13) |
| Ru3—N12 | 2.083 (7) | C84—H84 | 0.9500 |
| Ru3—C84 | 2.199 (8) | C84—C94 | 1.378 (13) |
| Ru3—C94 | 2.197 (9) | C84—C149 | 1.435 (13) |
| Ru3—C149 | 2.240 (9) | C86—H86 | 0.9500 |
| Ru3—C176 | 2.168 (9) | C86—C103 | 1.424 (12) |
| Ru3—C190 | 2.246 (8) | C86—C133 | 1.396 (12) |
| C1AA—H1AA | 0.9500 | C85—H85 | 0.9500 |
| C1AA—C0AA | 1.400 (15) | C87—H87 | 0.9500 |
| C1AA—C2AA | 1.421 (14) | C87—C154 | 1.414 (12) |
| Ru2—Cl1X | 2.404 (2) | C88—H88A | 0.9900 |
| Ru2—C2 | 2.175 (9) | C88—H88B | 0.9900 |
| Ru2—N32 | 2.100 (8) | C88—N148 | 1.449 (12) |
| Ru2—N34 | 2.036 (9) | C89—H89 | 0.9500 |
| Ru2—C40 | 2.202 (9) | C90—H90 | 0.9500 |
| Ru2—C89 | 2.191 (9) | B91—C93 | 1.630 (12) |
| Ru2—C101 | 2.172 (9) | C92—H92 | 0.9500 |
| Ru2—C105 | 2.235 (8) | C93—C157 | 1.400 (11) |
| Ru2—C160 | 2.249 (9) | C94—H94 | 0.9500 |
| Ru4—Cl5 | 2.398 (2) | C94—C176 | 1.410 (13) |
| Ru4—N3 | 2.029 (8) | C95—H95 | 0.9500 |
| Ru4—N4 | 2.082 (7) | N96—N148 | 1.383 (11) |
| Ru4—C8 | 2.193 (8) | N96—C185 | 1.323 (14) |
| Ru4—C14 | 2.173 (9) | C97—H97 | 0.9500 |
| Ru4—C65 | 2.247 (9) | C97—C164 | 1.404 (13) |
| Ru4—C87 | 2.200 (8) | C98—C108 | 1.412 (12) |
| Ru4—C154 | 2.203 (8) | C98—B208 | 1.645 (14) |
| Ru4—C201 | 2.249 (10) | C100—H100 | 0.9500 |
| C2—H2 | 0.9500 | C100—C158 | 1.372 (13) |
| C2—C89 | 1.416 (14) | C100—C195 | 1.393 (12) |
| C2—C101 | 1.369 (14) | C99—H99 | 0.9500 |
| N3—N13 | 1.364 (10) | C99—C3 | 1.413 (13) |
| N3—N1X | 1.342 (10) | C101—H101 | 0.9500 |
| N4—N11 | 1.361 (9) | C101—C160 | 1.428 (13) |
| N4—C61 | 1.339 (11) | C102—H102 | 0.9500 |

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| N5—C99 | 1.313 (11) | C102—C150 | 1.411 (14) |
| N5—N215 | 1.342 (9) | C102—C2AA | 1.406 (14) |
| N6—N52 | 1.349 (10) | C103—B191 | 1.640 (13) |
| N6—C165 | 1.326 (11) | C103—C195 | 1.418 (12) |
| N7—N19 | 1.363 (10) | C104—H10A | 0.9900 |
| N7—N2X | 1.362 (10) | C104—H10B | 0.9900 |
| C8—H8 | 0.9500 | C105—H105 | 0.9500 |
| C8—C14 | 1.388 (12) | C105—C160 | 1.387 (13) |
| C8—C154 | 1.418 (12) | C107—C110 | 1.400 (12) |
| C9—H9 | 0.9500 | C107—B191 | 1.637 (13) |
| C9—N19 | 1.378 (11) | C107—C198 | 1.409 (12) |
| C9—C109 | 1.320 (13) | C106—H106 | 0.9500 |
| C10—H10 | 0.9500 | C106—C141 | 1.368 (14) |
| C10—C176 | 1.390 (12) | C109—H109 | 0.9500 |
| C10—C190 | 1.418 (13) | C108—H108 | 0.9500 |
| N11—C47 | 1.442 (11) | C110—H110 | 0.9500 |
| N11—C159 | 1.351 (10) | C110—C121 | 1.385 (12) |
| N12—N29 | 1.373 (10) | C111—H111 | 0.9500 |
| N12—C156 | 1.312 (11) | C112—H112 | 0.9500 |
| N13—C18 | 1.373 (11) | C112—C165 | 1.395 (13) |
| N13—C47 | 1.450 (10) | C113—H113 | 0.9500 |
| C14—H14 | 0.9500 | C113—C164 | 1.376 (15) |
| C14—C201 | 1.448 (13) | C113—C193 | 1.379 (15) |
| N15—N34 | 1.362 (11) | C115—H115 | 0.9500 |
| N15—C67 | 1.386 (12) | C115—C152 | 1.380 (13) |
| N15—C119 | 1.456 (12) | C115—C188 | 1.375 (14) |
| N17—N34 | 1.351 (11) | C116—H116 | 0.9500 |
| N17—C118 | 1.449 (11) | C117—H117 | 0.9500 |
| N17—C123 | 1.386 (11) | C117—C122 | 1.324 (14) |
| C18—H18 | 0.9500 | C118—H11A | 0.9900 |
| C18—C90 | 1.341 (13) | C118—H11B | 0.9900 |
| N19—C25 | 1.461 (11) | C119—H11C | 0.9900 |
| C21—H21 | 0.9500 | C119—H11D | 0.9900 |
| C21—C61 | 1.392 (12) | C120—H120 | 0.9500 |
| C21—C159 | 1.360 (13) | C120—C173 | 1.382 (14) |
| C22—H22 | 0.9500 | C120—C175 | 1.371 (14) |
| C22—C62 | 1.409 (12) | C121—H121 | 0.9500 |
| C22—C77 | 1.372 (12) | C121—C129 | 1.401 (13) |
| N2X—C27 | 1.482 (11) | C122—H122 | 0.9500 |
| N2X—C109 | 1.375 (10) | C123—H123 | 0.9500 |
| N24—C104 | 1.449 (11) | C125—H125 | 0.9500 |

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| N24—C114 | 1.352 (11) | C125—C132 | 1.386 (12) |
| N24—C117 | 1.379 (12) | C125—C137 | 1.408 (12) |
| C25—H25A | 0.9900 | C126—H126 | 0.9500 |
| C25—H25B | 0.9900 | C126—C180 | 1.386 (13) |
| C25—N29 | 1.444 (11) | B127—C136 | 1.620 (12) |
| N26—N41 | 1.356 (10) | B127—C147 | 1.647 (12) |
| N26—C192 | 1.322 (13) | C128—H128 | 0.9500 |
| C27—H27A | 0.9900 | C128—C183 | 1.391 (14) |
| C27—H27B | 0.9900 | C129—H129 | 0.9500 |
| C27—N52 | 1.469 (11) | C129—C172 | 1.380 (13) |
| C28—H28 | 0.9500 | C130—H130 | 0.9500 |
| C28—C85 | 1.386 (12) | C130—C151 | 1.362 (15) |
| C28—C111 | 1.394 (13) | C131—H131 | 0.9500 |
| N29—C76 | 1.325 (11) | C132—H132 | 0.9500 |
| C30—C85 | 1.373 (12) | C132—C169 | 1.389 (13) |
| C30—B91 | 1.649 (12) | C133—H133 | 0.9500 |
| C30—C144 | 1.420 (12) | C133—C158 | 1.385 (14) |
| N31—C33 | 1.349 (12) | C135—H135 | 0.9500 |
| N31—N54 | 1.355 (10) | C135—C182 | 1.396 (14) |
| N31—C118 | 1.473 (12) | C136—C168 | 1.398 (12) |
| N32—N44 | 1.364 (10) | C137—B208 | 1.641 (13) |
| N32—C131 | 1.332 (12) | C138—H138 | 0.9500 |
| C33—H33 | 0.9500 | C138—C151 | 1.397 (15) |
| C33—C38 | 1.360 (14) | C138—C168 | 1.379 (13) |
| N1X—C71 | 1.459 (10) | C139—H139 | 0.9500 |
| N1X—C90 | 1.385 (11) | C139—C163 | 1.405 (13) |
| C37—C60 | 1.403 (12) | C140—H140 | 0.9500 |
| C37—C183 | 1.403 (13) | C141—H141 | 0.9500 |
| C37—B191 | 1.642 (13) | C142—H142 | 0.9500 |
| C38—H38 | 0.9500 | C142—C166 | 1.376 (13) |
| C38—C181 | 1.377 (14) | C144—H144 | 0.9500 |
| C39—H39 | 0.9500 | C146—H146 | 0.9500 |
| C39—C66 | 1.356 (13) | C146—C169 | 1.383 (13) |
| C39—C69 | 1.390 (13) | C147—C162 | 1.393 (12) |
| C40—H40 | 0.9500 | N148—C4 | 1.335 (13) |
| C40—C89 | 1.403 (12) | C149—H149 | 0.9500 |
| C40—C105 | 1.420 (13) | C149—C190 | 1.393 (13) |
| N41—C104 | 1.460 (12) | C150—H150 | 0.9500 |
| N41—C179 | 1.342 (12) | C150—C184 | 1.387 (13) |
| C42—C46 | 1.411 (12) | C151—H151 | 0.9500 |
| C42—B91 | 1.658 (13) | C152—H152 | 0.9500 |

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| C42—C189 | 1.393 (12) |
| C43—C50 | 1.394 (12) |
| C43—C97 | 1.405 (12) |
| C43—B127 | 1.644 (12) |
| N44—C92 | 1.366 (12) |
| N44—C119 | 1.432 (12) |
| N45—C88 | 1.454 (11) |
| N45—C114 | 1.354 (11) |
| N45—C122 | 1.388 (11) |
| C46—H46 | 0.9500 |
| C46—C173 | 1.397 (13) |
| C47—H47A | 0.9900 |
| C47—H47B | 0.9900 |
| C48—H48 | 0.9500 |
| C48—C141 | 1.385 (14) |
| C48—C162 | 1.381 (13) |
| C50—H50 | 0.9500 |
| C50—C193 | 1.400 (13) |
| N52—C55 | 1.336 (11) |
| C53—H53 | 0.9500 |
| C53—C157 | 1.377 (12) |
| C53—C166 | 1.371 (13) |
| N54—C181 | 1.319 (12) |
| C55—H55 | 0.9500 |
| C55—C112 | 1.370 (13) |
| C56—H56 | 0.9500 |
| C56—C130 | 1.424 (13) |
| C56—C136 | 1.391 (12) |
| C57—H57 | 0.9500 |
| C57—C72 | 1.387 (13) |
| C57—C135 | 1.371 (12) |
| C58—C116 | 1.404 (12) |
| C58—C140 | 1.409 (12) |
| C58—B208 | 1.640 (12) |
| C60—H60 | 0.9500 |
| C60—C202 | 1.369 (14) |
| C61—H61 | 0.9500 |
| C62—B127 | 1.636 (12) |
| C62—C153 | 1.416 (11) |
| C63—H63 | 0.9500 |
| C63—C93 | 1.411 (11) |
| C153—H153 | 0.9500 |
| C153—C180 | 1.373 (12) |
| C154—H154 | 0.9500 |
| C155—H155 | 0.9500 |
| C155—C187 | 1.385 (14) |
| C156—H156 | 0.9500 |
| C156—C167 | 1.379 (13) |
| C157—H157 | 0.9500 |
| C158—H158 | 0.9500 |
| C159—H159 | 0.9500 |
| C160—H160 | 0.9500 |
| C162—H162 | 0.9500 |
| C161—C171 | 1.394 (12) |
| C161—B208 | 1.655 (12) |
| C163—H163 | 0.9500 |
| C163—C188 | 1.379 (14) |
| C164—H164 | 0.9500 |
| C165—H165 | 0.9500 |
| C166—H166 | 0.9500 |
| C167—H167 | 0.9500 |
| C168—H168 | 0.9500 |
| C169—H169 | 0.9500 |
| C171—H171 | 0.9500 |
| C171—C174 | 1.392 (13) |
| C172—H172 | 0.9500 |
| C172—C198 | 1.392 (13) |
| C173—H173 | 0.9500 |
| C174—H174 | 0.9500 |
| C174—C187 | 1.353 (14) |
| C175—H175 | 0.9500 |
| C175—C189 | 1.378 (12) |
| C176—H176 | 0.9500 |
| C179—H179 | 0.9500 |
| C179—C197 | 1.375 (15) |
| C180—H180 | 0.9500 |
| C181—H181 | 0.9500 |
| C182—H182 | 0.9500 |
| C182—C200 | 1.390 (15) |
| C183—H183 | 0.9500 |
| C184—H184 | 0.9500 |
| C184—C0AA | 1.403 (14) |

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|---|---|
| C63—C142 | 1.395 (12) |
| C64—H64 | 0.9500 |
| C64—C106 | 1.395 (13) |
| C64—C147 | 1.408 (12) |
| C65—H65 | 0.9500 |
| C65—C87 | 1.428 (13) |
| C65—C201 | 1.359 (13) |
| C66—H66 | 0.9500 |
| C66—C116 | 1.390 (12) |
| C67—H67 | 0.9500 |
| C67—C123 | 1.326 (14) |
| C68—H68 | 0.9500 |
| C68—C128 | 1.378 (15) |
| C68—C202 | 1.373 (15) |
| C69—H69 | 0.9500 |
| C69—C140 | 1.366 (12) |
| C70—H70 | 0.9500 |
| C70—N215 | 1.376 (11) |
| C70—C3 | 1.358 (14) |
| C71—H71A | 0.9900 |
| C71—H71B | 0.9900 |
| C71—N215 | 1.462 (11) |
| C72—B91 | 1.632 (12) |
| C72—C194 | 1.421 (12) |
| C73—H73 | 0.9500 |
| C73—C95 | 1.373 (13) |
| C73—C108 | 1.406 (13) |
| C74—H74 | 0.9500 |
| C74—C111 | 1.381 (12) |
| C74—C144 | 1.388 (12) |
| C75—H75 | 0.9500 |
| C75—C78 | 1.387 (13) |
| C75—C95 | 1.385 (13) |
| C76—H76 | 0.9500 |
| C76—C167 | 1.364 (14) |
| C77—H77 | 0.9500 |
| C77—C126 | 1.395 (13) |
| C78—H78 | 0.9500 |
| C78—C98 | 1.396 (12) |
| C185—H185 | 0.9500 |
| C185—C207 | 1.409 (17) |
| C187—H187 | 0.9500 |
| C188—H188 | 0.9500 |
| C189—H189 | 0.9500 |
| C190—H190 | 0.9500 |
| C192—H192 | 0.9500 |
| C192—C197 | 1.385 (15) |
| C193—H193 | 0.9500 |
| C194—H194 | 0.9500 |
| C194—C200 | 1.397 (13) |
| C195—H195 | 0.9500 |
| C197—H197 | 0.9500 |
| C198—H198 | 0.9500 |
| C200—H200 | 0.9500 |
| C201—H201 | 0.9500 |
| C202—H202 | 0.9500 |
| C207—H207 | 0.9500 |
| C207—C4 | 1.375 (15) |
| C0AA—H0AA | 0.9500 |
| C3—H3 | 0.9500 |
| C2AA—H2AA | 0.9500 |
| C4—H4 | 0.9500 |
| O1—H1 | 0.8400 |
| O1—C4AA | 1.399 (12) |
| O2—H2A | 0.8400 |
| O2—C5AA | 1.401 (13) |
| C4AA—H4AA | 0.9800 |
| C4AA—H4AB | 0.9800 |
| C4AA—H4AC | 0.9800 |
| O8—H8A | 0.8400 |
| O8—C3AA | 1.477 (19) |
| C5AA—H5AA | 0.9800 |
| C5AA—H5AB | 0.9800 |
| C5AA—H5AC | 0.9800 |
| C3AA—H3AA | 0.9800 |
| C3AA—H3AB | 0.9800 |
| C3AA—H3AC | 0.9800 |

Selected geometric parameters (º)

| | | | |
|---|---|---|---|
| C1AA—Ru1—Cl7 | 162.3 (3) | N148—C88—H88A | 109.4 |
| C1AA—Ru1—C102 | 67.6 (4) | N148—C88—H88B | 109.4 |
| C1AA—Ru1—C150 | 79.2 (4) | Ru2—C89—H89 | 130.0 |
| C1AA—Ru1—C184 | 67.0 (4) | C2—C89—Ru2 | 70.5 (5) |
| C1AA—Ru1—C2AA | 37.8 (4) | C2—C89—H89 | 120.2 |
| N26—Ru1—C1AA | 111.9 (4) | C40—C89—Ru2 | 71.8 (5) |
| N26—Ru1—Cl7 | 85.5 (2) | C40—C89—C2 | 119.7 (9) |
| N26—Ru1—C102 | 161.9 (4) | C40—C89—H89 | 120.2 |
| N26—Ru1—C150 | 124.8 (3) | C18—C90—N1X | 106.7 (8) |
| N26—Ru1—C184 | 96.4 (3) | C18—C90—H90 | 126.7 |
| N26—Ru1—C0AA | 89.8 (4) | N1X—C90—H90 | 126.7 |
| N26—Ru1—C2AA | 148.8 (3) | C30—B91—C42 | 111.2 (7) |
| C102—Ru1—Cl7 | 94.9 (3) | C72—B91—C30 | 102.7 (7) |
| C102—Ru1—C150 | 37.2 (4) | C72—B91—C42 | 114.0 (7) |
| C102—Ru1—C184 | 66.3 (4) | C93—B91—C30 | 110.5 (6) |
| C102—Ru1—C2AA | 37.4 (4) | C93—B91—C42 | 106.2 (7) |
| C114—Ru1—C1AA | 96.1 (4) | C93—B91—C72 | 112.3 (7) |
| C114—Ru1—Cl7 | 88.9 (2) | N44—C92—C80 | 107.7 (9) |
| C114—Ru1—N26 | 83.1 (3) | N44—C92—H92 | 126.1 |
| C114—Ru1—C102 | 115.0 (4) | C80—C92—H92 | 126.1 |
| C114—Ru1—C150 | 151.5 (4) | C63—C93—B91 | 121.3 (7) |
| C114—Ru1—C184 | 161.6 (4) | C157—C93—C63 | 114.9 (7) |
| C114—Ru1—C0AA | 124.6 (4) | C157—C93—B91 | 123.8 (7) |
| C114—Ru1—C2AA | 91.8 (4) | Ru3—C94—H94 | 131.0 |
| C150—Ru1—Cl7 | 88.3 (3) | C84—C94—Ru3 | 71.8 (5) |
| C184—Ru1—Cl7 | 109.4 (3) | C84—C94—H94 | 119.8 |
| C184—Ru1—C150 | 36.2 (3) | C84—C94—C176 | 120.3 (9) |
| C0AA—Ru1—C1AA | 37.5 (4) | C176—C94—Ru3 | 70.0 (5) |
| C0AA—Ru1—Cl7 | 145.4 (3) | C176—C94—H94 | 119.8 |
| C0AA—Ru1—C102 | 79.6 (4) | C73—C95—C75 | 119.0 (9) |
| C0AA—Ru1—C150 | 66.6 (4) | C73—C95—H95 | 120.5 |
| C0AA—Ru1—C184 | 37.1 (4) | C75—C95—H95 | 120.5 |
| C0AA—Ru1—C2AA | 67.9 (4) | C185—N96—N148 | 103.5 (9) |
| C2AA—Ru1—Cl7 | 125.3 (3) | C43—C97—H97 | 118.9 |
| C2AA—Ru1—C150 | 67.2 (4) | C164—C97—C43 | 122.2 (9) |
| C2AA—Ru1—C184 | 79.1 (4) | C164—C97—H97 | 118.9 |
| N7—Ru3—Cl8 | 86.9 (2) | C78—C98—C108 | 115.2 (8) |
| N7—Ru3—C10 | 120.7 (3) | C78—C98—B208 | 122.7 (8) |
| N7—Ru3—N12 | 84.5 (3) | C108—C98—B208 | 121.9 (8) |

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| N7—Ru3—C84 | 117.7 (3) | C158—C100—H100 | 118.9 |
| N7—Ru3—C94 | 93.8 (3) | C158—C100—C195 | 122.2 (9) |
| N7—Ru3—C149 | 155.3 (3) | C195—C100—H100 | 118.9 |
| N7—Ru3—C176 | 94.8 (3) | N5—C99—H99 | 123.9 |
| N7—Ru3—C190 | 158.1 (3) | N5—C99—C3 | 112.1 (8) |
| C10—Ru3—Cl8 | 151.4 (3) | C3—C99—H99 | 123.9 |
| C10—Ru3—C84 | 80.5 (3) | Ru2—C101—H101 | 126.9 |
| C10—Ru3—C94 | 67.9 (3) | C2—C101—Ru2 | 71.8 (6) |
| C10—Ru3—C149 | 66.8 (3) | C2—C101—H101 | 119.2 |
| C10—Ru3—C190 | 37.4 (3) | C2—C101—C160 | 121.5 (9) |
| N12—Ru3—Cl8 | 84.5 (2) | C160—C101—Ru2 | 74.1 (5) |
| N12—Ru3—C10 | 90.5 (3) | C160—C101—H101 | 119.2 |
| N12—Ru3—C84 | 157.6 (3) | Ru1—C102—H102 | 127.4 |
| N12—Ru3—C94 | 153.8 (3) | C150—C102—Ru1 | 73.4 (5) |
| N12—Ru3—C149 | 119.9 (3) | C150—C102—H102 | 119.4 |
| N12—Ru3—C176 | 116.3 (3) | C2AA—C102—Ru1 | 72.0 (6) |
| N12—Ru3—C190 | 93.4 (3) | C2AA—C102—H102 | 119.4 |
| C84—Ru3—Cl8 | 93.7 (3) | C2AA—C102—C150 | 121.3 (9) |
| C84—Ru3—C149 | 37.7 (3) | C86—C103—B191 | 123.0 (8) |
| C84—Ru3—C190 | 67.1 (3) | C195—C103—C86 | 114.2 (8) |
| C94—Ru3—Cl8 | 121.6 (2) | C195—C103—B191 | 122.3 (8) |
| C94—Ru3—C84 | 36.5 (3) | N24—C104—N41 | 109.4 (7) |
| C94—Ru3—C149 | 66.2 (3) | N24—C104—H10A | 109.8 |
| C94—Ru3—C190 | 78.5 (3) | N24—C104—H10B | 109.8 |
| C149—Ru3—Cl8 | 91.4 (2) | N41—C104—H10A | 109.8 |
| C149—Ru3—C190 | 36.2 (3) | N41—C104—H10B | 109.8 |
| C176—Ru3—Cl8 | 159.3 (2) | H10A—C104—H10B | 108.3 |
| C176—Ru3—C10 | 37.4 (3) | Ru2—C105—H105 | 131.1 |
| C176—Ru3—C84 | 67.3 (3) | C40—C105—Ru2 | 70.1 (5) |
| C176—Ru3—C94 | 37.7 (3) | C40—C105—H105 | 119.2 |
| C176—Ru3—C149 | 78.4 (3) | C160—C105—Ru2 | 72.5 (5) |
| C176—Ru3—C190 | 66.6 (3) | C160—C105—C40 | 121.7 (8) |
| C190—Ru3—Cl8 | 114.7 (3) | C160—C105—H105 | 119.2 |
| Ru1—C1AA—H1AA | 129.6 | C110—C107—B191 | 122.3 (8) |
| C0AA—C1AA—Ru1 | 70.9 (6) | C110—C107—C198 | 114.9 (8) |
| C0AA—C1AA—H1AA | 120.0 | C198—C107—B191 | 122.6 (7) |
| C0AA—C1AA—C2AA | 119.9 (10) | C64—C106—H106 | 119.7 |
| C2AA—C1AA—Ru1 | 71.9 (6) | C141—C106—C64 | 120.5 (9) |
| C2AA—C1AA—H1AA | 120.0 | C141—C106—H106 | 119.7 |

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| C2—Ru2—Cl1X | 161.9 (3) | C9—C109—N2X | 107.3 (8) |
| C2—Ru2—C40 | 67.7 (3) | C9—C109—H109 | 126.3 |
| C2—Ru2—C89 | 37.8 (4) | N2X—C109—H109 | 126.3 |
| C2—Ru2—C105 | 78.6 (3) | C73—C108—C98 | 122.0 (8) |
| C2—Ru2—C160 | 66.9 (4) | C73—C108—H108 | 119.0 |
| N32—Ru2—Cl1X | 85.4 (2) | C98—C108—H108 | 119.0 |
| N32—Ru2—C2 | 112.5 (4) | C107—C110—H110 | 118.8 |
| N32—Ru2—C40 | 162.7 (3) | C121—C110—C107 | 122.4 (8) |
| N32—Ru2—C89 | 149.3 (3) | C121—C110—H110 | 118.8 |
| N32—Ru2—C101 | 90.9 (3) | C28—C111—H111 | 121.5 |
| N32—Ru2—C105 | 125.4 (3) | C74—C111—C28 | 117.1 (8) |
| N32—Ru2—C160 | 96.9 (3) | C74—C111—H111 | 121.5 |
| N34—Ru2—Cl1X | 89.0 (2) | C55—C112—H112 | 127.9 |
| N34—Ru2—C2 | 95.4 (4) | C55—C112—C165 | 104.1 (8) |
| N34—Ru2—N32 | 83.1 (3) | C165—C112—H112 | 127.9 |
| N34—Ru2—C40 | 114.2 (3) | C164—C113—H113 | 120.5 |
| N34—Ru2—C89 | 91.1 (3) | C164—C113—C193 | 119.0 (9) |
| N34—Ru2—C101 | 123.4 (3) | C193—C113—H113 | 120.5 |
| N34—Ru2—C105 | 151.1 (4) | N24—C114—Ru1 | 122.2 (7) |
| N34—Ru2—C160 | 160.9 (3) | N24—C114—N45 | 104.0 (8) |
| C40—Ru2—Cl1X | 94.6 (2) | N45—C114—Ru1 | 133.8 (6) |
| C40—Ru2—C105 | 37.3 (3) | C152—C115—H115 | 119.5 |
| C40—Ru2—C160 | 66.8 (3) | C188—C115—H115 | 119.5 |
| C89—Ru2—Cl1X | 124.8 (2) | C188—C115—C152 | 120.9 (9) |
| C89—Ru2—C40 | 37.2 (3) | C58—C116—H116 | 119.2 |
| C89—Ru2—C105 | 66.6 (3) | C66—C116—C58 | 121.6 (8) |
| C89—Ru2—C160 | 79.1 (3) | C66—C116—H116 | 119.2 |
| C101—Ru2—Cl1X | 146.7 (3) | N24—C117—H117 | 126.7 |
| C101—Ru2—C2 | 36.7 (4) | C122—C117—N24 | 106.6 (8) |
| C101—Ru2—C40 | 79.6 (3) | C122—C117—H117 | 126.7 |
| C101—Ru2—C89 | 67.2 (4) | N17—C118—N31 | 110.2 (7) |
| C101—Ru2—C105 | 66.3 (3) | N17—C118—H11A | 109.6 |
| C101—Ru2—C160 | 37.6 (3) | N17—C118—H11B | 109.6 |
| C105—Ru2—Cl1X | 89.1 (2) | N31—C118—H11A | 109.6 |
| C105—Ru2—C160 | 36.0 (3) | N31—C118—H11B | 109.6 |
| C160—Ru2—Cl1X | 110.0 (2) | H11A—C118—H11B | 108.1 |
| N3—Ru4—Cl5 | 87.6 (2) | N15—C119—H11C | 109.8 |
| N3—Ru4—N4 | 84.7 (3) | N15—C119—H11D | 109.8 |
| N3—Ru4—C8 | 93.3 (3) | N44—C119—N15 | 109.4 (7) |
| N3—Ru4—C14 | 120.8 (3) | N44—C119—H11C | 109.8 |
| N3—Ru4—C65 | 152.9 (3) | N44—C119—H11D | 109.8 |

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| N3—Ru4—C87 | 115.6 (3) | H11C—C119—H11D | 108.2 |
| N3—Ru4—C154 | 91.1 (3) | C173—C120—H120 | 120.4 |
| N3—Ru4—C201 | 158.9 (3) | C175—C120—H120 | 120.4 |
| N4—Ru4—Cl5 | 85.0 (2) | C175—C120—C173 | 119.2 (9) |
| N4—Ru4—C8 | 113.6 (3) | C110—C121—H121 | 119.3 |
| N4—Ru4—C14 | 90.2 (3) | C110—C121—C129 | 121.4 (8) |
| N4—Ru4—C65 | 122.3 (3) | C129—C121—H121 | 119.3 |
| N4—Ru4—C87 | 159.7 (3) | N45—C122—H122 | 126.3 |
| N4—Ru4—C154 | 150.7 (3) | C117—C122—N45 | 107.4 (8) |
| N4—Ru4—C201 | 95.1 (3) | C117—C122—H122 | 126.3 |
| C8—Ru4—Cl5 | 161.5 (2) | N17—C123—H123 | 126.3 |
| C8—Ru4—C65 | 78.8 (3) | C67—C123—N17 | 107.4 (9) |
| C8—Ru4—C87 | 67.9 (3) | C67—C123—H123 | 126.3 |
| C8—Ru4—C154 | 37.6 (3) | C132—C125—H125 | 118.7 |
| C8—Ru4—C201 | 67.4 (3) | C132—C125—C137 | 122.7 (8) |
| C14—Ru4—Cl5 | 150.6 (2) | C137—C125—H125 | 118.7 |
| C14—Ru4—C8 | 37.1 (3) | C77—C126—H126 | 121.0 |
| C14—Ru4—C65 | 66.4 (3) | C180—C126—C77 | 118.0 (9) |
| C14—Ru4—C87 | 79.9 (3) | C180—C126—H126 | 121.0 |
| C14—Ru4—C154 | 67.3 (3) | C43—B127—C147 | 110.3 (7) |
| C14—Ru4—C201 | 38.2 (3) | C62—B127—C43 | 103.9 (6) |
| C65—Ru4—Cl5 | 92.0 (2) | C62—B127—C147 | 112.2 (7) |
| C65—Ru4—C201 | 35.2 (3) | C136—B127—C43 | 115.1 (7) |
| C87—Ru4—Cl5 | 95.0 (3) | C136—B127—C62 | 112.8 (7) |
| C87—Ru4—C65 | 37.4 (3) | C136—B127—C147 | 102.7 (6) |
| C87—Ru4—C154 | 37.5 (3) | C68—C128—H128 | 119.9 |
| C87—Ru4—C201 | 66.2 (3) | C68—C128—C183 | 120.3 (10) |
| C154—Ru4—Cl5 | 123.9 (2) | C183—C128—H128 | 119.9 |
| C154—Ru4—C65 | 66.8 (3) | C121—C129—H129 | 121.3 |
| C154—Ru4—C201 | 78.8 (3) | C172—C129—C121 | 117.5 (8) |
| C201—Ru4—Cl5 | 113.4 (3) | C172—C129—H129 | 121.3 |
| Ru2—C2—H2 | 129.3 | C56—C130—H130 | 120.0 |
| C89—C2—Ru2 | 71.7 (5) | C151—C130—C56 | 120.0 (10) |
| C89—C2—H2 | 119.9 | C151—C130—H130 | 120.0 |
| C101—C2—Ru2 | 71.5 (6) | N32—C131—C80 | 112.1 (10) |
| C101—C2—H2 | 119.9 | N32—C131—H131 | 123.9 |
| C101—C2—C89 | 120.2 (9) | C80—C131—H131 | 123.9 |
| N13—N3—Ru4 | 123.5 (6) | C125—C132—H132 | 119.8 |
| N1X—N3—Ru4 | 132.8 (6) | C125—C132—C169 | 120.4 (8) |
| N1X—N3—N13 | 103.7 (7) | C169—C132—H132 | 119.8 |
| N11—N4—Ru4 | 123.6 (5) | C86—C133—H133 | 119.4 |

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| C61—N4—Ru4 | 130.6 (6) | C158—C133—C86 | 121.3 (9) |
| C61—N4—N11 | 105.7 (7) | C158—C133—H133 | 119.4 |
| C99—N5—N215 | 104.0 (7) | C57—C135—H135 | 120.1 |
| C165—N6—N52 | 103.4 (7) | C57—C135—C182 | 119.8 (9) |
| N19—N7—Ru3 | 124.0 (6) | C182—C135—H135 | 120.1 |
| N2X—N7—Ru3 | 132.8 (6) | C56—C136—B127 | 124.5 (8) |
| N2X—N7—N19 | 103.1 (7) | C56—C136—C168 | 114.9 (8) |
| Ru4—C8—H8 | 129.9 | C168—C136—B127 | 120.4 (8) |
| C14—C8—Ru4 | 70.7 (5) | C79—C137—C125 | 115.1 (8) |
| C14—C8—H8 | 120.3 | C79—C137—B208 | 123.3 (7) |
| C14—C8—C154 | 119.4 (8) | C125—C137—B208 | 121.5 (7) |
| C154—C8—Ru4 | 71.6 (5) | C151—C138—H138 | 120.2 |
| C154—C8—H8 | 120.3 | C168—C138—H138 | 120.2 |
| N19—C9—H9 | 126.4 | C168—C138—C151 | 119.5 (10) |
| C109—C9—H9 | 126.4 | C82—C139—H139 | 118.2 |
| C109—C9—N19 | 107.1 (8) | C82—C139—C163 | 123.5 (9) |
| Ru3—C10—H10 | 125.9 | C163—C139—H139 | 118.2 |
| C176—C10—Ru3 | 71.3 (5) | C58—C140—H140 | 118.6 |
| C176—C10—H10 | 120.4 | C69—C140—C58 | 122.8 (8) |
| C176—C10—C190 | 119.3 (9) | C69—C140—H140 | 118.6 |
| C190—C10—Ru3 | 74.3 (5) | C48—C141—H141 | 120.9 |
| C190—C10—H10 | 120.4 | C106—C141—C48 | 118.2 (9) |
| N4—N11—C47 | 119.5 (7) | C106—C141—H141 | 120.9 |
| C159—N11—N4 | 110.3 (7) | C63—C142—H142 | 119.8 |
| C159—N11—C47 | 129.3 (7) | C166—C142—C63 | 120.4 (9) |
| N29—N12—Ru3 | 124.3 (6) | C166—C142—H142 | 119.8 |
| C156—N12—Ru3 | 130.8 (6) | C30—C144—H144 | 118.6 |
| C156—N12—N29 | 104.8 (7) | C74—C144—C30 | 122.9 (8) |
| N3—N13—C18 | 111.5 (7) | C74—C144—H144 | 118.6 |
| N3—N13—C47 | 121.6 (7) | C79—C146—H146 | 119.7 |
| C18—N13—C47 | 126.9 (7) | C169—C146—C79 | 120.5 (8) |
| Ru4—C14—H14 | 126.2 | C169—C146—H146 | 119.7 |
| C8—C14—Ru4 | 72.2 (5) | C64—C147—B127 | 122.7 (8) |
| C8—C14—H14 | 119.7 | C162—C147—C64 | 113.2 (8) |
| C8—C14—C201 | 120.7 (8) | C162—C147—B127 | 123.7 (8) |
| C201—C14—Ru4 | 73.8 (5) | N96—N148—C88 | 119.1 (8) |
| C201—C14—H14 | 119.7 | C4—N148—C88 | 129.2 (9) |
| N34—N15—C67 | 110.5 (8) | C4—N148—N96 | 111.7 (9) |
| N34—N15—C119 | 122.4 (8) | Ru3—C149—H149 | 131.3 |
| C67—N15—C119 | 127.0 (8) | C84—C149—Ru3 | 69.6 (5) |
| N34—N17—C118 | 125.3 (7) | C84—C149—H149 | 119.7 |

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| N34—N17—C123 | 110.6 (8) | C190—C149—Ru3 | 72.2 (5) |
| C123—N17—C118 | 124.0 (8) | C190—C149—C84 | 120.6 (8) |
| N13—C18—H18 | 126.7 | C190—C149—H149 | 119.7 |
| C90—C18—N13 | 106.5 (7) | Ru1—C150—H150 | 131.2 |
| C90—C18—H18 | 126.7 | C102—C150—Ru1 | 69.4 (5) |
| N7—N19—C9 | 111.2 (7) | C102—C150—H150 | 120.3 |
| N7—N19—C25 | 121.4 (7) | C184—C150—Ru1 | 71.8 (5) |
| C9—N19—C25 | 127.4 (7) | C184—C150—C102 | 119.5 (9) |
| C61—C21—H21 | 127.2 | C184—C150—H150 | 120.3 |
| C159—C21—H21 | 127.2 | C130—C151—C138 | 119.2 (9) |
| C159—C21—C61 | 105.6 (8) | C130—C151—H151 | 120.4 |
| C62—C22—H22 | 118.2 | C138—C151—H151 | 120.4 |
| C77—C22—H22 | 118.2 | C82—C152—H152 | 118.5 |
| C77—C22—C62 | 123.7 (8) | C115—C152—C82 | 123.0 (9) |
| N7—N2X—C27 | 124.9 (7) | C115—C152—H152 | 118.5 |
| N7—N2X—C109 | 111.3 (7) | C62—C153—H153 | 118.1 |
| C109—N2X—C27 | 123.8 (7) | C180—C153—C62 | 123.8 (8) |
| C114—N24—C104 | 122.6 (8) | C180—C153—H153 | 118.1 |
| C114—N24—C117 | 111.5 (8) | Ru4—C154—H154 | 130.7 |
| C117—N24—C104 | 125.8 (7) | C8—C154—Ru4 | 70.8 (5) |
| N19—C25—H25A | 109.5 | C8—C154—H154 | 120.0 |
| N19—C25—H25B | 109.5 | C87—C154—Ru4 | 71.1 (5) |
| H25A—C25—H25B | 108.1 | C87—C154—C8 | 120.0 (8) |
| N29—C25—N19 | 110.7 (7) | C87—C154—H154 | 120.0 |
| N29—C25—H25A | 109.5 | C81—C155—H155 | 119.7 |
| N29—C25—H25B | 109.5 | C81—C155—C187 | 120.6 (9) |
| N41—N26—Ru1 | 123.2 (6) | C187—C155—H155 | 119.7 |
| C192—N26—Ru1 | 132.2 (7) | N12—C156—H156 | 124.1 |
| C192—N26—N41 | 104.6 (8) | N12—C156—C167 | 111.8 (8) |
| N2X—C27—H27A | 109.6 | C167—C156—H156 | 124.1 |
| N2X—C27—H27B | 109.6 | C53—C157—C93 | 122.9 (8) |
| H27A—C27—H27B | 108.1 | C53—C157—H157 | 118.6 |
| N52—C27—N2X | 110.4 (7) | C93—C157—H157 | 118.6 |
| N52—C27—H27A | 109.6 | C100—C158—C133 | 117.6 (8) |
| N52—C27—H27B | 109.6 | C100—C158—H158 | 121.2 |
| C85—C28—H28 | 119.7 | C133—C158—H158 | 121.2 |
| C85—C28—C111 | 120.7 (8) | N11—C159—C21 | 108.0 (8) |
| C111—C28—H28 | 119.7 | N11—C159—H159 | 126.0 |
| N12—N29—C25 | 118.7 (7) | C21—C159—H159 | 126.0 |
| C76—N29—N12 | 110.6 (7) | Ru2—C160—H160 | 131.9 |
| C76—N29—C25 | 130.5 (8) | C101—C160—Ru2 | 68.3 (5) |

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| C85—C30—B91 | 122.7 (7) | C101—C160—H160 | 121.1 |
| C85—C30—C144 | 113.8 (7) | C105—C160—Ru2 | 71.4 (5) |
| C144—C30—B91 | 123.3 (7) | C105—C160—C101 | 117.9 (9) |
| C33—N31—N54 | 112.9 (8) | C105—C160—H160 | 121.1 |
| C33—N31—C118 | 127.6 (8) | C48—C162—C147 | 124.4 (9) |
| N54—N31—C118 | 119.4 (7) | C48—C162—H162 | 117.8 |
| N44—N32—Ru2 | 121.9 (6) | C147—C162—H162 | 117.8 |
| C131—N32—Ru2 | 132.7 (7) | C81—C161—B208 | 121.1 (8) |
| C131—N32—N44 | 105.4 (8) | C171—C161—C81 | 114.6 (8) |
| N31—C33—H33 | 127.4 | C171—C161—B208 | 123.8 (8) |
| N31—C33—C38 | 105.1 (9) | C139—C163—H163 | 120.6 |
| C38—C33—H33 | 127.4 | C188—C163—C139 | 118.8 (9) |
| N15—N34—Ru2 | 121.9 (7) | C188—C163—H163 | 120.6 |
| N17—N34—Ru2 | 133.7 (6) | C97—C164—H164 | 119.8 |
| N17—N34—N15 | 104.5 (8) | C113—C164—C97 | 120.4 (10) |
| N3—N1X—C71 | 125.7 (7) | C113—C164—H164 | 119.8 |
| N3—N1X—C90 | 111.5 (7) | N6—C165—C112 | 112.5 (8) |
| C90—N1X—C71 | 122.8 (8) | N6—C165—H165 | 123.7 |
| C60—C37—C183 | 114.5 (9) | C112—C165—H165 | 123.7 |
| C60—C37—B191 | 121.2 (8) | C53—C166—C142 | 118.9 (9) |
| C183—C37—B191 | 124.1 (8) | C53—C166—H166 | 120.5 |
| C33—C38—H38 | 126.7 | C142—C166—H166 | 120.5 |
| C33—C38—C181 | 106.5 (9) | C76—C167—C156 | 104.8 (8) |
| C181—C38—H38 | 126.7 | C76—C167—H167 | 127.6 |
| C66—C39—H39 | 120.8 | C156—C167—H167 | 127.6 |
| C66—C39—C69 | 118.3 (8) | C136—C168—H168 | 118.0 |
| C69—C39—H39 | 120.8 | C138—C168—C136 | 124.0 (9) |
| Ru2—C40—H40 | 128.0 | C138—C168—H168 | 118.0 |
| C89—C40—Ru2 | 70.9 (5) | C132—C169—H169 | 120.9 |
| C89—C40—H40 | 120.5 | C146—C169—C132 | 118.2 (8) |
| C89—C40—C105 | 119.0 (8) | C146—C169—H169 | 120.9 |
| C105—C40—Ru2 | 72.6 (5) | C161—C171—H171 | 118.6 |
| C105—C40—H40 | 120.5 | C174—C171—C161 | 122.8 (9) |
| N26—N41—C104 | 119.6 (7) | C174—C171—H171 | 118.6 |
| C179—N41—N26 | 111.5 (9) | C129—C172—H172 | 119.6 |
| C179—N41—C104 | 128.8 (8) | C129—C172—C198 | 120.8 (9) |
| C46—C42—B91 | 121.9 (7) | C198—C172—H172 | 119.6 |
| C189—C42—C46 | 115.7 (8) | C46—C173—H173 | 120.0 |
| C189—C42—B91 | 122.4 (8) | C120—C173—C46 | 120.0 (9) |
| C50—C43—C97 | 115.4 (8) | C120—C173—H173 | 120.0 |
| C50—C43—B127 | 124.0 (8) | C171—C174—H174 | 119.8 |

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| C97—C43—B127 | 120.6 (7) | C187—C174—C171 | 120.4 (9) |
| N32—N44—C92 | 109.6 (8) | C187—C174—H174 | 119.8 |
| N32—N44—C119 | 120.9 (7) | C120—C175—H175 | 119.7 |
| C92—N44—C119 | 129.4 (8) | C120—C175—C189 | 120.5 (9) |
| C114—N45—C88 | 125.4 (8) | C189—C175—H175 | 119.7 |
| C114—N45—C122 | 110.5 (8) | Ru3—C176—H176 | 129.4 |
| C122—N45—C88 | 124.0 (8) | C10—C176—Ru3 | 71.3 (5) |
| C42—C46—H46 | 119.2 | C10—C176—C94 | 121.0 (9) |
| C173—C46—C42 | 121.6 (9) | C10—C176—H176 | 119.5 |
| C173—C46—H46 | 119.2 | C94—C176—Ru3 | 72.3 (5) |
| N11—C47—N13 | 110.3 (7) | C94—C176—H176 | 119.5 |
| N11—C47—H47A | 109.6 | N41—C179—H179 | 126.4 |
| N11—C47—H47B | 109.6 | N41—C179—C197 | 107.2 (9) |
| N13—C47—H47A | 109.6 | C197—C179—H179 | 126.4 |
| N13—C47—H47B | 109.6 | C126—C180—H180 | 119.8 |
| H47A—C47—H47B | 108.1 | C153—C180—C126 | 120.5 (9) |
| C141—C48—H48 | 119.9 | C153—C180—H180 | 119.8 |
| C162—C48—H48 | 119.9 | C38—C181—H181 | 124.1 |
| C162—C48—C141 | 120.2 (9) | N54—C181—C38 | 111.7 (9) |
| C43—C50—H50 | 118.6 | N54—C181—H181 | 124.1 |
| C43—C50—C193 | 122.7 (9) | C135—C182—H182 | 120.7 |
| C193—C50—H50 | 118.6 | C200—C182—C135 | 118.6 (9) |
| N6—N52—C27 | 121.7 (8) | C200—C182—H182 | 120.7 |
| C55—N52—N6 | 113.0 (8) | C37—C183—H183 | 118.8 |
| C55—N52—C27 | 125.2 (8) | C128—C183—C37 | 122.4 (9) |
| C157—C53—H53 | 119.6 | C128—C183—H183 | 118.8 |
| C166—C53—H53 | 119.6 | Ru1—C184—H184 | 131.9 |
| C166—C53—C157 | 120.8 (8) | C150—C184—Ru1 | 72.0 (5) |
| C181—N54—N31 | 103.7 (8) | C150—C184—H184 | 119.9 |
| N52—C55—H55 | 126.6 | C150—C184—C0AA | 120.2 (10) |
| N52—C55—C112 | 106.9 (9) | C0AA—C184—Ru1 | 69.0 (5) |
| C112—C55—H55 | 126.6 | C0AA—C184—H184 | 119.9 |
| C130—C56—H56 | 118.8 | N96—C185—H185 | 123.5 |
| C136—C56—H56 | 118.8 | N96—C185—C207 | 113.1 (10) |
| C136—C56—C130 | 122.4 (9) | C207—C185—H185 | 123.5 |
| C72—C57—H57 | 117.6 | C155—C187—H187 | 120.5 |
| C135—C57—H57 | 117.6 | C174—C187—C155 | 119.1 (9) |
| C135—C57—C72 | 124.8 (9) | C174—C187—H187 | 120.5 |
| C116—C58—C140 | 115.0 (8) | C115—C188—C163 | 119.2 (9) |
| C116—C58—B208 | 123.0 (8) | C115—C188—H188 | 120.4 |
| C140—C58—B208 | 121.7 (8) | C163—C188—H188 | 120.4 |

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| C37—C60—H60 | 118.3 | C42—C189—H189 | 118.7 |
| C202—C60—C37 | 123.4 (10) | C175—C189—C42 | 122.7 (9) |
| C202—C60—H60 | 118.3 | C175—C189—H189 | 118.7 |
| N4—C61—C21 | 110.4 (8) | Ru3—C190—H190 | 132.8 |
| N4—C61—H61 | 124.8 | C10—C190—Ru3 | 68.3 (5) |
| C21—C61—H61 | 124.8 | C10—C190—H190 | 120.2 |
| C22—C62—B127 | 122.3 (7) | C149—C190—Ru3 | 71.7 (5) |
| C22—C62—C153 | 113.4 (8) | C149—C190—C10 | 119.6 (9) |
| C153—C62—B127 | 124.1 (7) | C149—C190—H190 | 120.2 |
| C93—C63—H63 | 119.0 | C37—B191—C82 | 112.1 (7) |
| C142—C63—H63 | 119.0 | C103—B191—C37 | 109.6 (7) |
| C142—C63—C93 | 122.0 (8) | C103—B191—C82 | 102.9 (7) |
| C106—C64—H64 | 118.3 | C107—B191—C37 | 106.1 (7) |
| C106—C64—C147 | 123.4 (9) | C107—B191—C82 | 111.8 (7) |
| C147—C64—H64 | 118.3 | C107—B191—C103 | 114.5 (7) |
| Ru4—C65—H65 | 131.8 | N26—C192—H192 | 123.9 |
| C87—C65—Ru4 | 69.5 (5) | N26—C192—C197 | 112.2 (10) |
| C87—C65—H65 | 119.3 | C197—C192—H192 | 123.9 |
| C201—C65—Ru4 | 72.5 (6) | C50—C193—H193 | 119.9 |
| C201—C65—H65 | 119.3 | C113—C193—C50 | 120.2 (9) |
| C201—C65—C87 | 121.5 (9) | C113—C193—H193 | 119.9 |
| C39—C66—H66 | 119.2 | C72—C194—H194 | 118.8 |
| C39—C66—C116 | 121.6 (9) | C200—C194—C72 | 122.3 (9) |
| C116—C66—H66 | 119.2 | C200—C194—H194 | 118.8 |
| N15—C67—H67 | 126.5 | C100—C195—C103 | 122.2 (8) |
| C123—C67—N15 | 106.9 (8) | C100—C195—H195 | 118.9 |
| C123—C67—H67 | 126.5 | C103—C195—H195 | 118.9 |
| C128—C68—H68 | 120.6 | C179—C197—C192 | 104.5 (10) |
| C202—C68—H68 | 120.6 | C179—C197—H197 | 127.8 |
| C202—C68—C128 | 118.9 (10) | C192—C197—H197 | 127.8 |
| C39—C69—H69 | 119.7 | C107—C198—H198 | 118.5 |
| C140—C69—C39 | 120.6 (9) | C172—C198—C107 | 123.0 (8) |
| C140—C69—H69 | 119.7 | C172—C198—H198 | 118.5 |
| N215—C70—H70 | 127.4 | C182—C200—C194 | 120.2 (9) |
| C3—C70—H70 | 127.4 | C182—C200—H200 | 119.9 |
| C3—C70—N215 | 105.1 (8) | C194—C200—H200 | 119.9 |
| N1X—C71—H71A | 109.5 | Ru4—C201—H201 | 131.9 |
| N1X—C71—H71B | 109.5 | C14—C201—Ru4 | 68.1 (5) |
| N1X—C71—N215 | 110.6 (7) | C14—C201—H201 | 120.4 |
| H71A—C71—H71B | 108.1 | C65—C201—Ru4 | 72.3 (6) |
| N215—C71—H71A | 109.5 | C65—C201—C14 | 119.1 (9) |

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| N215—C71—H71B | 109.5 | C65—C201—H201 | 120.4 |
| C57—C72—B91 | 122.5 (8) | C60—C202—C68 | 120.5 (10) |
| C57—C72—C194 | 114.4 (8) | C60—C202—H202 | 119.7 |
| C194—C72—B91 | 122.8 (8) | C68—C202—H202 | 119.7 |
| C95—C73—H73 | 119.8 | C185—C207—H207 | 128.3 |
| C95—C73—C108 | 120.4 (8) | C4—C207—C185 | 103.4 (10) |
| C108—C73—H73 | 119.8 | C4—C207—H207 | 128.3 |
| C111—C74—H74 | 119.4 | C58—B208—C98 | 111.4 (7) |
| C111—C74—C144 | 121.1 (8) | C58—B208—C137 | 111.8 (7) |
| C144—C74—H74 | 119.4 | C58—B208—C161 | 103.8 (6) |
| C78—C75—H75 | 119.8 | C98—B208—C161 | 112.0 (7) |
| C95—C75—H75 | 119.8 | C137—B208—C98 | 106.5 (7) |
| C95—C75—C78 | 120.5 (9) | C137—B208—C161 | 111.5 (7) |
| N29—C76—H76 | 126.0 | N5—N215—C70 | 113.3 (7) |
| N29—C76—C167 | 108.0 (8) | N5—N215—C71 | 121.9 (7) |
| C167—C76—H76 | 126.0 | C70—N215—C71 | 124.7 (7) |
| C22—C77—H77 | 119.7 | Ru1—C0AA—H0AA | 126.9 |
| C22—C77—C126 | 120.5 (9) | C1AA—C0AA—Ru1 | 71.6 (6) |
| C126—C77—H77 | 119.7 | C1AA—C0AA—C184 | 120.6 (10) |
| C75—C78—H78 | 118.6 | C1AA—C0AA—H0AA | 119.7 |
| C75—C78—C98 | 122.9 (9) | C184—C0AA—Ru1 | 73.8 (6) |
| C98—C78—H78 | 118.6 | C184—C0AA—H0AA | 119.7 |
| C137—C79—H79 | 118.5 | C70—C3—C99 | 105.4 (8) |
| C137—C79—C146 | 123.0 (8) | C70—C3—H3 | 127.3 |
| C146—C79—H79 | 118.5 | C99—C3—H3 | 127.3 |
| C92—C80—H80 | 127.4 | Ru1—C2AA—H2AA | 130.8 |
| C131—C80—H80 | 127.4 | C1AA—C2AA—Ru1 | 70.2 (6) |
| C131—C80—C92 | 105.1 (9) | C1AA—C2AA—H2AA | 120.8 |
| C155—C81—H81 | 118.7 | C102—C2AA—Ru1 | 70.7 (6) |
| C155—C81—C161 | 122.5 (9) | C102—C2AA—C1AA | 118.4 (10) |
| C161—C81—H81 | 118.7 | C102—C2AA—H2AA | 120.8 |
| C139—C82—B191 | 119.4 (8) | N148—C4—C207 | 108.4 (10) |
| C152—C82—C139 | 114.5 (8) | N148—C4—H4 | 125.8 |
| C152—C82—B191 | 125.4 (8) | C207—C4—H4 | 125.8 |
| Ru3—C84—H84 | 127.1 | C4AA—O1—H1 | 109.5 |
| C94—C84—Ru3 | 71.6 (5) | C5AA—O2—H2A | 109.5 |
| C94—C84—H84 | 120.5 | O1—C4AA—H4AA | 109.5 |
| C94—C84—C149 | 119.0 (8) | O1—C4AA—H4AB | 109.5 |
| C149—C84—Ru3 | 72.7 (5) | O1—C4AA—H4AC | 109.5 |
| C149—C84—H84 | 120.5 | H4AA—C4AA— | 109.5 |

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| | | H4AB | |
| C103—C86—H86 | 118.8 | H4AA—C4AA—H4AC | 109.5 |
| C133—C86—H86 | 118.8 | H4AB—C4AA—H4AC | 109.5 |
| C133—C86—C103 | 122.5 (9) | C3AA—O8—H8A | 109.5 |
| C28—C85—H85 | 117.8 | O2—C5AA—H5AA | 109.5 |
| C30—C85—C28 | 124.4 (8) | O2—C5AA—H5AB | 109.5 |
| C30—C85—H85 | 117.8 | O2—C5AA—H5AC | 109.5 |
| Ru4—C87—H87 | 127.0 | H5AA—C5AA—H5AB | 109.5 |
| C65—C87—Ru4 | 73.1 (5) | H5AA—C5AA—H5AC | 109.5 |
| C65—C87—H87 | 120.5 | H5AB—C5AA—H5AC | 109.5 |
| C154—C87—Ru4 | 71.4 (5) | O8—C3AA—H3AA | 109.5 |
| C154—C87—C65 | 119.0 (8) | O8—C3AA—H3AB | 109.5 |
| C154—C87—H87 | 120.5 | O8—C3AA—H3AC | 109.5 |
| N45—C88—H88A | 109.4 | H3AA—C3AA—H3AB | 109.5 |
| N45—C88—H88B | 109.4 | H3AA—C3AA—H3AC | 109.5 |
| H88A—C88—H88B | 108.0 | H3AB—C3AA—H3AC | 109.5 |
| N148—C88—N45 | 111.0 (8) | | |

Selected geometric parameters (º)

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| Ru1—C1AA—C0AA—C184 | 57.4 (9) | C89—C40—C105—C160 | -2.3 (13) |
| Ru1—C1AA—C2AA—C102 | -53.6 (8) | C90—N1X—C71—N215 | -94.1 (10) |
| Ru1—N26—N41—C104 | 0.2 (11) | B91—C30—C85—C28 | 175.5 (8) |
| Ru1—N26—N41—C179 | -179.5 (6) | B91—C30—C144—C74 | -175.9 (8) |
| Ru1—N26—C192—C197 | 179.0 (7) | B91—C42—C46—C173 | 179.5 (8) |
| Ru1—C102—C150—C184 | -53.4 (8) | B91—C42—C189—C175 | -178.5 (8) |
| Ru1—C102—C2AA—C1AA | 53.4 (8) | B91—C72—C194—C200 | 173.2 (8) |
| Ru1—C150—C184—C0AA | -51.4 (9) | B91—C93—C157—C53 | -179.0 (8) |
| Ru1—C184—C0AA—C1AA | -56.4 (9) | C92—N44—C119—N15 | 122.7 (10) |
| Ru3—N7—N19—C9 | -178.6 (6) | C92—C80—C131— | -3.0 (12) |

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| | | N32 | |
| Ru3—N7—N19—C25 | 0.7 (11) | C93—C63—C142—C166 | -2.7 (13) |
| Ru3—N7—N2X—C27 | -4.6 (13) | C94—C84—C149—Ru3 | -56.6 (7) |
| Ru3—N7—N2X—C109 | 178.3 (7) | C94—C84—C149—C190 | -3.5 (13) |
| Ru3—C10—C176—C94 | 54.7 (7) | C95—C73—C108—C98 | 0.8 (13) |
| Ru3—C10—C190—C149 | -52.1 (8) | C95—C75—C78—C98 | -3.3 (14) |
| Ru3—N12—N29—C25 | 8.9 (10) | N96—N148—C4—C207 | 1.6 (12) |
| Ru3—N12—N29—C76 | -176.5 (6) | N96—C185—C207—C4 | 0.6 (14) |
| Ru3—N12—C156—C167 | 176.9 (6) | C97—C43—C50—C193 | 2.0 (13) |
| Ru3—C84—C94—C176 | -52.5 (7) | C97—C43—B127—C62 | -70.6 (10) |
| Ru3—C84—C149—C190 | 53.2 (8) | C97—C43—B127—C136 | 165.5 (8) |
| Ru3—C94—C176—C10 | -54.3 (8) | C97—C43—B127—C147 | 49.8 (10) |
| Ru3—C149—C190—C10 | 50.6 (7) | C99—N5—N215—C70 | 1.2 (10) |
| Ru2—C2—C89—C40 | 54.3 (7) | C99—N5—N215—C71 | 178.2 (8) |
| Ru2—C2—C101—C160 | -57.3 (8) | C101—C2—C89—Ru2 | -54.6 (8) |
| Ru2—N32—N44—C92 | -177.3 (6) | C101—C2—C89—C40 | -0.3 (13) |
| Ru2—N32—N44—C119 | -0.4 (11) | C102—C150—C184—Ru1 | 52.3 (8) |
| Ru2—N32—C131—C80 | 178.4 (7) | C102—C150—C184—C0AA | 0.9 (14) |
| Ru2—C40—C89—C2 | -53.7 (7) | C103—C86—C133—C158 | 1.5 (13) |
| Ru2—C40—C105—C160 | 53.3 (8) | C104—N24—C114—Ru1 | 1.0 (12) |
| Ru2—C101—C160—C105 | -53.2 (7) | C104—N24—C114—N45 | -178.6 (8) |
| Ru2—C105—C160—C101 | 51.7 (7) | C104—N24—C117—C122 | 178.6 (9) |
| Ru4—N3—N13—C18 | -176.2 (6) | C104—N41—C179—C197 | -179.7 (9) |
| Ru4—N3—N13—C47 | 3.0 (10) | C105—C40—C89—Ru2 | 56.4 (7) |
| Ru4—N3—N1X— | -5.0 (12) | C105—C40—C89— | 2.7 (12) |

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| C71 | | C2 | |
| Ru4—N3—N1X—C90 | 176.3 (6) | C107—C110—C121—C129 | 1.1 (14) |
| Ru4—N4—N11—C47 | 12.8 (10) | C106—C64—C147—B127 | 172.1 (8) |
| Ru4—N4—N11—C159 | -177.2 (6) | C106—C64—C147—C162 | -0.2 (12) |
| Ru4—N4—C61—C21 | 176.4 (6) | C109—C9—N19—N7 | -0.4 (11) |
| Ru4—C8—C14—C201 | -57.9 (8) | C109—C9—N19—C25 | -179.7 (8) |
| Ru4—C8—C154—C87 | 53.4 (7) | C109—N2X—C27—N52 | -96.2 (9) |
| Ru4—C14—C201—C65 | -53.2 (8) | C108—C73—C95—C75 | 0.1 (13) |
| Ru4—C65—C87—C154 | -56.6 (7) | C108—C98—B208—C58 | -151.4 (7) |
| Ru4—C65—C201—C14 | 51.2 (7) | C108—C98—B208—C137 | 86.5 (9) |
| Ru4—C87—C154—C8 | -53.2 (7) | C108—C98—B208—C161 | -35.7 (11) |
| C2—C101—C160—Ru2 | 56.2 (8) | C110—C107—B191—C37 | 77.7 (10) |
| C2—C101—C160—C105 | 3.0 (13) | C110—C107—B191—C82 | -44.7 (12) |
| N3—N13—C18—C90 | -1.7 (10) | C110—C107—B191—C103 | -161.3 (8) |
| N3—N13—C47—N11 | 52.1 (10) | C110—C107—C198—C172 | 2.0 (14) |
| N3—N1X—C71—N215 | 87.3 (10) | C110—C121—C129—C172 | -0.1 (14) |
| N3—N1X—C90—C18 | 0.9 (10) | C111—C28—C85—C30 | 1.5 (13) |
| N4—N11—C47—N13 | -59.9 (10) | C111—C74—C144—C30 | -0.8 (13) |
| N4—N11—C159—C21 | 1.0 (10) | C114—N24—C104—N41 | -55.7 (11) |
| N5—C99—C3—C70 | 2.9 (12) | C114—N24—C117—C122 | 1.3 (11) |
| N6—N52—C55—C112 | 0.1 (10) | C114—N45—C88—N148 | -102.4 (10) |
| N7—N19—C25—N29 | 53.7 (10) | C114—N45—C122—C117 | 0.1 (11) |
| N7—N2X—C27—N52 | 87.1 (10) | C116—C58—C140—C69 | -1.7 (12) |
| N7—N2X—C109—C9 | 1.0 (10) | C116—C58—B208—C98 | 31.7 (11) |
| C8—C14—C201—Ru4 | 57.1 (8) | C116—C58—B208—C137 | 150.7 (8) |

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| C8—C14—C201—C65 | 3.9 (13) |
| C9—N19—C25—N29 | -127.2 (9) |
| N11—N4—C61—C21 | 0.5 (10) |
| N12—N29—C76—C167 | -0.8 (10) |
| N12—C156—C167—C76 | -1.0 (11) |
| N13—N3—N1X—C71 | 176.8 (7) |
| N13—N3—N1X—C90 | -1.9 (9) |
| N13—C18—C90—N1X | 0.5 (9) |
| C14—C8—C154—Ru4 | -54.0 (7) |
| C14—C8—C154—C87 | -0.6 (12) |
| N15—C67—C123—N17 | -0.2 (10) |
| C18—N13—C47—N11 | -128.8 (8) |
| N19—N7—N2X—C27 | 175.9 (7) |
| N19—N7—N2X—C109 | -1.2 (9) |
| N19—C9—C109—N2X | -0.3 (10) |
| N19—C25—N29—N12 | -57.4 (10) |
| N19—C25—N29—C76 | 129.2 (9) |
| C22—C62—B127—C43 | -82.6 (9) |
| C22—C62—B127—C136 | 42.8 (11) |
| C22—C62—B127—C147 | 158.2 (8) |
| C22—C62—C153—C180 | -3.0 (13) |
| C22—C77—C126—C180 | -2.1 (14) |
| N2X—N7—N19—C9 | 1.0 (9) |
| N2X—N7—N19—C25 | -179.7 (7) |
| C116—C58—B208—C161 | -88.9 (10) |
| C117—N24—C104—N41 | 127.3 (9) |
| C117—N24—C114—Ru1 | 178.4 (6) |
| C117—N24—C114—N45 | -1.3 (10) |
| C118—N17—N34—Ru2 | -3.7 (13) |
| C118—N17—N34—N15 | 176.1 (7) |
| C118—N17—C123—C67 | -176.1 (8) |
| C118—N31—C33—C38 | -174.6 (9) |
| C118—N31—N54—C181 | 175.4 (8) |
| C119—N15—N34—Ru2 | -0.1 (11) |
| C119—N15—N34—N17 | -180.0 (8) |
| C119—N15—C67—C123 | -179.9 (8) |
| C119—N44—C92—C80 | -177.7 (9) |
| C120—C175—C189—C42 | -4.1 (14) |
| C121—C129—C172—C198 | 0.2 (15) |
| C122—N45—C88—N148 | 81.6 (11) |
| C122—N45—C114—Ru1 | -178.9 (7) |
| C122—N45—C114—N24 | 0.7 (10) |
| C123—N17—N34—Ru2 | 179.9 (7) |
| C123—N17—N34—N15 | -0.2 (9) |
| C123—N17—C118—N31 | -87.4 (10) |
| C125—C132—C169—C146 | 1.6 (14) |
| C125—C137—B208—C58 | -34.9 (11) |
| C125—C137—B208—C98 | 87.0 (9) |

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| N2X—C27—N52—N6 | 37.1 (11) |
| N2X—C27—N52—C55 | -145.1 (9) |
| N24—C117—C122—N45 | -0.8 (10) |
| C25—N29—C76—C167 | 173.1 (9) |
| N26—N41—C104—N24 | 53.6 (11) |
| N26—N41—C179—C197 | 0.0 (11) |
| N26—C192—C197—C179 | 1.7 (13) |
| C27—N2X—C109—C9 | -176.2 (8) |
| C27—N52—C55—C112 | -177.9 (8) |
| N29—N12—C156—C167 | 0.6 (10) |
| N29—C76—C167—C156 | 1.1 (11) |
| C30—B91—C93—C63 | -146.8 (7) |
| C30—B91—C93—C157 | 34.1 (11) |
| N31—C33—C38—C181 | -0.6 (12) |
| N31—N54—C181—C38 | -0.2 (11) |
| N32—N44—C92—C80 | -1.1 (11) |
| N32—N44—C119—N15 | -53.6 (11) |
| C33—N31—N54—C181 | -0.2 (10) |
| C33—N31—C118—N17 | -132.4 (9) |
| C33—C38—C181—N54 | 0.5 (13) |
| N34—N15—C67—C123 | 0.1 (10) |
| N34—N15—C119—N44 | 55.3 (11) |
| N34—N17—C118—N31 | 96.7 (10) |
| N34—N17—C123—C67 | 0.3 (10) |
| C125—C137—B208—C161 | -150.6 (8) |
| B127—C43—C50—C193 | -175.8 (8) |
| B127—C43—C97—C164 | 177.3 (8) |
| B127—C62—C153—C180 | -177.7 (8) |
| B127—C136—C168—C138 | -174.9 (8) |
| B127—C147—C162—C48 | -171.3 (8) |
| C128—C68—C202—C60 | 1.4 (15) |
| C129—C172—C198—C107 | -1.2 (16) |
| C130—C56—C136—B127 | 174.4 (8) |
| C130—C56—C136—C168 | 0.5 (12) |
| C131—N32—N44—C92 | -0.7 (10) |
| C131—N32—N44—C119 | 176.2 (9) |
| C131—C80—C92—N44 | 2.4 (11) |
| C132—C125—C137—C79 | -2.3 (13) |
| C132—C125—C137—B208 | -178.3 (8) |
| C133—C86—C103—B191 | -173.0 (8) |
| C133—C86—C103—C195 | -1.6 (12) |
| C135—C57—C72—B91 | -174.7 (8) |
| C135—C57—C72—C194 | -0.8 (13) |
| C135—C182—C200—C194 | -1.0 (14) |
| C136—C56—C130—C151 | 0.1 (14) |
| C136—B127—C147—C64 | -99.9 (9) |
| C136—B127—C147—C162 | 71.5 (9) |
| C137—C79—C146—C169 | -1.1 (14) |

| | |
|---|---|
| N1X—N3—N13—C18 | 2.2 (9) |
| N1X—N3—N13—C47 | -178.5 (7) |
| N1X—C71—N215—N5 | 37.8 (11) |
| N1X—C71—N215—C70 | -145.6 (8) |
| C37—C60—C202—C68 | 0.2 (15) |
| C39—C66—C116—C58 | -2.1 (13) |
| C39—C69—C140—C58 | -0.3 (13) |
| C40—C105—C160—Ru2 | -52.2 (8) |
| C40—C105—C160—C101 | -0.5 (13) |
| N41—N26—C192—C197 | -1.7 (12) |
| N41—C179—C197—C192 | -0.9 (12) |
| C42—C46—C173—C120 | 2.1 (14) |
| C42—B91—C93—C63 | 92.5 (9) |
| C42—B91—C93—C157 | -86.7 (9) |
| C43—C50—C193—C113 | -2.6 (15) |
| C43—C97—C164—C113 | -0.2 (15) |
| C43—B127—C136—C56 | 136.9 (8) |
| C43—B127—C136—C168 | -49.5 (10) |
| C43—B127—C147—C64 | 23.3 (11) |
| C43—B127—C147—C162 | -165.2 (8) |
| N44—N32—C131—C80 | 2.3 (11) |
| N45—C88—N148—N96 | -57.2 (11) |
| N45—C88—N148—C4 | 123.4 (10) |
| C46—C42—B91—C30 | 145.6 (8) |
| C137—C125—C132—C169 | 0.2 (14) |
| C139—C82—C152—C115 | -1.6 (12) |
| C139—C82—B191—C37 | 52.0 (10) |
| C139—C82—B191—C103 | -65.7 (10) |
| C139—C82—B191—C107 | 171.0 (7) |
| C139—C163—C188—C115 | -0.5 (13) |
| C140—C58—C116—C66 | 2.8 (12) |
| C140—C58—B208—C98 | -154.8 (8) |
| C140—C58—B208—C137 | -35.7 (11) |
| C140—C58—B208—C161 | 84.6 (9) |
| C141—C48—C162—C147 | -1.8 (14) |
| C142—C63—C93—B91 | -178.8 (8) |
| C142—C63—C93—C157 | 0.4 (12) |
| C144—C30—C85—C28 | 0.6 (12) |
| C144—C30—B91—C42 | -29.9 (11) |
| C144—C30—B91—C72 | 92.5 (9) |
| C144—C30—B91—C93 | -147.6 (8) |
| C144—C74—C111—C28 | 2.9 (12) |
| C146—C79—C137—C125 | 2.8 (13) |
| C146—C79—C137—B208 | 178.7 (8) |
| C147—C64—C106—C141 | 0.4 (14) |
| C147—B127—C136—C56 | -103.1 (9) |
| C147—B127—C136—C168 | 70.5 (9) |
| N148—N96—C185—C207 | 0.3 (12) |

| | |
|---|---|
| C46—C42—B91—C72 | 30.0 (11) |
| C46—C42—B91—C93 | -94.2 (9) |
| C46—C42—C189—C175 | 2.0 (13) |
| C47—N11—C159—C21 | 169.8 (8) |
| C47—N13—C18—C90 | 179.1 (8) |
| C50—C43—C97—C164 | -0.6 (13) |
| C50—C43—B127—C62 | 107.1 (9) |
| C50—C43—B127—C136 | -16.8 (12) |
| C50—C43—B127—C147 | -132.5 (8) |
| N52—N6—C165—C112 | 0.1 (10) |
| N52—C55—C112—C165 | 0.0 (10) |
| N54—N31—C33—C38 | 0.5 (11) |
| N54—N31—C118—N17 | 52.8 (10) |
| C55—C112—C165—N6 | -0.1 (11) |
| C56—C130—C151—C138 | -0.5 (14) |
| C56—C136—C168—C138 | -0.7 (12) |
| C57—C72—B91—C30 | 84.6 (9) |
| C57—C72—B91—C42 | -154.9 (8) |
| C57—C72—B91—C93 | -34.1 (11) |
| C57—C72—C194—C200 | -0.7 (13) |
| C57—C135—C182—C200 | -0.4 (14) |
| C60—C37—C183—C128 | 2.4 (13) |
| C60—C37—B191—C82 | -164.7 (8) |
| C60—C37—B191—C103 | -51.1 (11) |
| C149—C84—C94—Ru3 | 57.2 (7) |
| C149—C84—C94—C176 | 4.6 (13) |
| C150—C102—C2AA—Ru1 | -56.6 (8) |
| C150—C102—C2AA—C1AA | -3.3 (14) |
| C150—C184—C0AA—Ru1 | 52.8 (9) |
| C150—C184—C0AA—C1AA | -3.6 (15) |
| C151—C138—C168—C136 | 0.3 (14) |
| C152—C82—C139—C163 | 1.1 (12) |
| C152—C82—B191—C37 | -137.3 (8) |
| C152—C82—B191—C103 | 105.0 (9) |
| C152—C82—B191—C107 | -18.3 (12) |
| C152—C115—C188—C163 | 0.0 (14) |
| C153—C62—B127—C43 | 91.6 (10) |
| C153—C62—B127—C136 | -143.0 (8) |
| C153—C62—B127—C147 | -27.6 (11) |
| C154—C8—C14—Ru4 | 54.4 (7) |
| C154—C8—C14—C201 | -3.5 (13) |
| C155—C81—C161—C171 | -0.8 (13) |
| C155—C81—C161—B208 | 171.7 (8) |
| C156—N12—N29—C25 | -174.5 (8) |
| C156—N12—N29—C76 | 0.1 (10) |
| C157—C53—C166—C142 | -0.6 (14) |
| C158—C100—C195—C103 | -0.9 (13) |
| C159—N11—C47—N13 | 132.2 (9) |

| | |
|---|---|
| C60—C37—B191—C107 | 73.0 (10) |
| C61—N4—N11—C47 | -171.0 (7) |
| C61—N4—N11—C159 | -1.0 (9) |
| C61—C21—C159—N11 | -0.7 (10) |
| C62—C22—C77—C126 | -1.3 (14) |
| C62—B127—C136—C56 | 17.8 (11) |
| C62—B127—C136—C168 | -168.6 (7) |
| C62—B127—C147—C64 | 138.7 (8) |
| C62—B127—C147—C162 | -49.8 (11) |
| C62—C153—C180—C126 | -0.1 (15) |
| C63—C93—C157—C53 | 1.8 (13) |
| C63—C142—C166—C53 | 2.8 (13) |
| C64—C106—C141—C48 | -1.2 (13) |
| C64—C147—C162—C48 | 0.9 (12) |
| C65—C87—C154—Ru4 | 57.5 (7) |
| C65—C87—C154—C8 | 4.3 (12) |
| C66—C39—C69—C140 | 1.1 (13) |
| C67—N15—N34—Ru2 | 180.0 (6) |
| C67—N15—N34—N17 | 0.1 (9) |
| C67—N15—C119—N44 | -124.8 (9) |
| C68—C128—C183—C37 | -0.9 (15) |
| C69—C39—C66—C116 | 0.0 (13) |
| C71—N1X—C90—C18 | -177.8 (7) |
| C72—C57—C135—C182 | 1.4 (14) |
| C159—C21—C61—N4 | 0.1 (11) |
| C162—C48—C141—C106 | 1.8 (13) |
| C161—C81—C155—C187 | 1.1 (15) |
| C161—C171—C174—C187 | -0.3 (14) |
| C164—C113—C193—C50 | 1.7 (15) |
| C165—N6—N52—C27 | 177.9 (7) |
| C165—N6—N52—C55 | -0.1 (10) |
| C166—C53—C157—C93 | -1.7 (14) |
| C168—C138—C151—C130 | 0.3 (14) |
| C171—C161—B208—C58 | 88.5 (10) |
| C171—C161—B208—C98 | -31.7 (11) |
| C171—C161—B208—C137 | -150.9 (8) |
| C171—C174—C187—C155 | 0.6 (14) |
| C173—C120—C175—C189 | 5.0 (14) |
| C175—C120—C173—C46 | -4.1 (15) |
| C176—C10—C190—Ru3 | 57.3 (7) |
| C176—C10—C190—C149 | 5.2 (13) |
| C179—N41—C104—N24 | -126.8 (9) |
| C183—C37—C60—C202 | -2.1 (13) |
| C183—C37—B191—C82 | 20.1 (12) |
| C183—C37—B191—C103 | 133.8 (8) |
| C183—C37—B191—C107 | -102.2 (9) |
| C185—N96—N148—C88 | 179.3 (8) |
| C185—N96—N148—C4 | -1.2 (11) |

| | |
|---|---|
| C72—B91—C93—C63 | -32.7 (11) |
| C72—B91—C93—C157 | 148.1 (8) |
| C72—C194—C200—C182 | 1.6 (14) |
| C75—C78—C98—C108 | 4.0 (12) |
| C75—C78—C98—B208 | 179.3 (8) |
| C77—C22—C62—B127 | 178.5 (8) |
| C77—C22—C62—C153 | 3.7 (13) |
| C77—C126—C180—C153 | 2.7 (14) |
| C78—C75—C95—C73 | 1.1 (13) |
| C78—C98—C108—C73 | -2.7 (12) |
| C78—C98—B208—C58 | 33.6 (11) |
| C78—C98—B208—C137 | -88.6 (9) |
| C78—C98—B208—C161 | 149.2 (8) |
| C79—C137—B208—C58 | 149.4 (8) |
| C79—C137—B208—C98 | -88.7 (10) |
| C79—C137—B208—C161 | 33.7 (12) |
| C79—C146—C169—C132 | -1.2 (14) |
| C81—C155—C187—C174 | -1.0 (14) |
| C81—C161—C171—C174 | 0.3 (12) |
| C81—C161—B208—C58 | -83.2 (9) |
| C81—C161—B208—C98 | 156.6 (8) |
| C81—C161—B208—C137 | 37.3 (11) |
| C82—C139—C163—C188 | -0.1 (13) |
| C84—C94—C176—Ru3 | 53.4 (7) |
| C185—C207—C4—N148 | -1.3 (12) |
| C188—C115—C152—C82 | 1.1 (14) |
| C189—C42—C46—C173 | -1.0 (13) |
| C189—C42—B91—C30 | -33.9 (11) |
| C189—C42—B91—C72 | -149.5 (8) |
| C189—C42—B91—C93 | 86.4 (9) |
| C190—C10—C176—Ru3 | -58.8 (8) |
| C190—C10—C176—C94 | -4.1 (13) |
| B191—C37—C60—C202 | -177.7 (8) |
| B191—C37—C183—C128 | 177.8 (9) |
| B191—C82—C139—C163 | 172.8 (8) |
| B191—C82—C152—C115 | -172.7 (8) |
| B191—C103—C195—C100 | 172.7 (8) |
| B191—C107—C110—C121 | -176.7 (8) |
| B191—C107—C198—C172 | 176.7 (9) |
| C192—N26—N41—C104 | -179.3 (8) |
| C192—N26—N41—C179 | 1.0 (10) |
| C193—C113—C164—C97 | -0.4 (15) |
| C194—C72—B91—C30 | -88.8 (9) |
| C194—C72—B91—C42 | 31.7 (11) |
| C194—C72—B91—C93 | 152.4 (8) |
| C195—C100—C158—C133 | 0.7 (13) |
| C195—C103—B191—C37 | 164.3 (8) |
| C195—C103—B191—C82 | -76.3 (9) |

| | | | |
|---|---|---|---|
| C84—C94—C176—C10 | -0.9 (13) | C195—C103—B191—C107 | 45.3 (11) |
| C84—C149—C190—Ru3 | -52.0 (7) | C198—C107—C110—C121 | -1.9 (13) |
| C84—C149—C190—C10 | -1.4 (13) | C198—C107—B191—C37 | -96.7 (10) |
| C86—C103—B191—C37 | -25.0 (11) | C198—C107—B191—C82 | 140.9 (9) |
| C86—C103—B191—C82 | 94.4 (9) | C198—C107—B191—C103 | 24.3 (13) |
| C86—C103—B191—C107 | -144.1 (8) | C201—C65—C87—Ru4 | 52.7 (8) |
| C86—C103—C195—C100 | 1.3 (12) | C201—C65—C87—C154 | -3.9 (13) |
| C86—C133—C158—C100 | -1.0 (13) | C202—C68—C128—C183 | -1.1 (15) |
| C85—C28—C111—C74 | -3.2 (12) | B208—C58—C116—C66 | 176.8 (8) |
| C85—C30—B91—C42 | 155.7 (8) | B208—C58—C140—C69 | -175.7 (8) |
| C85—C30—B91—C72 | -82.0 (9) | B208—C98—C108—C73 | -178.2 (8) |
| C85—C30—B91—C93 | 38.0 (11) | B208—C161—C171—C174 | -171.9 (8) |
| C85—C30—C144—C74 | -1.0 (12) | N215—N5—C99—C3 | -2.5 (11) |
| C87—C65—C201—Ru4 | -51.4 (8) | N215—C70—C3—C99 | -1.9 (10) |
| C87—C65—C201—C14 | -0.2 (13) | C0AA—C1AA—C2AA—Ru1 | 54.2 (9) |
| C88—N45—C114—Ru1 | 4.7 (14) | C0AA—C1AA—C2AA—C102 | 0.6 (14) |
| C88—N45—C114—N24 | -175.7 (8) | C3—C70—N215—N5 | 0.5 (11) |
| C88—N45—C122—C117 | 176.5 (8) | C3—C70—N215—C71 | -176.3 (8) |
| C88—N148—C4—C207 | -179.0 (9) | C2AA—C1AA—C0AA—Ru1 | -54.7 (9) |
| C89—C2—C101—Ru2 | 54.7 (8) | C2AA—C1AA—C0AA—C184 | 2.8 (15) |
| C89—C2—C101—C160 | -2.6 (14) | C2AA—C102—C150—Ru1 | 56.0 (8) |
| C89—C40—C105—Ru2 | -55.6 (7) | C2AA—C102—C150—C184 | 2.5 (14) |

### 7.1.5. Crystal data for complex 4a

Selected geometric parameters (Å)

| | | | |
|---|---|---|---|
| Ru01—Cl02 | 2.4080 (6) | C3A—H3A | 0.9500 |
| Ru01—N2A | 2.086 (2) | C3B—H3B | 0.9500 |
| Ru01—C1B | 2.046 (2) | C3C—H3C | 0.9500 |
| Ru01—C1D | 2.236 (3) | C3D—H3D | 0.9500 |
| Ru01—C2D | 2.225 (2) | C3D—C4D | 1.431 (3) |
| Ru01—C3D | 2.242 (2) | C4D—C5D | 1.402 (3) |
| Ru01—C4D | 2.226 (2) | C4D—C8D | 1.514 (4) |
| Ru01—C5D | 2.182 (2) | C5D—H5D | 0.9500 |
| Ru01—C6D | 2.195 (2) | C5D—C6D | 1.416 (4) |
| N1A—N2A | 1.355 (3) | C6D—H6D | 0.9500 |
| N1A—C1 | 1.452 (3) | C7D—H7DA | 0.9800 |
| N1A—C3A | 1.340 (3) | C7D—H7DB | 0.9800 |
| N1B—C1 | 1.450 (3) | C7D—H7DC | 0.9800 |
| N1B—C1B | 1.350 (3) | C8D—H8D | 1.0000 |
| N1B—C2B | 1.394 (3) | C8D—C9D | 1.540 (4) |
| N1C—N2C | 1.350 (3) | C8D—C10D | 1.511 (4) |
| N1C—C2 | 1.443 (3) | C9D—H9DA | 0.9800 |
| N1C—C3C | 1.349 (3) | C9D—H9DB | 0.9800 |
| N2A—C1A | 1.334 (3) | C9D—H9DC | 0.9800 |
| N2B—C1B | 1.350 (3) | C10D—H10A | 0.9800 |
| N2B—C2 | 1.467 (3) | C10D—H10B | 0.9800 |
| N2B—C3B | 1.390 (3) | C10D—H10C | 0.9800 |
| N2C—C1C | 1.321 (4) | O1—B1 | 1.485 (3) |
| C1—H1A | 0.9900 | O1—B2 | 1.342 (3) |
| C1—H1B | 0.9900 | O2—B2 | 1.388 (3) |
| C1A—H1AA | 0.9500 | O2—B3 | 1.384 (3) |
| C1A—C2A | 1.392 (4) | O3—B1 | 1.477 (3) |
| C1C—H1C | 0.9500 | O3—B3 | 1.350 (3) |
| C1C—C2C | 1.390 (4) | O4—H4 | 0.864 (17) |
| C1D—C2D | 1.429 (4) | O4—B2 | 1.358 (3) |
| C1D—C6D | 1.395 (4) | O5—H5 | 0.857 (17) |
| C1D—C7D | 1.497 (4) | O5—B3 | 1.354 (3) |
| C2—H2A | 0.9900 | O6—B1 | 1.454 (3) |
| C2—H2B | 0.9900 | O6—B5 | 1.340 (3) |
| C2A—H2AA | 0.9500 | O7—B1 | 1.463 (3) |
| C2A—C3A | 1.371 (4) | O7—B4 | 1.338 (4) |
| C2B—H2BA | 0.9500 | O8—B4 | 1.373 (4) |
| C2B—C3B | 1.336 (4) | O8—B5 | 1.387 (4) |
| C2C—H2C | 0.9500 | O9—H9 | 0.909 (17) |

| | | | |
|---|---|---|---|
| C2C—C3C | 1.359 (4) | O9—B5 | 1.357 (4) |
| C2D—H2D | 0.9500 | O10—H10 | 0.8400 |
| C2D—C3D | 1.383 (4) | O10—B4 | 1.366 (3) |

Selected geometric parameters (º)

| | | | |
|---|---|---|---|
| N2A—Ru01—Cl02 | 84.44 (5) | C1D—C2D—H2D | 119.1 |
| N2A—Ru01—C1D | 158.31 (9) | C3D—C2D—Ru01 | 72.61 (14) |
| N2A—Ru01—C2D | 121.01 (9) | C3D—C2D—C1D | 121.8 (2) |
| N2A—Ru01—C3D | 94.98 (8) | C3D—C2D—H2D | 119.1 |
| N2A—Ru01—C4D | 92.61 (8) | N1A—C3A—C2A | 107.2 (2) |
| N2A—Ru01—C5D | 117.22 (9) | N1A—C3A—H3A | 126.4 |
| N2A—Ru01—C6D | 154.70 (9) | C2A—C3A—H3A | 126.4 |
| C1B—Ru01—Cl02 | 87.89 (6) | N2B—C3B—H3B | 126.4 |
| C1B—Ru01—N2A | 83.50 (8) | C2B—C3B—N2B | 107.3 (2) |
| C1B—Ru01—C1D | 117.90 (10) | C2B—C3B—H3B | 126.4 |
| C1B—Ru01—C2D | 155.05 (10) | N1C—C3C—C2C | 107.4 (2) |
| C1B—Ru01—C3D | 158.45 (9) | N1C—C3C—H3C | 126.3 |
| C1B—Ru01—C4D | 121.10 (9) | C2C—C3C—H3C | 126.3 |
| C1B—Ru01—C5D | 94.77 (9) | Ru01—C3D—H3D | 130.7 |
| C1B—Ru01—C6D | 93.77 (9) | C2D—C3D—Ru01 | 71.33 (14) |
| C1D—Ru01—Cl02 | 92.41 (7) | C2D—C3D—H3D | 119.9 |
| C1D—Ru01—C3D | 66.56 (10) | C2D—C3D—C4D | 120.2 (2) |
| C2D—Ru01—Cl02 | 89.90 (7) | C4D—C3D—Ru01 | 70.72 (13) |
| C2D—Ru01—C1D | 37.37 (10) | C4D—C3D—H3D | 119.9 |
| C2D—Ru01—C3D | 36.06 (9) | C3D—C4D—Ru01 | 71.91 (13) |
| C2D—Ru01—C4D | 66.46 (9) | C3D—C4D—C8D | 122.1 (2) |
| C3D—Ru01—Cl02 | 113.42 (7) | C5D—C4D—Ru01 | 69.78 (14) |
| C4D—Ru01—Cl02 | 150.41 (6) | C5D—C4D—C3D | 118.4 (2) |
| C4D—Ru01—C1D | 79.59 (9) | C5D—C4D—C8D | 119.3 (2) |
| C4D—Ru01—C3D | 37.36 (9) | C8D—C4D—Ru01 | 134.90 (17) |
| C5D—Ru01—Cl02 | 158.33 (7) | Ru01—C5D—H5D | 127.7 |
| C5D—Ru01—C1D | 67.34 (10) | C4D—C5D—Ru01 | 73.15 (14) |
| C5D—Ru01—C2D | 78.66 (10) | C4D—C5D—H5D | 119.7 |
| C5D—Ru01—C3D | 66.73 (9) | C4D—C5D—C6D | 120.7 (2) |
| C5D—Ru01—C4D | 37.07 (9) | C6D—C5D—Ru01 | 71.63 (14) |
| C5D—Ru01—C6D | 37.74 (10) | C6D—C5D—H5D | 119.7 |
| C6D—Ru01—Cl02 | 120.68 (7) | Ru01—C6D—H6D | 129.2 |
| C6D—Ru01—C1D | 36.68 (10) | C1D—C6D—Ru01 | 73.26 (15) |
| C6D—Ru01—C2D | 66.25 (10) | C1D—C6D—C5D | 121.3 (2) |

| | | | |
|---|---|---|---|
| C6D—Ru01—C3D | 78.42 (9) | C1D—C6D—H6D | 119.3 |
| C6D—Ru01—C4D | 67.25 (10) | C5D—C6D—Ru01 | 70.63 (14) |
| N2A—N1A—C1 | 119.92 (19) | C5D—C6D—H6D | 119.3 |
| C3A—N1A—N2A | 111.3 (2) | C1D—C7D—H7DA | 109.5 |
| C3A—N1A—C1 | 128.7 (2) | C1D—C7D—H7DB | 109.5 |
| C1B—N1B—C1 | 122.05 (19) | C1D—C7D—H7DC | 109.5 |
| C1B—N1B—C2B | 112.2 (2) | H7DA—C7D—H7DB | 109.5 |
| C2B—N1B—C1 | 125.7 (2) | H7DA—C7D—H7DC | 109.5 |
| N2C—N1C—C2 | 120.0 (2) | H7DB—C7D—H7DC | 109.5 |
| C3C—N1C—N2C | 111.5 (2) | C4D—C8D—H8D | 107.7 |
| C3C—N1C—C2 | 128.4 (2) | C4D—C8D—C9D | 105.9 (2) |
| N1A—N2A—Ru01 | 123.94 (14) | C9D—C8D—H8D | 107.7 |
| C1A—N2A—Ru01 | 130.45 (17) | C10D—C8D—C4D | 116.2 (2) |
| C1A—N2A—N1A | 105.6 (2) | C10D—C8D—H8D | 107.7 |
| C1B—N2B—C2 | 125.25 (19) | C10D—C8D—C9D | 111.3 (3) |
| C1B—N2B—C3B | 111.33 (19) | C8D—C9D—H9DA | 109.5 |
| C3B—N2B—C2 | 123.41 (19) | C8D—C9D—H9DB | 109.5 |
| C1C—N2C—N1C | 104.5 (2) | C8D—C9D—H9DC | 109.5 |
| N1A—C1—H1A | 109.8 | H9DA—C9D—H9DB | 109.5 |
| N1A—C1—H1B | 109.8 | H9DA—C9D—H9DC | 109.5 |
| N1B—C1—N1A | 109.49 (18) | H9DB—C9D—H9DC | 109.5 |
| N1B—C1—H1A | 109.8 | C8D—C10D—H10A | 109.5 |
| N1B—C1—H1B | 109.8 | C8D—C10D—H10B | 109.5 |
| H1A—C1—H1B | 108.2 | C8D—C10D—H10C | 109.5 |
| N2A—C1A—H1AA | 124.8 | H10A—C10D—H10B | 109.5 |
| N2A—C1A—C2A | 110.4 (2) | H10A—C10D—H10C | 109.5 |
| C2A—C1A—H1AA | 124.8 | H10B—C10D—H10C | 109.5 |
| N1B—C1B—Ru01 | 123.36 (16) | B2—O1—B1 | 123.55 (18) |
| N1B—C1B—N2B | 103.62 (19) | B3—O2—B2 | 119.17 (19) |
| N2B—C1B—Ru01 | 133.01 (17) | B3—O3—B1 | 123.04 (18) |
| N2C—C1C—H1C | 123.9 | B2—O4—H4 | 109.6 (17) |
| N2C—C1C—C2C | 112.2 (2) | B3—O5—H5 | 112.1 (19) |
| C2C—C1C—H1C | 123.9 | B5—O6—B1 | 122.6 (2) |
| C2D—C1D—Ru01 | 70.90 (14) | B4—O7—B1 | 122.5 (2) |
| C2D—C1D—C7D | 120.7 (2) | B4—O8—B5 | 118.3 (2) |
| C6D—C1D—Ru01 | 70.06 (15) | B5—O9—H9 | 107.4 (18) |
| C6D—C1D—C2D | 117.6 (2) | B4—O10—H10 | 109.5 |
| C6D—C1D—C7D | 121.7 (3) | O3—B1—O1 | 109.61 (19) |
| C7D—C1D—Ru01 | 131.26 (19) | O6—B1—O1 | 108.11 (19) |
| N1C—C2—N2B | 110.3 (2) | O6—B1—O3 | 109.08 (19) |
| N1C—C2—H2A | 109.6 | O6—B1—O7 | 112.2 (2) |

| | | | |
|---|---|---|---|
| N1C—C2—H2B | 109.6 | O7—B1—O1 | 107.83 (18) |
| N2B—C2—H2A | 109.6 | O7—B1—O3 | 109.93 (19) |
| N2B—C2—H2B | 109.6 | O1—B2—O2 | 120.9 (2) |
| H2A—C2—H2B | 108.1 | O1—B2—O4 | 123.0 (2) |
| C1A—C2A—H2AA | 127.2 | O4—B2—O2 | 116.1 (2) |
| C3A—C2A—C1A | 105.6 (2) | O3—B3—O2 | 121.0 (2) |
| C3A—C2A—H2AA | 127.2 | O3—B3—O5 | 123.0 (2) |
| N1B—C2B—H2BA | 127.2 | O5—B3—O2 | 116.0 (2) |
| C3B—C2B—N1B | 105.6 (2) | O7—B4—O8 | 122.2 (2) |
| C3B—C2B—H2BA | 127.2 | O7—B4—O10 | 119.5 (3) |
| C1C—C2C—H2C | 127.8 | O10—B4—O8 | 118.2 (3) |
| C3C—C2C—C1C | 104.5 (3) | O6—B5—O8 | 121.7 (2) |
| C3C—C2C—H2C | 127.8 | O6—B5—O9 | 122.6 (3) |
| Ru01—C2D—H2D | 129.0 | O9—B5—O8 | 115.8 (2) |
| C1D—C2D—Ru01 | 71.73 (15) | | |

## Selected geometric parameters, torsion angles (º)

| | | | |
|---|---|---|---|
| Ru01—N2A—C1A—C2A | -178.55 (16) | C3B—N2B—C1B—Ru01 | 179.17 (17) |
| Ru01—C1D—C2D—C3D | -54.9 (2) | C3B—N2B—C1B—N1B | 0.3 (2) |
| Ru01—C1D—C6D—C5D | 54.0 (2) | C3B—N2B—C2—N1C | -50.1 (3) |
| Ru01—C2D—C3D—C4D | -53.2 (2) | C3C—N1C—N2C—C1C | -0.7 (3) |
| Ru01—C3D—C4D—C5D | -53.84 (19) | C3C—N1C—C2—N2B | -73.9 (3) |
| Ru01—C3D—C4D—C8D | 132.2 (2) | C3D—C4D—C5D—Ru01 | 54.87 (19) |
| Ru01—C4D—C5D—C6D | -55.8 (2) | C3D—C4D—C5D—C6D | -0.9 (3) |
| Ru01—C4D—C8D—C9D | 179.6 (2) | C3D—C4D—C8D—C9D | 83.4 (3) |
| Ru01—C4D—C8D—C10D | 55.4 (3) | C3D—C4D—C8D—C10D | -40.8 (3) |
| Ru01—C5D—C6D—C1D | -55.2 (2) | C4D—C5D—C6D—Ru01 | 56.5 (2) |
| N1A—N2A—C1A—C2A | -0.3 (2) | C4D—C5D—C6D—C1D | 1.3 (4) |
| N1B—C2B—C3B—N2B | 0.7 (3) | C5D—C4D—C8D—C9D | -90.5 (3) |
| N1C—N2C—C1C—C2C | 1.0 (4) | C5D—C4D—C8D—C10D | 145.3 (2) |

| | | | |
|---|---|---|---|
| N2A—N1A—C1—N1B | 56.1 (3) | C6D—C1D—C2D—Ru01 | 54.0 (2) |
| N2A—N1A—C3A—C2A | -0.1 (3) | C6D—C1D—C2D—C3D | -0.9 (4) |
| N2A—C1A—C2A—C3A | 0.3 (3) | C7D—C1D—C2D—Ru01 | -127.3 (2) |
| N2C—N1C—C2—N2B | 102.5 (2) | C7D—C1D—C2D—C3D | 177.8 (2) |
| N2C—N1C—C3C—C2C | 0.2 (3) | C7D—C1D—C6D—Ru01 | 126.9 (2) |
| N2C—C1C—C2C—C3C | -0.9 (4) | C7D—C1D—C6D—C5D | -179.1 (2) |
| C1—N1A—N2A—Ru01 | -5.2 (3) | C8D—C4D—C5D—Ru01 | -131.0 (2) |
| C1—N1A—N2A—C1A | 176.44 (19) | C8D—C4D—C5D—C6D | 173.2 (2) |
| C1—N1A—C3A—C2A | -175.9 (2) | B1—O1—B2—O2 | -4.5 (4) |
| C1—N1B—C1B—Ru01 | 1.4 (3) | B1—O1—B2—O4 | 175.7 (2) |
| C1—N1B—C1B—N2B | -179.55 (19) | B1—O3—B3—O2 | 11.3 (4) |
| C1—N1B—C2B—C3B | 179.1 (2) | B1—O3—B3—O5 | -171.2 (2) |
| C1A—C2A—C3A—N1A | -0.1 (3) | B1—O6—B5—O8 | 7.8 (4) |
| C1B—N1B—C1—N1A | -55.1 (3) | B1—O6—B5—O9 | -171.3 (3) |
| C1B—N1B—C2B—C3B | -0.6 (3) | B1—O7—B4—O8 | -2.9 (4) |
| C1B—N2B—C2—N1C | 128.3 (2) | B1—O7—B4—O10 | 172.9 (2) |
| C1B—N2B—C3B—C2B | -0.7 (3) | B2—O1—B1—O3 | 15.6 (3) |
| C1C—C2C—C3C—N1C | 0.4 (3) | B2—O1—B1—O6 | 134.3 (2) |
| C1D—C2D—C3D—Ru01 | 54.5 (2) | B2—O1—B1—O7 | -104.1 (2) |
| C1D—C2D—C3D—C4D | 1.3 (4) | B2—O2—B3—O3 | 2.1 (3) |
| C2—N1C—N2C—C1C | -177.7 (2) | B2—O2—B3—O5 | -175.5 (2) |
| C2—N1C—C3C—C2C | 176.9 (2) | B3—O2—B2—O1 | -5.5 (3) |
| C2—N2B—C1B—Ru01 | 0.6 (3) | B3—O2—B2—O4 | 174.3 (2) |
| C2—N2B—C1B—N1B | -178.3 (2) | B3—O3—B1—O1 | -18.9 (3) |

| | | | |
|---|---|---|---|
| C2—N2B—C3B—C2B | 177.9 (2) | B3—O3—B1—O6 | -137.1 (2) |
| C2B—N1B—C1—N1A | 125.2 (2) | B3—O3—B1—O7 | 99.5 (2) |
| C2B—N1B—C1B—Ru01 | -178.83 (16) | B4—O7—B1—O1 | -113.7 (2) |
| C2B—N1B—C1B—N2B | 0.2 (2) | B4—O7—B1—O3 | 126.9 (2) |
| C2D—C1D—C6D—Ru01 | -54.4 (2) | B4—O7—B1—O6 | 5.3 (3) |
| C2D—C1D—C6D—C5D | -0.4 (4) | B4—O8—B5—O6 | -4.6 (4) |
| C2D—C3D—C4D—Ru01 | 53.4 (2) | B4—O8—B5—O9 | 174.6 (3) |
| C2D—C3D—C4D—C5D | -0.4 (3) | B5—O6—B1—O1 | 111.1 (3) |
| C2D—C3D—C4D—C8D | -174.4 (2) | B5—O6—B1—O3 | -129.8 (2) |
| C3A—N1A—N2A—Ru01 | 178.65 (15) | B5—O6—B1—O7 | -7.7 (3) |
| C3A—N1A—N2A—C1A | 0.3 (2) | B5—O8—B4—O7 | 2.1 (4) |
| C3A—N1A—C1—N1B | -128.5 (2) | B5—O8—B4—O10 | -173.7 (3) |

### 7.1.6. Crystal data for complex 5

Selected geometric parameters (Å)

| | | | |
|---|---|---|---|
| Ru1A—H | 1.50 (4) | C12'—C13' | 1.269 (17) |
| Ru1A—P1A | 2.3683 (12) | C12C—H12C | 0.9500 |
| Ru1A—P1B | 2.3697 (11) | C12C—C13C | 1.382 (7) |
| Ru1A—N2E | 2.123 (5) | C12D—H12D | 0.9500 |
| Ru1A—C1F | 1.812 (6) | C12D—C13D | 1.385 (7) |
| Ru1A—C7E | 2.121 (6) | C12G—H12G | 0.9500 |
| P1A—C11A | 1.829 (5) | C12G—C13G | 1.280 (13) |
| P1A—C21A | 1.835 (6) | C13'—H13' | 0.9500 |
| P1A—C31A | 1.816 (5) | C13C—H13C | 0.9500 |
| P1B—C11B | 1.853 (5) | C13C—C14C | 1.390 (7) |
| P1B—C21B | 1.833 (5) | C13D—H13D | 0.9500 |
| P1B—C31B | 1.815 (5) | C13D—C14D | 1.378 (7) |
| O1F—C1F | 1.171 (5) | C13G—H13G | 0.9500 |
| N1E—N2E | 1.377 (5) | C14C—H14C | 0.9500 |
| N1E—C5E | 1.353 (7) | C14C—C15C | 1.389 (7) |
| N1E—C6E | 1.444 (6) | C14D—H14D | 0.9500 |

| | | | |
|---|---|---|---|
| N2E—C3E | 1.333 (7) | C14D—C15D | 1.388 (7) |
| N3E—C6E | 1.439 (6) | C15C—H15C | 0.9500 |
| N3E—C7E | 1.384 (6) | C15C—C16C | 1.378 (7) |
| N3E—C8E | 1.376 (7) | C15D—H15D | 0.9500 |
| N4E—C7E | 1.377 (6) | C15D—C16D | 1.374 (7) |
| N4E—C9E | 1.409 (7) | C16C—H16C | 0.9500 |
| N4E—C10E | 1.453 (6) | C16D—H16D | 0.9500 |
| N5E—N6E | 1.365 (6) | C21C—C22C | 1.385 (6) |
| N5E—C10E | 1.454 (6) | C21C—C26C | 1.391 (6) |
| N5E—C13E | 1.360 (7) | C21D—C22D | 1.391 (6) |
| N6E—C11E | 1.345 (7) | C21D—C26D | 1.389 (7) |
| C3E—H3E | 0.9500 | C22C—H22C | 0.9500 |
| C3E—C4E | 1.387 (7) | C22C—C23C | 1.397 (7) |
| C4E—H4E | 0.9500 | C22D—H22D | 0.9500 |
| C4E—C5E | 1.340 (8) | C22D—C23D | 1.386 (7) |
| C5E—H5E | 0.9500 | C23C—H23C | 0.9500 |
| C6E—H6EA | 0.9900 | C23C—C24C | 1.368 (7) |
| C6E—H6EB | 0.9900 | C23D—H23D | 0.9500 |
| C8E—H8E | 0.9500 | C23D—C24D | 1.388 (7) |
| C8E—C9E | 1.298 (7) | C24C—H24C | 0.9500 |
| C9E—H9E | 0.9500 | C24C—C25C | 1.378 (7) |
| C10E—H10E | 0.9900 | C24D—H24D | 0.9500 |
| C10E—H10F | 0.9900 | C24D—C25D | 1.384 (7) |
| C11A—C12A | 1.405 (7) | C25C—H25C | 0.9500 |
| C11A—C16A | 1.383 (7) | C25C—C26C | 1.394 (7) |
| C11B—C12B | 1.394 (6) | C25D—H25D | 0.9500 |
| C11B—C16B | 1.363 (7) | C25D—C26D | 1.368 (7) |
| C11E—H11E | 0.9500 | C26C—H26C | 0.9500 |
| C11E—C12E | 1.388 (8) | C26D—H26D | 0.9500 |
| C12A—H12A | 0.9500 | C31C—C32C | 1.392 (6) |
| C12A—C13A | 1.389 (7) | C31C—C36C | 1.383 (7) |
| C12B—H12B | 0.9500 | C31D—C32D | 1.403 (7) |
| C12B—C13B | 1.368 (7) | C31D—C36D | 1.387 (6) |
| C12E—H12E | 0.9500 | C32C—H32C | 0.9500 |
| C12E—C13E | 1.356 (8) | C32C—C33C | 1.380 (7) |
| C13A—H13A | 0.9500 | C32D—H32D | 0.9500 |
| C13A—C14A | 1.378 (7) | C32D—C33D | 1.371 (6) |
| C13B—H13B | 0.9500 | C33C—H33C | 0.9500 |
| C13B—C14B | 1.363 (8) | C33C—C34C | 1.384 (7) |
| C13E—H13E | 0.9500 | C33D—H33D | 0.9500 |
| C14A—H14A | 0.9500 | C33D—C34D | 1.394 (7) |

| | | | |
|---|---|---|---|
| C14A—C15A | 1.367 (8) | C34C—H34C | 0.9500 |
| C14B—H14B | 0.9500 | C34C—C35C | 1.380 (7) |
| C14B—C15B | 1.379 (7) | C34D—H34D | 0.9500 |
| C15A—H15A | 0.9500 | C34D—C35D | 1.367 (7) |
| C15A—C16A | 1.382 (7) | C35C—H35C | 0.9500 |
| C15B—H15B | 0.9500 | C35C—C36C | 1.383 (7) |
| C15B—C16B | 1.364 (8) | C35D—H35D | 0.9500 |
| C16A—H16A | 0.9500 | C35D—C36D | 1.422 (7) |
| C16B—H16B | 0.9500 | C36C—H36C | 0.9500 |
| C21A—C22A | 1.371 (7) | C36D—H36D | 0.9500 |
| C21A—C26A | 1.397 (7) | C11M—C12M | 1.391 (8) |
| C21B—C22B | 1.392 (7) | C11M—C16M | 1.402 (7) |
| C21B—C26B | 1.406 (7) | C11M—B1M | 1.641 (9) |
| C22A—H22A | 0.9500 | C12M—H12M | 0.9500 |
| C22A—C23A | 1.376 (8) | C12M—C13M | 1.399 (8) |
| C22B—H22B | 0.9500 | C13M—H13M | 0.9500 |
| C22B—C23B | 1.376 (7) | C13M—C14M | 1.370 (8) |
| C23A—H23A | 0.9500 | C14M—H14M | 0.9500 |
| C23A—C24A | 1.376 (8) | C14M—C15M | 1.373 (8) |
| C23B—H23B | 0.9500 | C15M—H15M | 0.9500 |
| C23B—C24B | 1.383 (7) | C15M—C16M | 1.404 (8) |
| C24A—H24A | 0.9500 | C16M—H16M | 0.9500 |
| C24A—C25A | 1.377 (8) | C21M—C22M | 1.413 (7) |
| C24B—H24B | 0.9500 | C21M—C26M | 1.378 (7) |
| C24B—C25B | 1.391 (8) | C21M—B1M | 1.627 (8) |
| C25A—H25A | 0.9500 | C22M—H22M | 0.9500 |
| C25A—C26A | 1.390 (7) | C22M—C23M | 1.376 (8) |
| C25B—H25B | 0.9500 | C23M—H23M | 0.9500 |
| C25B—C26B | 1.367 (7) | C23M—C24M | 1.384 (8) |
| C26A—H26A | 0.9500 | C24M—H24M | 0.9500 |
| C26B—H26B | 0.9500 | C24M—C25M | 1.361 (8) |
| C31A—C32A | 1.404 (6) | C25M—H25M | 0.9500 |
| C31A—C36A | 1.401 (7) | C25M—C26M | 1.399 (8) |
| C31B—C32B | 1.387 (7) | C26M—H26M | 0.9500 |
| C31B—C36B | 1.402 (7) | C31M—C32M | 1.408 (7) |
| C32A—H32A | 0.9500 | C31M—C36M | 1.386 (7) |
| C32A—C33A | 1.400 (8) | C31M—B1M | 1.674 (7) |
| C32B—H32B | 0.9500 | C32M—H32M | 0.9500 |
| C32B—C33B | 1.395 (7) | C32M—C33M | 1.388 (7) |
| C33A—H33A | 0.9500 | C33M—H33M | 0.9500 |
| C33A—C34A | 1.381 (8) | C33M—C34M | 1.375 (7) |

| | | | |
|---|---|---|---|
| C33B—H33B | 0.9500 | C34M—H34M | 0.9500 |
| C33B—C34B | 1.385 (8) | C34M—C35M | 1.384 (7) |
| C34A—H34A | 0.9500 | C35M—H35M | 0.9500 |
| C34A—C35A | 1.389 (8) | C35M—C36M | 1.375 (7) |
| C34B—H34B | 0.9500 | C36M—H36M | 0.9500 |
| C34B—C35B | 1.364 (8) | C41M—C42M | 1.398 (8) |
| C35A—H35A | 0.9500 | C41M—C46M | 1.389 (7) |
| C35A—C36A | 1.376 (7) | C41M—B1M | 1.654 (8) |
| C35B—H35B | 0.9500 | C42M—H42M | 0.9500 |
| C35B—C36B | 1.409 (7) | C42M—C43M | 1.401 (8) |
| C36A—H36A | 0.9500 | C43M—H43M | 0.9500 |
| C36B—H36B | 0.9500 | C43M—C44M | 1.378 (8) |
| Ru1B—HA | 1.71 (4) | C44M—H44M | 0.9500 |
| Ru1B—P1C | 2.3784 (11) | C44M—C45M | 1.364 (8) |
| Ru1B—P1D | 2.3758 (11) | C45M—H45M | 0.9500 |
| Ru1B—N2G | 2.164 (4) | C45M—C46M | 1.402 (8) |
| Ru1B—C1H | 1.813 (6) | C46M—H46M | 0.9500 |
| Ru1B—C7G | 2.114 (5) | C11N—C12N | 1.398 (7) |
| P1C—C11C | 1.826 (5) | C11N—C16N | 1.403 (6) |
| P1C—C21C | 1.838 (5) | C11N—B1N | 1.655 (7) |
| P1C—C31C | 1.843 (5) | C12N—H12N | 0.9500 |
| P1D—C11D | 1.827 (5) | C12N—C13N | 1.389 (6) |
| P1D—C21D | 1.840 (5) | C13N—H13N | 0.9500 |
| P1D—C31D | 1.825 (5) | C13N—C14N | 1.379 (7) |
| O1H—C1H | 1.170 (5) | C14N—H14N | 0.9500 |
| N1G—N2G | 1.364 (5) | C14N—C15N | 1.360 (7) |
| N1G—C5G | 1.344 (6) | C15N—H15N | 0.9500 |
| N1G—C6G | 1.453 (6) | C15N—C16N | 1.401 (7) |
| N2G—C3G | 1.344 (6) | C16N—H16N | 0.9500 |
| N3G—C6G | 1.433 (6) | C21N—C22N | 1.411 (7) |
| N3G—C7G | 1.385 (6) | C21N—C26N | 1.390 (7) |
| N3G—C9G | 1.374 (6) | C21N—B1N | 1.637 (7) |
| N4G—C7G | 1.378 (6) | C22N—H22N | 0.9500 |
| N4G—C8G | 1.386 (6) | C22N—C23N | 1.396 (7) |
| N4G—C10G | 1.445 (6) | C23N—H23N | 0.9500 |
| N5G—N6G | 1.341 (9) | C23N—C24N | 1.374 (7) |
| N5G—C10G | 1.558 (8) | C24N—H24N | 0.9500 |
| N5G—C13G | 1.338 (13) | C24N—C25N | 1.365 (7) |
| N5G'—N6G' | 1.305 (17) | C25N—H25N | 0.9500 |
| N5G'—C10G | 1.408 (14) | C25N—C26N | 1.393 (7) |
| N5G'—C13' | 1.380 (16) | C26N—H26N | 0.9500 |

| | | | |
|---|---|---|---|
| N6G—C11G | 1.374 (10) | C31N—C32N | 1.395 (7) |
| N6G'—C11' | 1.347 (18) | C31N—C36N | 1.397 (7) |
| C3G—H3G | 0.9500 | C31N—B1N | 1.634 (8) |
| C3G—C4G | 1.375 (7) | C32N—H32N | 0.9500 |
| C4G—H4G | 0.9500 | C32N—C33N | 1.393 (7) |
| C4G—C5G | 1.385 (8) | C33N—H33N | 0.9500 |
| C5G—H5G | 0.9500 | C33N—C34N | 1.378 (7) |
| C6G—H6GA | 0.9900 | C34N—H34N | 0.9500 |
| C6G—H6GB | 0.9900 | C34N—C35N | 1.373 (7) |
| C8G—H8G | 0.9500 | C35N—H35N | 0.9500 |
| C8G—C9G | 1.341 (7) | C35N—C36N | 1.393 (7) |
| C9G—H9G | 0.9500 | C36N—H36N | 0.9500 |
| C10G—H10A | 0.9900 | C41N—C42N | 1.419 (6) |
| C10G—H10B | 0.9900 | C41N—C46N | 1.385 (7) |
| C10G—H10C | 0.9900 | C41N—B1N | 1.654 (7) |
| C10G—H10D | 0.9900 | C42N—H42N | 0.9500 |
| C11'—H11' | 0.9500 | C42N—C43N | 1.401 (7) |
| C11'—C12' | 1.482 (17) | C43N—H43N | 0.9500 |
| C11C—C12C | 1.393 (7) | C43N—C44N | 1.367 (7) |
| C11C—C16C | 1.393 (6) | C44N—H44N | 0.9500 |
| C11D—C12D | 1.380 (6) | C44N—C45N | 1.390 (7) |
| C11D—C16D | 1.391 (7) | C45N—H45N | 0.9500 |
| C11G—H11G | 0.9500 | C45N—C46N | 1.402 (6) |
| C11G—C12G | 1.441 (11) | C46N—H46N | 0.9500 |
| C12'—H12' | 0.9500 | | |

Selected geometric parameters (º)

| | | | |
|---|---|---|---|
| P1A—Ru1A—H | 80.9 (12) | C16C—C11C—P1C | 121.8 (4) |
| P1A—Ru1A—P1B | 168.78 (5) | C16C—C11C—C12C | 119.8 (5) |
| P1B—Ru1A—H | 88.0 (12) | C12D—C11D—P1D | 123.9 (4) |
| N2E—Ru1A—H | 87.7 (13) | C12D—C11D—C16D | 118.6 (5) |
| N2E—Ru1A—P1A | 92.80 (10) | C16D—C11D—P1D | 117.4 (4) |
| N2E—Ru1A—P1B | 88.27 (10) | N6G—C11G—H11G | 126.5 |
| C1F—Ru1A—H | 86.9 (13) | N6G—C11G—C12G | 107.0 (8) |
| C1F—Ru1A—P1A | 89.31 (13) | C12G—C11G—H11G | 126.5 |
| C1F—Ru1A—P1B | 88.54 (13) | C11'—C12'—H12' | 128.4 |
| C1F—Ru1A—N2E | 173.8 (2) | C13'—C12'—C11' | 103.2 (14) |
| C1F—Ru1A—C7E | 99.0 (2) | C13'—C12'—H12' | 128.4 |
| C7E—Ru1A—H | 173.7 (13) | C11C—C12C—H12C | 120.1 |

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|---|---|---|---|
| C7E—Ru1A—P1A | 96.89 (12) | C13C—C12C—C11C | 119.7 (5) |
| C7E—Ru1A—P1B | 94.32 (12) | C13C—C12C—H12C | 120.1 |
| C7E—Ru1A—N2E | 86.5 (2) | C11D—C12D—H12D | 119.9 |
| C11A—P1A—Ru1A | 112.31 (15) | C11D—C12D—C13D | 120.2 (5) |
| C11A—P1A—C21A | 102.1 (2) | C13D—C12D—H12D | 119.9 |
| C21A—P1A—Ru1A | 118.11 (16) | C11G—C12G—H12G | 126.3 |
| C31A—P1A—Ru1A | 115.79 (16) | C13G—C12G—C11G | 107.4 (11) |
| C31A—P1A—C11A | 102.7 (2) | C13G—C12G—H12G | 126.3 |
| C31A—P1A—C21A | 103.8 (2) | N5G'—C13'—H13' | 123.7 |
| C11B—P1B—Ru1A | 116.32 (16) | C12'—C13'—N5G' | 112.5 (15) |
| C21B—P1B—Ru1A | 116.01 (15) | C12'—C13'—H13' | 123.7 |
| C21B—P1B—C11B | 101.7 (2) | C12C—C13C—H13C | 119.8 |
| C31B—P1B—Ru1A | 115.03 (15) | C12C—C13C—C14C | 120.5 (6) |
| C31B—P1B—C11B | 102.7 (2) | C14C—C13C—H13C | 119.8 |
| C31B—P1B—C21B | 103.0 (2) | C12D—C13D—H13D | 119.7 |
| N2E—N1E—C6E | 119.7 (4) | C14D—C13D—C12D | 120.6 (5) |
| C5E—N1E—N2E | 112.2 (5) | C14D—C13D—H13D | 119.7 |
| C5E—N1E—C6E | 127.2 (5) | N5G—C13G—H13G | 125.6 |
| N1E—N2E—Ru1A | 125.2 (4) | C12G—C13G—N5G | 108.7 (12) |
| C3E—N2E—Ru1A | 130.4 (4) | C12G—C13G—H13G | 125.6 |
| C3E—N2E—N1E | 103.6 (5) | C13C—C14C—H14C | 120.2 |
| C7E—N3E—C6E | 123.4 (5) | C15C—C14C—C13C | 119.6 (5) |
| C8E—N3E—C6E | 123.3 (5) | C15C—C14C—H14C | 120.2 |
| C8E—N3E—C7E | 112.8 (5) | C13D—C14D—H14D | 120.1 |
| C7E—N4E—C9E | 112.2 (5) | C13D—C14D—C15D | 119.7 (5) |
| C7E—N4E—C10E | 126.3 (5) | C15D—C14D—H14D | 120.1 |
| C9E—N4E—C10E | 121.3 (5) | C14C—C15C—H15C | 119.8 |
| N6E—N5E—C10E | 119.3 (5) | C16C—C15C—C14C | 120.3 (5) |
| C13E—N5E—N6E | 112.1 (5) | C16C—C15C—H15C | 119.8 |
| C13E—N5E—C10E | 128.5 (5) | C14D—C15D—H15D | 120.4 |
| C11E—N6E—N5E | 102.7 (5) | C16D—C15D—C14D | 119.2 (5) |
| O1F—C1F—Ru1A | 176.5 (5) | C16D—C15D—H15D | 120.4 |
| N2E—C3E—H3E | 124.6 | C11C—C16C—H16C | 119.9 |
| N2E—C3E—C4E | 110.7 (6) | C15C—C16C—C11C | 120.1 (5) |
| C4E—C3E—H3E | 124.6 | C15C—C16C—H16C | 119.9 |
| C3E—C4E—H4E | 126.2 | C11D—C16D—H16D | 119.2 |
| C5E—C4E—C3E | 107.7 (6) | C15D—C16D—C11D | 121.6 (5) |
| C5E—C4E—H4E | 126.2 | C15D—C16D—H16D | 119.2 |
| N1E—C5E—H5E | 127.1 | C22C—C21C—P1C | 122.0 (4) |
| C4E—C5E—N1E | 105.8 (6) | C22C—C21C—C26C | 118.7 (5) |
| C4E—C5E—H5E | 127.1 | C26C—C21C—P1C | 119.2 (4) |

| | | |
|---|---|---|
| N1E—C6E—H6EA | 109.2 | |
| N1E—C6E—H6EB | 109.2 | |
| N3E—C6E—N1E | 112.3 | (4) |
| N3E—C6E—H6EA | 109.2 | |
| N3E—C6E—H6EB | 109.2 | |
| H6EA—C6E—H6EB | 107.9 | |
| N3E—C7E—Ru1A | 122.8 | (4) |
| N4E—C7E—Ru1A | 136.5 | (4) |
| N4E—C7E—N3E | 100.5 | (5) |
| N3E—C8E—H8E | 126.0 | |
| C9E—C8E—N3E | 107.9 | (6) |
| C9E—C8E—H8E | 126.0 | |
| N4E—C9E—H9E | 126.7 | |
| C8E—C9E—N4E | 106.6 | (6) |
| C8E—C9E—H9E | 126.7 | |
| N4E—C10E—N5E | 110.8 | (4) |
| N4E—C10E—H10E | 109.5 | |
| N4E—C10E—H10F | 109.5 | |
| N5E—C10E—H10E | 109.5 | |
| N5E—C10E—H10F | 109.5 | |
| H10E—C10E—H10F | 108.1 | |
| C12A—C11A—P1A | 118.0 | (4) |
| C16A—C11A—P1A | 123.3 | (4) |
| C16A—C11A—C12A | 118.6 | (5) |
| C12B—C11B—P1B | 120.9 | (4) |
| C16B—C11B—P1B | 122.0 | (4) |
| C16B—C11B—C12B | 117.1 | (5) |
| N6E—C11E—H11E | 123.4 | |
| N6E—C11E—C12E | 113.1 | (6) |
| C12E—C11E—H11E | 123.4 | |
| C11A—C12A—H12A | 119.6 | |
| C13A—C12A—C11A | 120.9 | (5) |
| C13A—C12A—H12A | 119.6 | |
| C11B—C12B—H12B | 119.7 | |
| C13B—C12B—C11B | 120.7 | (5) |
| C13B—C12B—H12B | 119.7 | |
| C11E—C12E—H12E | 127.7 | |
| C13E—C12E—C11E | 104.6 | (6) |
| C13E—C12E—H12E | 127.7 | |
| C12A—C13A—H13A | 120.5 | |
| C14A—C13A—C12A | 119.1 | (6) |

| | | |
|---|---|---|
| C22D—C21D—P1D | 121.1 | (4) |
| C26D—C21D—P1D | 121.1 | (4) |
| C26D—C21D—C22D | 117.8 | (5) |
| C21C—C22C—H22C | 120.1 | |
| C21C—C22C—C23C | 119.8 | (5) |
| C23C—C22C—H22C | 120.1 | |
| C21D—C22D—H22D | 119.1 | |
| C23D—C22D—C21D | 121.8 | (5) |
| C23D—C22D—H22D | 119.1 | |
| C22C—C23C—H23C | 119.3 | |
| C24C—C23C—C22C | 121.4 | (5) |
| C24C—C23C—H23C | 119.3 | |
| C22D—C23D—H23D | 120.5 | |
| C22D—C23D—C24D | 119.1 | (5) |
| C24D—C23D—H23D | 120.5 | |
| C23C—C24C—H24C | 120.4 | |
| C23C—C24C—C25C | 119.1 | (5) |
| C25C—C24C—H24C | 120.4 | |
| C23D—C24D—H24D | 120.3 | |
| C25D—C24D—C23D | 119.5 | (5) |
| C25D—C24D—H24D | 120.3 | |
| C24C—C25C—H25C | 119.9 | |
| C24C—C25C—C26C | 120.3 | (5) |
| C26C—C25C—H25C | 119.9 | |
| C24D—C25D—H25D | 119.6 | |
| C26D—C25D—C24D | 120.9 | (5) |
| C26D—C25D—H25D | 119.6 | |
| C21C—C26C—C25C | 120.7 | (5) |
| C21C—C26C—H26C | 119.7 | |
| C25C—C26C—H26C | 119.7 | |
| C21D—C26D—H26D | 119.5 | |
| C25D—C26D—C21D | 121.0 | (5) |
| C25D—C26D—H26D | 119.5 | |
| C32C—C31C—P1C | 122.1 | (4) |
| C36C—C31C—P1C | 120.0 | (4) |
| C36C—C31C—C32C | 117.7 | (5) |
| C32D—C31D—P1D | 118.9 | (4) |
| C36D—C31D—P1D | 121.7 | (4) |
| C36D—C31D—C32D | 119.2 | (4) |
| C31C—C32C—H32C | 119.3 | |
| C33C—C32C—C31C | 121.4 | (5) |

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|---|---|---|---|
| C14A—C13A—H13A | 120.5 | C33C—C32C—H32C | 119.3 |
| C12B—C13B—H13B | 119.2 | C31D—C32D—H32D | 119.6 |
| C14B—C13B—C12B | 121.5 (5) | C33D—C32D—C31D | 120.7 (5) |
| C14B—C13B—H13B | 119.2 | C33D—C32D—H32D | 119.6 |
| N5E—C13E—H13E | 126.3 | C32C—C33C—H33C | 120.1 |
| C12E—C13E—N5E | 107.5 (6) | C32C—C33C—C34C | 119.7 (5) |
| C12E—C13E—H13E | 126.3 | C34C—C33C—H33C | 120.1 |
| C13A—C14A—H14A | 119.8 | C32D—C33D—H33D | 119.8 |
| C15A—C14A—C13A | 120.5 (5) | C32D—C33D—C34D | 120.4 (5) |
| C15A—C14A—H14A | 119.8 | C34D—C33D—H33D | 119.8 |
| C13B—C14B—H14B | 121.0 | C33C—C34C—H34C | 120.2 |
| C13B—C14B—C15B | 118.0 (6) | C35C—C34C—C33C | 119.7 (5) |
| C15B—C14B—H14B | 121.0 | C35C—C34C—H34C | 120.2 |
| C14A—C15A—H15A | 119.5 | C33D—C34D—H34D | 120.0 |
| C14A—C15A—C16A | 121.0 (6) | C35D—C34D—C33D | 119.9 (5) |
| C16A—C15A—H15A | 119.5 | C35D—C34D—H34D | 120.0 |
| C14B—C15B—H15B | 119.7 | C34C—C35C—H35C | 120.1 |
| C16B—C15B—C14B | 120.5 (6) | C34C—C35C—C36C | 119.9 (6) |
| C16B—C15B—H15B | 119.7 | C36C—C35C—H35C | 120.1 |
| C11A—C16A—H16A | 120.0 | C34D—C35D—H35D | 119.8 |
| C15A—C16A—C11A | 120.0 (5) | C34D—C35D—C36D | 120.3 (5) |
| C15A—C16A—H16A | 120.0 | C36D—C35D—H35D | 119.8 |
| C11B—C16B—C15B | 122.2 (6) | C31C—C36C—C35C | 121.5 (5) |
| C11B—C16B—H16B | 118.9 | C31C—C36C—H36C | 119.3 |
| C15B—C16B—H16B | 118.9 | C35C—C36C—H36C | 119.3 |
| C22A—C21A—P1A | 122.5 (4) | C31D—C36D—C35D | 119.4 (5) |
| C22A—C21A—C26A | 117.3 (5) | C31D—C36D—H36D | 120.3 |
| C26A—C21A—P1A | 120.2 (4) | C35D—C36D—H36D | 120.3 |
| C22B—C21B—P1B | 123.0 (4) | C12M—C11M—C16M | 114.3 (6) |
| C22B—C21B—C26B | 117.7 (5) | C12M—C11M—B1M | 124.2 (5) |
| C26B—C21B—P1B | 119.4 (4) | C16M—C11M—B1M | 121.3 (5) |
| C21A—C22A—H22A | 119.0 | C11M—C12M—H12M | 118.0 |
| C21A—C22A—C23A | 122.1 (6) | C11M—C12M—C13M | 124.0 (6) |
| C23A—C22A—H22A | 119.0 | C13M—C12M—H12M | 118.0 |
| C21B—C22B—H22B | 119.7 | C12M—C13M—H13M | 120.3 |
| C23B—C22B—C21B | 120.6 (5) | C14M—C13M—C12M | 119.5 (6) |
| C23B—C22B—H22B | 119.7 | C14M—C13M— | 120.3 |

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|---|---|---|---|
| | | H13M | |
| C22A—C23A—H23A | 119.9 | C13M—C14M—H14M | 120.3 |
| C24A—C23A—C22A | 120.3 (6) | C13M—C14M—C15M | 119.4 (7) |
| C24A—C23A—H23A | 119.9 | C15M—C14M—H14M | 120.3 |
| C22B—C23B—H23B | 119.1 | C14M—C15M—H15M | 119.9 |
| C22B—C23B—C24B | 121.8 (6) | C14M—C15M—C16M | 120.3 (6) |
| C24B—C23B—H23B | 119.1 | C16M—C15M—H15M | 119.9 |
| C23A—C24A—H24A | 120.3 | C11M—C16M—C15M | 122.6 (6) |
| C23A—C24A—C25A | 119.3 (6) | C11M—C16M—H16M | 118.7 |
| C25A—C24A—H24A | 120.3 | C15M—C16M—H16M | 118.7 |
| C23B—C24B—H24B | 121.2 | C22M—C21M—B1M | 122.3 (5) |
| C23B—C24B—C25B | 117.6 (6) | C26M—C21M—C22M | 113.8 (6) |
| C25B—C24B—H24B | 121.2 | C26M—C21M—B1M | 123.2 (5) |
| C24A—C25A—H25A | 120.1 | C21M—C22M—H22M | 118.7 |
| C24A—C25A—C26A | 119.9 (6) | C23M—C22M—C21M | 122.5 (6) |
| C26A—C25A—H25A | 120.1 | C23M—C22M—H22M | 118.7 |
| C24B—C25B—H25B | 119.3 | C22M—C23M—H23M | 119.5 |
| C26B—C25B—C24B | 121.4 (6) | C22M—C23M—C24M | 120.9 (6) |
| C26B—C25B—H25B | 119.3 | C24M—C23M—H23M | 119.5 |
| C21A—C26A—H26A | 119.4 | C23M—C24M—H24M | 120.6 |
| C25A—C26A—C21A | 121.2 (5) | C25M—C24M—C23M | 118.8 (6) |
| C25A—C26A—H26A | 119.4 | C25M—C24M—H24M | 120.6 |
| C21B—C26B—H26B | 119.6 | C24M—C25M—H25M | 120.4 |
| C25B—C26B—C21B | 120.8 (5) | C24M—C25M—C26M | 119.2 (6) |
| C25B—C26B—H26B | 119.6 | C26M—C25M—H25M | 120.4 |
| C32A—C31A—P1A | 124.2 (5) | C21M—C26M— | 124.7 (6) |

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|---|---|---|---|
| | | C25M | |
| C36A—C31A—P1A | 117.5 (4) | C21M—C26M—H26M | 117.7 |
| C36A—C31A—C32A | 118.3 (5) | C25M—C26M—H26M | 117.7 |
| C32B—C31B—P1B | 119.3 (4) | C32M—C31M—B1M | 122.3 (5) |
| C32B—C31B—C36B | 117.4 (5) | C36M—C31M—C32M | 114.6 (5) |
| C36B—C31B—P1B | 123.3 (4) | C36M—C31M—B1M | 123.1 (5) |
| C31A—C32A—H32A | 120.6 | C31M—C32M—H32M | 118.7 |
| C33A—C32A—C31A | 118.8 (6) | C33M—C32M—C31M | 122.6 (5) |
| C33A—C32A—H32A | 120.6 | C33M—C32M—H32M | 118.7 |
| C31B—C32B—H32B | 119.1 | C32M—C33M—H33M | 119.9 |
| C31B—C32B—C33B | 121.9 (5) | C34M—C33M—C32M | 120.2 (6) |
| C33B—C32B—H32B | 119.1 | C34M—C33M—H33M | 119.9 |
| C32A—C33A—H33A | 119.3 | C33M—C34M—H34M | 120.6 |
| C34A—C33A—C32A | 121.4 (6) | C33M—C34M—C35M | 118.8 (5) |
| C34A—C33A—H33A | 119.3 | C35M—C34M—H34M | 120.6 |
| C32B—C33B—H33B | 119.9 | C34M—C35M—H35M | 120.0 |
| C34B—C33B—C32B | 120.2 (6) | C36M—C35M—C34M | 120.0 (5) |
| C34B—C33B—H33B | 119.9 | C36M—C35M—H35M | 120.0 |
| C33A—C34A—H34A | 119.9 | C31M—C36M—H36M | 118.1 |
| C33A—C34A—C35A | 120.2 (6) | C35M—C36M—C31M | 123.8 (6) |
| C35A—C34A—H34A | 119.9 | C35M—C36M—H36M | 118.1 |
| C33B—C34B—H34B | 120.5 | C42M—C41M—B1M | 123.6 (5) |
| C35B—C34B—C33B | 119.1 (6) | C46M—C41M—C42M | 114.0 (5) |
| C35B—C34B—H34B | 120.5 | C46M—C41M—B1M | 122.4 (5) |
| C34A—C35A—H35A | 120.7 | C41M—C42M—H42M | 118.0 |
| C36A—C35A—C34A | 118.7 (6) | C41M—C42M—C43M | 124.0 (6) |
| C36A—C35A—H35A | 120.7 | C43M—C42M— | 118.0 |

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| | | H42M | |
| C34B—C35B—H35B | 119.4 | C42M—C43M—H43M | 120.5 |
| C34B—C35B—C36B | 121.3 (6) | C44M—C43M—C42M | 119.1 (6) |
| C36B—C35B—H35B | 119.4 | C44M—C43M—H43M | 120.5 |
| C31A—C36A—H36A | 118.7 | C43M—C44M—H44M | 120.3 |
| C35A—C36A—C31A | 122.6 (5) | C45M—C44M—C43M | 119.4 (6) |
| C35A—C36A—H36A | 118.7 | C45M—C44M—H44M | 120.3 |
| C31B—C36B—C35B | 120.3 (5) | C44M—C45M—H45M | 119.8 |
| C31B—C36B—H36B | 119.9 | C44M—C45M—C46M | 120.4 (6) |
| C35B—C36B—H36B | 119.9 | C46M—C45M—H45M | 119.8 |
| P1C—Ru1B—HA | 91.1 (11) | C41M—C46M—C45M | 123.2 (6) |
| P1D—Ru1B—HA | 78.6 (11) | C41M—C46M—H46M | 118.4 |
| P1D—Ru1B—P1C | 169.30 (5) | C45M—C46M—H46M | 118.4 |
| N2G—Ru1B—HA | 88.9 (12) | C11M—B1M—C31M | 111.9 (4) |
| N2G—Ru1B—P1C | 88.00 (10) | C11M—B1M—C41M | 109.9 (5) |
| N2G—Ru1B—P1D | 94.75 (10) | C21M—B1M—C11M | 112.2 (5) |
| C1H—Ru1B—HA | 87.0 (12) | C21M—B1M—C31M | 106.5 (5) |
| C1H—Ru1B—P1C | 89.61 (13) | C21M—B1M—C41M | 108.2 (5) |
| C1H—Ru1B—P1D | 86.87 (13) | C41M—B1M—C31M | 108.1 (4) |
| C1H—Ru1B—N2G | 175.2 (2) | C12N—C11N—C16N | 114.8 (4) |
| C1H—Ru1B—C7G | 99.2 (2) | C12N—C11N—B1N | 123.4 (4) |
| C7G—Ru1B—HA | 170.8 (12) | C16N—C11N—B1N | 121.4 (5) |
| C7G—Ru1B—P1C | 95.63 (11) | C11N—C12N—H12N | 118.4 |
| C7G—Ru1B—P1D | 94.91 (11) | C13N—C12N—C11N | 123.2 (5) |
| C7G—Ru1B—N2G | 85.18 (19) | C13N—C12N—H12N | 118.4 |
| C11C—P1C—Ru1B | 114.18 (15) | C12N—C13N—H13N | 120.0 |
| C11C—P1C—C21C | 103.1 (2) | C14N—C13N—C12N | 119.9 (5) |
| C11C—P1C—C31C | 103.2 (2) | C14N—C13N—H13N | 120.0 |
| C21C—P1C—Ru1B | 117.23 (14) | C13N—C14N—H14N | 120.4 |
| C21C—P1C—C31C | 100.4 (2) | C15N—C14N—C13N | 119.2 (5) |
| C31C—P1C—Ru1B | 116.64 (15) | C15N—C14N—H14N | 120.4 |
| C11D—P1D—Ru1B | 114.46 (15) | C14N—C15N—H15N | 119.6 |
| C11D—P1D—C21D | 103.9 (2) | C14N—C15N—C16N | 120.8 (5) |

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| C21D—P1D—Ru1B | 119.47 (16) | C16N—C15N—H15N | 119.6 |
| C31D—P1D—Ru1B | 113.35 (15) | C11N—C16N—H16N | 119.0 |
| C31D—P1D—C11D | 102.7 (2) | C15N—C16N—C11N | 122.0 (5) |
| C31D—P1D—C21D | 100.8 (2) | C15N—C16N—H16N | 119.0 |
| N2G—N1G—C6G | 119.9 (4) | C22N—C21N—B1N | 123.6 (5) |
| C5G—N1G—N2G | 112.2 (4) | C26N—C21N—C22N | 114.1 (5) |
| C5G—N1G—C6G | 126.7 (4) | C26N—C21N—B1N | 122.3 (5) |
| N1G—N2G—Ru1B | 124.6 (3) | C21N—C22N—H22N | 118.8 |
| C3G—N2G—Ru1B | 131.0 (4) | C23N—C22N—C21N | 122.4 (5) |
| C3G—N2G—N1G | 103.8 (4) | C23N—C22N—H22N | 118.8 |
| C7G—N3G—C6G | 123.7 (5) | C22N—C23N—H23N | 119.5 |
| C9G—N3G—C6G | 122.9 (4) | C24N—C23N—C22N | 121.0 (5) |
| C9G—N3G—C7G | 113.1 (5) | C24N—C23N—H23N | 119.5 |
| C7G—N4G—C8G | 113.5 (5) | C23N—C24N—H24N | 121.0 |
| C7G—N4G—C10G | 124.5 (4) | C25N—C24N—C23N | 118.0 (5) |
| C8G—N4G—C10G | 122.0 (5) | C25N—C24N—H24N | 121.0 |
| N6G—N5G—C10G | 123.8 (7) | C24N—C25N—H25N | 119.5 |
| C13G—N5G—N6G | 112.6 (8) | C24N—C25N—C26N | 121.1 (6) |
| C13G—N5G—C10G | 123.6 (7) | C26N—C25N—H25N | 119.5 |
| N6G'—N5G'—C10G | 116.9 (13) | C21N—C26N—C25N | 123.3 (5) |
| N6G'—N5G'—C13' | 108.5 (14) | C21N—C26N—H26N | 118.4 |
| C13'—N5G'—C10G | 134.6 (12) | C25N—C26N—H26N | 118.4 |
| N5G—N6G—C11G | 104.3 (8) | C32N—C31N—C36N | 114.1 (5) |
| N5G'—N6G'—C11' | 107.9 (15) | C32N—C31N—B1N | 122.4 (5) |
| O1H—C1H—Ru1B | 176.5 (5) | C36N—C31N—B1N | 123.5 (5) |
| N2G—C3G—H3G | 123.9 | C31N—C32N—H32N | 118.3 |
| N2G—C3G—C4G | 112.1 (5) | C33N—C32N—C31N | 123.4 (5) |
| C4G—C3G—H3G | 123.9 | C33N—C32N—H32N | 118.3 |
| C3G—C4G—H4G | 127.4 | C32N—C33N—H33N | 120.0 |
| C3G—C4G—C5G | 105.3 (5) | C34N—C33N—C32N | 120.0 (5) |
| C5G—C4G—H4G | 127.4 | C34N—C33N—H33N | 120.0 |
| N1G—C5G—C4G | 106.6 (5) | C33N—C34N—H34N | 120.4 |
| N1G—C5G—H5G | 126.7 | C35N—C34N—C33N | 119.2 (6) |
| C4G—C5G—H5G | 126.7 | C35N—C34N—H34N | 120.4 |
| N1G—C6G—H6GA | 109.1 | C34N—C35N—H35N | 120.2 |
| N1G—C6G—H6GB | 109.1 | C34N—C35N—C36N | 119.6 (5) |
| N3G—C6G—N1G | 112.3 (4) | C36N—C35N—H35N | 120.2 |
| N3G—C6G—H6GA | 109.1 | C31N—C36N—H36N | 118.1 |
| N3G—C6G—H6GB | 109.1 | C35N—C36N—C31N | 123.8 (5) |
| H6GA—C6G—H6GB | 107.9 | C35N—C36N—H36N | 118.1 |
| N3G—C7G—Ru1B | 123.2 (4) | C42N—C41N—B1N | 118.7 (5) |

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| N4G—C7G—Ru1B | 136.3 (4) | C46N—C41N—C42N | 115.9 (4) |
| N4G—C7G—N3G | 100.5 (4) | C46N—C41N—B1N | 124.3 (4) |
| N4G—C8G—H8G | 127.1 | C41N—C42N—H42N | 119.4 |
| C9G—C8G—N4G | 105.9 (5) | C43N—C42N—C41N | 121.1 (5) |
| C9G—C8G—H8G | 127.1 | C43N—C42N—H42N | 119.4 |
| N3G—C9G—H9G | 126.5 | C42N—C43N—H43N | 119.6 |
| C8G—C9G—N3G | 107.0 (5) | C44N—C43N—C42N | 120.7 (5) |
| C8G—C9G—H9G | 126.5 | C44N—C43N—H43N | 119.6 |
| N4G—C10G—N5G | 111.3 (4) | C43N—C44N—H44N | 120.0 |
| N4G—C10G—H10A | 109.4 | C43N—C44N—C45N | 120.1 (5) |
| N4G—C10G—H10B | 109.4 | C45N—C44N—H44N | 120.0 |
| N4G—C10G—H10C | 110.0 | C44N—C45N—H45N | 120.7 |
| N4G—C10G—H10D | 110.0 | C44N—C45N—C46N | 118.7 (5) |
| N5G—C10G—H10A | 109.4 | C46N—C45N—H45N | 120.7 |
| N5G—C10G—H10B | 109.4 | C41N—C46N—C45N | 123.5 (5) |
| N5G'—C10G—N4G | 108.3 (7) | C41N—C46N—H46N | 118.3 |
| N5G'—C10G—H10C | 110.0 | C45N—C46N—H46N | 118.3 |
| N5G'—C10G—H10D | 110.0 | C21N—B1N—C11N | 110.3 (4) |
| H10A—C10G—H10B | 108.0 | C21N—B1N—C41N | 106.1 (4) |
| H10C—C10G—H10D | 108.4 | C31N—B1N—C11N | 107.3 (4) |
| N6G'—C11'—H11' | 126.3 | C31N—B1N—C21N | 112.0 (4) |
| N6G'—C11'—C12' | 107.4 (14) | C31N—B1N—C41N | 110.0 (4) |
| C12'—C11'—H11' | 126.3 | C41N—B1N—C11N | 111.2 (4) |
| C12C—C11C—P1C | 118.5 (4) | | |

Selected geometric parameters, torsion angles (º)

| | | | |
|---|---|---|---|
| Ru1A—P1A—C11A—C12A | 51.1 (4) | C10G—N4G—C8G—C9G | -179.6 (4) |
| Ru1A—P1A—C11A—C16A | -130.5 (4) | C10G—N5G—N6G—C11G | 178.7 (6) |
| Ru1A—P1A—C21A—C22A | -126.8 (4) | C10G—N5G—C13G—C12G | -176.7 (7) |
| Ru1A—P1A—C21A—C26A | 54.4 (5) | C10G—N5G'—N6G'—C11' | -176.2 (15) |
| Ru1A—P1A—C31A—C32A | -130.1 (4) | C10G—N5G'—C13'—C12' | -178.7 (15) |
| Ru1A—P1A—C31A—C36A | 47.6 (4) | C11'—C12'—C13'—N5G' | -4 (2) |
| Ru1A—P1B—C11B—C12B | 154.8 (4) | C11C—P1C—C21C—C22C | -7.8 (4) |
| Ru1A—P1B—C11B— | -26.9 (5) | C11C—P1C—C21C— | 170.0 (4) |

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|---|---|---|---|
| C16B | | C26C | |
| Ru1A—P1B—C21B—C22B | 105.5 (4) | C11C—P1C—C31C—C32C | -88.2 (4) |
| Ru1A—P1B—C21B—C26B | -74.5 (4) | C11C—P1C—C31C—C36C | 86.8 (4) |
| Ru1A—P1B—C31B—C32B | -48.1 (4) | C11C—C12C—C13C—C14C | -0.4 (8) |
| Ru1A—P1B—C31B—C36B | 128.2 (4) | C11D—P1D—C21D—C22D | 92.6 (4) |
| Ru1A—N2E—C3E—C4E | 170.4 (3) | C11D—P1D—C21D—C26D | -89.8 (4) |
| P1A—C11A—C12A—C13A | 178.1 (4) | C11D—P1D—C31D—C32D | 175.8 (4) |
| P1A—C11A—C16A—C15A | -177.4 (4) | C11D—P1D—C31D—C36D | -8.9 (5) |
| P1A—C21A—C22A—C23A | 179.8 (5) | C11D—C12D—C13D—C14D | -0.1 (7) |
| P1A—C21A—C26A—C25A | 179.9 (4) | C11G—C12G—C13G—N5G | -3.1 (13) |
| P1A—C31A—C32A—C33A | 175.2 (4) | C12C—C11C—C16C—C15C | 1.1 (7) |
| P1A—C31A—C36A—C35A | -177.0 (4) | C12C—C13C—C14C—C15C | 0.1 (8) |
| P1B—C11B—C12B—C13B | 179.1 (4) | C12D—C11D—C16D—C15D | 0.9 (7) |
| P1B—C11B—C16B—C15B | -177.7 (5) | C12D—C13D—C14D—C15D | 1.6 (8) |
| P1B—C21B—C22B—C23B | -179.6 (4) | C13'—N5G'—N6G'—C11' | 5 (2) |
| P1B—C21B—C26B—C25B | 179.0 (4) | C13'—N5G'—C10G—N4G | 97.6 (17) |
| P1B—C31B—C32B—C33B | 176.1 (4) | C13C—C14C—C15C—C16C | 0.8 (8) |
| P1B—C31B—C36B—C35B | -175.6 (4) | C13D—C14D—C15D—C16D | -1.9 (8) |
| N1E—N2E—C3E—C4E | 1.2 (5) | C13G—N5G—N6G—C11G | -0.1 (10) |
| N2E—N1E—C5E—C4E | 0.6 (6) | C13G—N5G—C10G—N4G | 83.2 (9) |
| N2E—N1E—C6E—N3E | -60.5 (6) | C14C—C15C—C16C—C11C | -1.4 (8) |
| N2E—C3E—C4E—C5E | -0.9 (6) | C14D—C15D—C16D—C11D | 0.6 (8) |
| N3E—C8E—C9E—N4E | 0.2 (6) | C16C—C11C—C12C—C13C | -0.1 (7) |
| N5E—N6E—C11E—C12E | 0.0 (7) | C16D—C11D—C12D—C13D | -1.2 (7) |
| N6E—N5E—C10E— | -96.0 (6) | C21C—P1C—C11C— | 77.4 (4) |

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|---|---|
| N4E | |
| N6E—N5E—C13E—C12E | 0.2 (7) |
| N6E—C11E—C12E—C13E | 0.1 (8) |
| C3E—C4E—C5E—N1E | 0.1 (6) |
| C5E—N1E—N2E—Ru1A | -171.1 (3) |
| C5E—N1E—N2E—C3E | -1.1 (5) |
| C5E—N1E—C6E—N3E | 131.8 (5) |
| C6E—N1E—N2E—Ru1A | 19.6 (5) |
| C6E—N1E—N2E—C3E | -170.5 (4) |
| C6E—N1E—C5E—C4E | 169.0 (5) |
| C6E—N3E—C7E—Ru1A | -10.0 (6) |
| C6E—N3E—C7E—N4E | 173.4 (4) |
| C6E—N3E—C8E—C9E | -173.4 (5) |
| C7E—N3E—C6E—N1E | 56.1 (6) |
| C7E—N3E—C8E—C9E | -0.5 (6) |
| C7E—N4E—C9E—C8E | 0.2 (6) |
| C7E—N4E—C10E—N5E | 108.0 (5) |
| C8E—N3E—C6E—N1E | -131.8 (5) |
| C8E—N3E—C7E—Ru1A | 177.2 (3) |
| C8E—N3E—C7E—N4E | 0.6 (5) |
| C9E—N4E—C7E—Ru1A | -176.3 (4) |
| C9E—N4E—C7E—N3E | -0.5 (5) |
| C9E—N4E—C10E—N5E | -66.4 (6) |
| C10E—N4E—C7E—Ru1A | 8.9 (7) |
| C10E—N4E—C7E— | -175.3 (4) |

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|---|---|
| C12C | |
| C21C—P1C—C11C—C16C | -103.5 (4) |
| C21C—P1C—C31C—C32C | 18.0 (5) |
| C21C—P1C—C31C—C36C | -167.0 (4) |
| C21C—C22C—C23C—C24C | -0.4 (8) |
| C21D—P1D—C11D—C12D | 5.8 (5) |
| C21D—P1D—C11D—C16D | -178.2 (4) |
| C21D—P1D—C31D—C32D | -77.1 (4) |
| C21D—P1D—C31D—C36D | 98.2 (4) |
| C21D—C22D—C23D—C24D | 0.1 (8) |
| C22C—C21C—C26C—C25C | -0.6 (7) |
| C22C—C23C—C24C—C25C | -1.3 (8) |
| C22D—C21D—C26D—C25D | -0.4 (7) |
| C22D—C23D—C24D—C25D | 0.0 (8) |
| C23C—C24C—C25C—C26C | 2.1 (8) |
| C23D—C24D—C25D—C26D | -0.3 (8) |
| C24C—C25C—C26C—C21C | -1.2 (7) |
| C24D—C25D—C26D—C21D | 0.5 (8) |
| C26C—C21C—C22C—C23C | 1.4 (7) |
| C26D—C21D—C22D—C23D | 0.1 (7) |
| C31C—P1C—C11C—C12C | -178.4 (4) |
| C31C—P1C—C11C—C16C | 0.7 (4) |
| C31C—P1C—C21C—C22C | -114.1 (4) |
| C31C—P1C—C21C—C26C | 63.7 (4) |
| C31C—C32C— | -3.8 (8) |

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|---|---|---|---|
| N3E | | C33C—C34C | |
| C10E—N4E—C9E—C8E | 175.3 (4) | C31D—P1D—C11D—C12D | 110.5 (4) |
| C10E—N5E—N6E—C11E | 176.6 (5) | C31D—P1D—C11D—C16D | -73.5 (4) |
| C10E—N5E—C13E—C12E | -176.2 (5) | C31D—P1D—C21D—C22D | -13.6 (4) |
| C11A—P1A—C21A—C22A | -3.1 (5) | C31D—P1D—C21D—C26D | 164.0 (4) |
| C11A—P1A—C21A—C26A | 178.1 (4) | C31D—C32D—C33D—C34D | -0.5 (8) |
| C11A—P1A—C31A—C32A | 107.2 (4) | C32C—C31C—C36C—C35C | -1.9 (8) |
| C11A—P1A—C31A—C36A | -75.2 (4) | C32C—C33C—C34C—C35C | 0.0 (9) |
| C11A—C12A—C13A—C14A | 0.2 (8) | C32D—C31D—C36D—C35D | -0.3 (7) |
| C11B—P1B—C21B—C22B | -127.2 (4) | C32D—C33D—C34D—C35D | 1.7 (8) |
| C11B—P1B—C21B—C26B | 52.7 (4) | C33C—C34C—C35C—C36C | 2.7 (9) |
| C11B—P1B—C31B—C32B | -175.5 (4) | C33D—C34D—C35D—C36D | -2.2 (8) |
| C11B—P1B—C31B—C36B | 0.8 (5) | C34C—C35C—C36C—C31C | -1.8 (9) |
| C11B—C12B—C13B—C14B | -0.9 (9) | C34D—C35D—C36D—C31D | 1.5 (8) |
| C11E—C12E—C13E—N5E | -0.2 (7) | C36C—C31C—C32C—C33C | 4.7 (8) |
| C12A—C11A—C16A—C15A | 0.9 (8) | C36D—C31D—C32D—C33D | -0.2 (8) |
| C12A—C13A—C14A—C15A | -0.6 (9) | C11M—C12M—C13M—C14M | -0.8 (9) |
| C12B—C11B—C16B—C15B | 0.7 (9) | C12M—C11M—C16M—C15M | -1.6 (8) |
| C12B—C13B—C14B—C15B | -0.3 (10) | C12M—C11M—B1M—C21M | 151.6 (5) |
| C13A—C14A—C15A—C16A | 1.2 (9) | C12M—C11M—B1M—C31M | 32.0 (7) |
| C13B—C14B—C15B—C16B | 1.7 (10) | C12M—C11M—B1M—C41M | -88.0 (6) |
| C13E—N5E—N6E—C11E | -0.1 (6) | C12M—C13M—C14M—C15M | 0.3 (9) |
| C13E—N5E—C10E—N4E | 80.1 (7) | C13M—C14M—C15M—C16M | -0.6 (9) |
| C14A—C15A—C16A—C11A | -1.4 (8) | C14M—C15M—C16M—C11M | 1.3 (9) |
| C14B—C15B— | -1.9 (11) | C16M—C11M— | 1.4 (8) |

| | |
|---|---|
| C16B—C11B | |
| C16A—C11A—C12A—C13A | -0.3 (8) |
| C16B—C11B—C12B—C13B | 0.7 (8) |
| C21A—P1A—C11A—C12A | -76.4 (4) |
| C21A—P1A—C11A—C16A | 101.9 (5) |
| C21A—P1A—C31A—C32A | 1.1 (5) |
| C21A—P1A—C31A—C36A | 178.7 (4) |
| C21A—C22A—C23A—C24A | 0.5 (10) |
| C21B—P1B—C11B—C12B | 27.8 (5) |
| C21B—P1B—C11B—C16B | -153.9 (5) |
| C21B—P1B—C31B—C32B | 79.1 (4) |
| C21B—P1B—C31B—C36B | -104.6 (4) |
| C21B—C22B—C23B—C24B | -0.2 (8) |
| C22A—C21A—C26A—C25A | 1.0 (8) |
| C22A—C23A—C24A—C25A | 0.8 (10) |
| C22B—C21B—C26B—C25B | -1.1 (7) |
| C22B—C23B—C24B—C25B | 0.4 (8) |
| C23A—C24A—C25A—C26A | -1.2 (9) |
| C23B—C24B—C25B—C26B | -1.0 (8) |
| C24A—C25A—C26A—C21A | 0.3 (8) |
| C24B—C25B—C26B—C21B | 1.4 (8) |
| C26A—C21A—C22A—C23A | -1.4 (9) |
| C26B—C21B—C22B—C23B | 0.5 (7) |
| C31A—P1A—C11A—C12A | 176.2 (4) |
| C31A—P1A— | -5.5 (5) |

| | |
|---|---|
| C12M—C13M | |
| C16M—C11M—B1M—C21M | -33.2 (7) |
| C16M—C11M—B1M—C31M | -152.8 (5) |
| C16M—C11M—B1M—C41M | 87.2 (6) |
| C21M—C22M—C23M—C24M | 1.3 (10) |
| C22M—C21M—C26M—C25M | -0.8 (9) |
| C22M—C21M—B1M—C11M | -37.1 (7) |
| C22M—C21M—B1M—C31M | 85.6 (6) |
| C22M—C21M—B1M—C41M | -158.4 (5) |
| C22M—C23M—C24M—C25M | -0.4 (10) |
| C23M—C24M—C25M—C26M | -1.1 (10) |
| C24M—C25M—C26M—C21M | 1.8 (10) |
| C26M—C21M—C22M—C23M | -0.7 (9) |
| C26M—C21M—B1M—C11M | 153.2 (5) |
| C26M—C21M—B1M—C31M | -84.2 (6) |
| C26M—C21M—B1M—C41M | 31.8 (7) |
| C31M—C32M—C33M—C34M | 0.2 (8) |
| C32M—C31M—C36M—C35M | -0.2 (8) |
| C32M—C31M—B1M—C11M | 106.8 (6) |
| C32M—C31M—B1M—C21M | -16.1 (7) |
| C32M—C31M—B1M—C41M | -132.1 (5) |
| C32M—C33M—C34M—C35M | 0.7 (8) |
| C33M—C34M—C35M—C36M | -1.3 (9) |
| C34M—C35M—C36M—C31M | 1.1 (9) |
| C36M—C31M— | -0.5 (8) |

| | |
|---|---|
| C11A—C16A | |
| C31A—P1A—C21A—C22A | 103.4 (5) |
| C31A—P1A—C21A—C26A | -75.4 (4) |
| C31A—C32A—C33A—C34A | 2.0 (8) |
| C31B—P1B—C11B—C12B | -78.6 (5) |
| C31B—P1B—C11B—C16B | 99.7 (5) |
| C31B—P1B—C21B—C22B | -21.0 (5) |
| C31B—P1B—C21B—C26B | 158.9 (4) |
| C31B—C32B—C33B—C34B | 0.1 (8) |
| C32A—C31A—C36A—C35A | 0.8 (8) |
| C32A—C33A—C34A—C35A | 0.1 (9) |
| C32B—C31B—C36B—C35B | 0.8 (7) |
| C32B—C33B—C34B—C35B | 0.0 (8) |
| C33A—C34A—C35A—C36A | -1.7 (9) |
| C33B—C34B—C35B—C36B | 0.4 (8) |
| C34A—C35A—C36A—C31A | 1.3 (8) |
| C34B—C35B—C36B—C31B | -0.8 (8) |
| C36A—C31A—C32A—C33A | -2.4 (7) |
| C36B—C31B—C32B—C33B | -0.5 (7) |
| Ru1B—P1C—C11C—C12C | -50.9 (4) |
| Ru1B—P1C—C11C—C16C | 128.3 (4) |
| Ru1B—P1C—C21C—C22C | 118.5 (4) |
| Ru1B—P1C—C21C—C26C | -63.7 (4) |
| Ru1B—P1C—C31C—C32C | 145.8 (4) |
| Ru1B—P1C—C31C— | -39.2 (5) |

| | |
|---|---|
| C32M—C33M | |
| C36M—C31M—B1M—C11M | -75.1 (7) |
| C36M—C31M—B1M—C21M | 162.0 (5) |
| C36M—C31M—B1M—C41M | 46.0 (7) |
| C41M—C42M—C43M—C44M | 0.6 (10) |
| C42M—C41M—C46M—C45M | 0.2 (8) |
| C42M—C41M—B1M—C11M | 149.8 (5) |
| C42M—C41M—B1M—C21M | -87.4 (6) |
| C42M—C41M—B1M—C31M | 27.5 (8) |
| C42M—C43M—C44M—C45M | -0.9 (10) |
| C43M—C44M—C45M—C46M | 0.8 (10) |
| C44M—C45M—C46M—C41M | -0.5 (9) |
| C46M—C41M—C42M—C43M | -0.2 (9) |
| C46M—C41M—B1M—C11M | -31.2 (7) |
| C46M—C41M—B1M—C21M | 91.5 (6) |
| C46M—C41M—B1M—C31M | -153.5 (5) |
| B1M—C11M—C12M—C13M | 176.9 (5) |
| B1M—C11M—C16M—C15M | -177.3 (5) |
| B1M—C21M—C22M—C23M | -171.4 (6) |
| B1M—C21M—C26M—C25M | 169.7 (6) |
| B1M—C31M—C32M—C33M | 177.8 (5) |
| B1M—C31M—C36M—C35M | -178.5 (5) |
| B1M—C41M—C42M—C43M | 178.8 (6) |
| B1M—C41M—C46M—C45M | -178.9 (5) |
| C11N—C12N— | 0.4 (8) |

| | | | |
|---|---|---|---|
| C36C | | C13N—C14N | |
| Ru1B—P1D—C11D—C12D | -126.2 (4) | C12N—C11N—C16N—C15N | -2.6 (8) |
| Ru1B—P1D—C11D—C16D | 49.8 (4) | C12N—C11N—B1N—C21N | 154.7 (5) |
| Ru1B—P1D—C21D—C22D | -138.4 (4) | C12N—C11N—B1N—C31N | -83.1 (6) |
| Ru1B—P1D—C21D—C26D | 39.2 (4) | C12N—C11N—B1N—C41N | 37.2 (7) |
| Ru1B—P1D—C31D—C32D | 51.8 (4) | C12N—C13N—C14N—C15N | -1.4 (9) |
| Ru1B—P1D—C31D—C36D | -132.9 (4) | C13N—C14N—C15N—C16N | 0.3 (9) |
| Ru1B—N2G—C3G—C4G | 173.2 (3) | C14N—C15N—C16N—C11N | 1.8 (9) |
| P1C—C11C—C12C—C13C | 179.0 (4) | C16N—C11N—C12N—C13N | 1.6 (8) |
| P1C—C11C—C16C—C15C | -178.1 (4) | C16N—C11N—B1N—C21N | -32.1 (7) |
| P1C—C21C—C22C—C23C | 179.1 (4) | C16N—C11N—B1N—C31N | 90.1 (6) |
| P1C—C21C—C26C—C25C | -178.4 (4) | C16N—C11N—B1N—C41N | -149.6 (5) |
| P1C—C31C—C32C—C33C | 179.9 (4) | C21N—C22N—C23N—C24N | 0.7 (8) |
| P1C—C31C—C36C—C35C | -177.2 (4) | C22N—C21N—C26N—C25N | -2.4 (8) |
| P1D—C11D—C12D—C13D | 174.8 (4) | C22N—C21N—B1N—C11N | -95.9 (5) |
| P1D—C11D—C16D—C15D | -175.3 (4) | C22N—C21N—B1N—C31N | 144.7 (5) |
| P1D—C21D—C22D—C23D | 177.7 (4) | C22N—C21N—B1N—C41N | 24.7 (6) |
| P1D—C21D—C26D—C25D | -178.1 (4) | C22N—C23N—C24N—C25N | -1.2 (8) |
| P1D—C31D—C32D—C33D | 175.2 (4) | C23N—C24N—C25N—C26N | 0.0 (9) |
| P1D—C31D—C36D—C35D | -175.6 (4) | C24N—C25N—C26N—C21N | 2.0 (9) |
| N1G—N2G—C3G—C4G | 1.9 (5) | C26N—C21N—C22N—C23N | 1.0 (7) |
| N2G—N1G—C5G—C4G | 1.2 (6) | C26N—C21N—B1N—C11N | 82.7 (6) |
| N2G—N1G—C6G—N3G | -60.0 (5) | C26N—C21N—B1N—C31N | -36.7 (6) |
| N2G—C3G—C4G—C5G | -1.2 (6) | C26N—C21N—B1N—C41N | -156.7 (5) |
| N4G—C8G—C9G— | 0.6 (5) | C31N—C32N— | 0.1 (8) |

| | | | |
|---|---|---|---|
| N3G | | C33N—C34N | |
| N5G—N6G—C11G—C12G | -1.8 (9) | C32N—C31N—C36N—C35N | -0.4 (7) |
| N5G'—N6G'—C11'—C12' | -7 (2) | C32N—C31N—B1N—C11N | -151.6 (5) |
| N6G—N5G—C10G—N4G | -95.4 (7) | C32N—C31N—B1N—C21N | -30.4 (6) |
| N6G—N5G—C13G—C12G | 2.1 (13) | C32N—C31N—B1N—C41N | 87.3 (6) |
| N6G—C11G—C12G—C13G | 3.1 (11) | C32N—C33N—C34N—C35N | 1.1 (9) |
| N6G'—N5G'—C10G—N4G | -80.7 (16) | C33N—C34N—C35N—C36N | -1.9 (9) |
| N6G'—N5G'—C13'—C12' | 0 (2) | C34N—C35N—C36N—C31N | 1.6 (8) |
| N6G'—C11'—C12'—C13' | 7 (2) | C36N—C31N—C32N—C33N | -0.5 (7) |
| C3G—C4G—C5G—N1G | 0.0 (6) | C36N—C31N—B1N—C11N | 29.3 (6) |
| C5G—N1G—N2G—Ru1B | -174.0 (3) | C36N—C31N—B1N—C21N | 150.4 (4) |
| C5G—N1G—N2G—C3G | -1.9 (5) | C36N—C31N—B1N—C41N | -91.8 (5) |
| C5G—N1G—C6G—N3G | 133.3 (5) | C41N—C42N—C43N—C44N | 0.1 (8) |
| C6G—N1G—N2G—Ru1B | 17.5 (5) | C42N—C41N—C46N—C45N | -1.0 (7) |
| C6G—N1G—N2G—C3G | -170.4 (4) | C42N—C41N—B1N—C11N | -158.1 (4) |
| C6G—N1G—C5G—C4G | 168.8 (5) | C42N—C41N—B1N—C21N | 81.9 (5) |
| C6G—N3G—C7G—Ru1B | -4.6 (5) | C42N—C41N—B1N—C31N | -39.4 (6) |
| C6G—N3G—C7G—N4G | 174.6 (4) | C42N—C43N—C44N—C45N | -1.2 (8) |
| C6G—N3G—C9G—C8G | -174.7 (4) | C43N—C44N—C45N—C46N | 1.2 (8) |
| C7G—N3G—C6G—N1G | 53.7 (6) | C44N—C45N—C46N—C41N | 0.0 (8) |
| C7G—N3G—C9G—C8G | -1.2 (5) | C46N—C41N—C42N—C43N | 1.0 (7) |
| C7G—N4G—C8G—C9G | 0.1 (5) | C46N—C41N—B1N—C11N | 34.1 (6) |
| C7G—N4G—C10G—N5G | 111.6 (5) | C46N—C41N—B1N—C21N | -85.9 (6) |
| C7G—N4G—C10G—N5G' | 159.0 (7) | C46N—C41N—B1N—C31N | 152.8 (4) |
| C8G—N4G—C7G— | 178.2 (3) | B1N—C11N— | 175.2 (5) |

| | | | |
|---|---|---|---|
| Ru1B | | C12N—C13N | |
| C8G—N4G—C7G—N3G | -0.8 (5) | B1N—C11N—C16N—C15N | -176.4 (5) |
| C8G—N4G—C10G—N5G | -68.7 (6) | B1N—C21N—C22N—C23N | 179.7 (5) |
| C8G—N4G—C10G—N5G' | -21.3 (8) | B1N—C21N—C26N—C25N | 178.9 (5) |
| C9G—N3G—C6G—N1G | -133.5 (4) | B1N—C31N—C32N—C33N | -179.7 (5) |
| C9G—N3G—C7G—Ru1B | -178.0 (3) | B1N—C31N—C36N—C35N | 178.8 (5) |
| C9G—N3G—C7G—N4G | 1.2 (4) | B1N—C41N—C42N—C43N | -167.8 (5) |
| C10G—N4G—C7G—Ru1B | -2.1 (7) | B1N—C41N—C46N—C45N | 167.1 (4) |
| C10G—N4G—C7G—N3G | 178.9 (4) | | |

### 7.1.7. Crystal data for complex 7

#### Selected geometric parameters (Å)

| | | | |
|---|---|---|---|
| Ru01—N1C | 2.076 (4) | C2—H2D | 0.9900 |
| Ru01—N1C$^{i}$ | 2.076 (4) | C11—C16 | 1.390 (6) |
| Ru01—N2A$^{i}$ | 2.088 (3) | C11—C12 | 1.407 (6) |
| Ru01—N2A | 2.088 (3) | C11—B1 | 1.631 (7) |
| Ru01—C1B | 2.043 (4) | C1C—H1C | 0.9500 |
| Ru01—C1B$^{i}$ | 2.043 (4) | C3B—H3B | 0.9500 |
| N1C—N2C | 1.376 (5) | C23—H23 | 0.9500 |
| N1C—C3C | 1.334 (5) | C23—C22 | 1.389 (6) |
| N2A—N1A | 1.371 (5) | C23—C24 | 1.369 (7) |
| N2A—C1A | 1.328 (5) | C43—H43 | 0.9500 |
| N1B—C1B | 1.346 (5) | C43—C44 | 1.375 (7) |
| N1B—C2B | 1.395 (6) | C16—H16 | 0.9500 |
| N1B—C1 | 1.444 (6) | C3A—H3A | 0.9500 |
| N1A—C3A | 1.346 (6) | C3A—C2A | 1.366 (6) |
| N1A—C1 | 1.470 (6) | C1—H1B | 0.9900 |
| N2C—C2 | 1.464 (5) | C1—H1D | 0.9900 |
| N2C—C1C | 1.341 (6) | C22—H22 | 0.9500 |
| N2B—C1B | 1.369 (5) | C44—H44 | 0.9500 |
| N2B—C2 | 1.437 (6) | C44—C45 | 1.378 (7) |

| | | | |
|---|---|---|---|
| N2B—C3B | 1.385 (6) | C12—H12 | 0.9500 |
| C21—C22 | 1.381 (6) | C12—C13 | 1.377 (6) |
| C21—C26 | 1.400 (7) | C36—H36 | 0.9500 |
| C21—B1 | 1.641 (7) | C36—C35 | 1.395 (7) |
| C15—H15 | 0.9500 | C46—H46 | 0.9500 |
| C15—C16 | 1.395 (6) | C46—C45 | 1.379 (7) |
| C15—C14 | 1.379 (6) | C45—H45 | 0.9500 |
| C2C—H2C | 0.9500 | C35—H35 | 0.9500 |
| C2C—C3C | 1.373 (6) | C35—C34 | 1.375 (8) |
| C2C—C1C | 1.360 (6) | C14—H14 | 0.9500 |
| C42—H42 | 0.9500 | C14—C13 | 1.366 (7) |
| C42—C41 | 1.388 (6) | C32—H32 | 0.9500 |
| C42—C43 | 1.378 (7) | C32—C33 | 1.390 (7) |
| C3C—H3C | 0.9500 | C26—H26 | 0.9500 |
| C1A—H1A | 0.9500 | C26—C25 | 1.389 (7) |
| C1A—C2A | 1.380 (6) | C13—H13 | 0.9500 |
| C2B—H2B | 0.9500 | C2A—H2AA | 0.9500 |
| C2B—C3B | 1.324 (7) | C33—H33 | 0.9500 |
| C41—C46 | 1.399 (6) | C33—C34 | 1.374 (8) |
| C41—B1 | 1.658 (7) | C34—H34 | 0.9500 |
| C31—C36 | 1.393 (7) | C24—H24 | 0.9500 |
| C31—C32 | 1.402 (7) | C24—C25 | 1.377 (8) |
| C31—B1 | 1.651 (7) | C25—H25 | 0.9500 |
| C2—H2A | 0.9900 | | |

Symmetry code(s): (i) -*x*, -*y*, -*z*+2.

## Selected geometric parameters (º)

| | | | |
|---|---|---|---|
| N1C—Ru01—N1C$^{i}$ | 180.0 | N2B—C3B—H3B | 126.4 |
| N1C$^{i}$—Ru01—N2A$^{i}$ | 90.51 (14) | C2B—C3B—N2B | 107.1 (4) |
| N1C—Ru01—N2A$^{i}$ | 89.49 (14) | C2B—C3B—H3B | 126.4 |
| N1C$^{i}$—Ru01—N2A | 89.49 (14) | C22—C23—H23 | 120.7 |
| N1C—Ru01—N2A | 90.51 (14) | C24—C23—H23 | 120.7 |
| N2A—Ru01—N2A$^{i}$ | 180.0 | C24—C23—C22 | 118.7 (5) |
| C1B—Ru01—N1C$^{i}$ | 95.88 (15) | C42—C43—H43 | 119.6 |
| C1B$^{i}$—Ru01—N1C$^{i}$ | 84.12 (15) | C44—C43—C42 | 120.8 (5) |
| C1B$^{i}$—Ru01—N1C | 95.88 (15) | C44—C43—H43 | 119.6 |
| C1B—Ru01—N1C | 84.12 (15) | C15—C16—H16 | 118.7 |
| C1B—Ru01—N2A$^{i}$ | 97.90 (15) | C11—C16—C15 | 122.6 (4) |
| C1B$^{i}$—Ru01—N2A | 97.90 (15) | C11—C16—H16 | 118.7 |

| | | | |
|---|---|---|---|
| C1B$^{i}$—Ru01—N2A$^{i}$ | 82.10 (15) | N1A—C3A—H3A | 126.5 |
| C1B—Ru01—N2A | 82.10 (15) | N1A—C3A—C2A | 107.0 (4) |
| C1B$^{i}$—Ru01—C1B | 180.0 (2) | C2A—C3A—H3A | 126.5 |
| N2C—N1C—Ru01 | 123.5 (3) | N1B—C1—N1A | 108.6 (4) |
| C3C—N1C—Ru01 | 132.8 (3) | N1B—C1—H1B | 110.0 |
| C3C—N1C—N2C | 103.6 (4) | N1B—C1—H1D | 110.0 |
| N1A—N2A—Ru01 | 124.0 (3) | N1A—C1—H1B | 110.0 |
| C1A—N2A—Ru01 | 132.0 (3) | N1A—C1—H1D | 110.0 |
| C1A—N2A—N1A | 103.5 (4) | H1B—C1—H1D | 108.3 |
| C1B—N1B—C2B | 112.6 (4) | C21—C22—C23 | 124.1 (4) |
| C1B—N1B—C1 | 119.1 (4) | C21—C22—H22 | 118.0 |
| C2B—N1B—C1 | 125.8 (4) | C23—C22—H22 | 118.0 |
| N2A—N1A—C1 | 120.7 (4) | C43—C44—H44 | 120.7 |
| C3A—N1A—N2A | 111.8 (4) | C43—C44—C45 | 118.5 (5) |
| C3A—N1A—C1 | 127.5 (4) | C45—C44—H44 | 120.7 |
| N1C—N2C—C2 | 121.0 (4) | C11—C12—H12 | 118.3 |
| C1C—N2C—N1C | 110.9 (4) | C13—C12—C11 | 123.4 (5) |
| C1C—N2C—C2 | 128.0 (4) | C13—C12—H12 | 118.3 |
| C1B—N2B—C2 | 119.6 (4) | C31—C36—H36 | 118.4 |
| C1B—N2B—C3B | 111.7 (4) | C31—C36—C35 | 123.3 (5) |
| C3B—N2B—C2 | 127.3 (4) | C35—C36—H36 | 118.4 |
| N1B—C1B—Ru01 | 128.0 (3) | C41—C46—H46 | 118.2 |
| N1B—C1B—N2B | 102.5 (4) | C45—C46—C41 | 123.6 (5) |
| N2B—C1B—Ru01 | 126.2 (3) | C45—C46—H46 | 118.2 |
| C22—C21—C26 | 115.2 (4) | C44—C45—C46 | 119.7 (5) |
| C22—C21—B1 | 120.9 (4) | C44—C45—H45 | 120.1 |
| C26—C21—B1 | 123.8 (4) | C46—C45—H45 | 120.1 |
| C16—C15—H15 | 119.9 | C36—C35—H35 | 120.4 |
| C14—C15—H15 | 119.9 | C34—C35—C36 | 119.3 (6) |
| C14—C15—C16 | 120.3 (5) | C34—C35—H35 | 120.4 |
| C3C—C2C—H2C | 127.5 | C15—C14—H14 | 120.5 |
| C1C—C2C—H2C | 127.5 | C13—C14—C15 | 119.0 (5) |
| C1C—C2C—C3C | 105.0 (4) | C13—C14—H14 | 120.5 |
| C41—C42—H42 | 118.5 | C31—C32—H32 | 118.4 |
| C43—C42—H42 | 118.5 | C33—C32—C31 | 123.1 (5) |
| C43—C42—C41 | 122.9 (5) | C33—C32—H32 | 118.4 |
| N1C—C3C—C2C | 112.5 (4) | C21—C26—H26 | 119.1 |
| N1C—C3C—H3C | 123.8 | C25—C26—C21 | 121.9 (5) |
| C2C—C3C—H3C | 123.8 | C25—C26—H26 | 119.1 |
| N2A—C1A—H1A | 123.7 | C12—C13—H13 | 119.9 |
| N2A—C1A—C2A | 112.6 (4) | C14—C13—C12 | 120.2 (5) |

| | | | |
|---|---|---|---|
| C2A—C1A—H1A | 123.7 | C14—C13—H13 | 119.9 |
| N1B—C2B—H2B | 127.0 | C1A—C2A—H2AA | 127.4 |
| C3B—C2B—N1B | 106.0 (4) | C3A—C2A—C1A | 105.2 (4) |
| C3B—C2B—H2B | 127.0 | C3A—C2A—H2AA | 127.4 |
| C42—C41—C46 | 114.5 (5) | C32—C33—H33 | 120.3 |
| C42—C41—B1 | 124.5 (4) | C34—C33—C32 | 119.5 (6) |
| C46—C41—B1 | 120.9 (4) | C34—C33—H33 | 120.3 |
| C36—C31—C32 | 114.7 (5) | C35—C34—H34 | 120.0 |
| C36—C31—B1 | 120.7 (4) | C33—C34—C35 | 120.1 (6) |
| C32—C31—B1 | 124.6 (5) | C33—C34—H34 | 120.0 |
| N2C—C2—H2A | 109.8 | C21—B1—C41 | 109.5 (4) |
| N2C—C2—H2D | 109.8 | C21—B1—C31 | 105.4 (4) |
| N2B—C2—N2C | 109.5 (4) | C31—B1—C41 | 111.5 (4) |
| N2B—C2—H2A | 109.8 | C11—B1—C21 | 110.3 (4) |
| N2B—C2—H2D | 109.8 | C11—B1—C41 | 107.0 (4) |
| H2A—C2—H2D | 108.2 | C11—B1—C31 | 113.1 (4) |
| C16—C11—C12 | 114.5 (4) | C23—C24—H24 | 120.0 |
| C16—C11—B1 | 123.5 (4) | C23—C24—C25 | 120.0 (5) |
| C12—C11—B1 | 121.8 (4) | C25—C24—H24 | 120.0 |
| N2C—C1C—C2C | 107.9 (4) | C26—C25—H25 | 119.9 |
| N2C—C1C—H1C | 126.0 | C24—C25—C26 | 120.2 (6) |
| C2C—C1C—H1C | 126.0 | C24—C25—H25 | 119.9 |

Symmetry code(s): (i) -*x*, -*y*, -*z*+2.

## Selected geometric parameters (º)

| | | | |
|---|---|---|---|
| Ru01—N1C—N2C—C2 | -6.2 (5) | C43—C42—C41—C46 | 1.1 (7) |
| Ru01—N1C—N2C—C1C | 176.4 (3) | C43—C42—C41—B1 | -176.0 (4) |
| Ru01—N1C—C3C—C2C | -175.6 (3) | C43—C44—C45—C46 | 0.6 (7) |
| Ru01—N2A—N1A—C3A | -172.0 (3) | C16—C15—C14—C13 | -0.6 (7) |
| Ru01—N2A—N1A—C1 | 6.6 (5) | C16—C11—C12—C13 | -1.7 (7) |
| Ru01—N2A—C1A—C2A | 171.4 (3) | C16—C11—B1—C21 | 6.1 (6) |
| N1C—N2C—C2—N2B | 56.8 (5) | C16—C11—B1—C41 | -113.0 (5) |

| | | | |
|---|---|---|---|
| N1C—N2C—C1C—C2C | -0.3 (5) | C16—C11—B1—C31 | 123.9 (5) |
| N2A—N1A—C3A—C2A | -0.5 (5) | C3A—N1A—C1—N1B | 120.9 (5) |
| N2A—N1A—C1—N1B | -57.5 (5) | C1—N1B—C1B—Ru01 | -3.6 (6) |
| N2A—C1A—C2A—C3A | -0.2 (6) | C1—N1B—C1B—N2B | -163.8 (4) |
| N1B—C2B—C3B—N2B | 0.9 (5) | C1—N1B—C2B—C3B | 161.7 (4) |
| N1A—N2A—C1A—C2A | -0.1 (5) | C1—N1A—C3A—C2A | -179.0 (4) |
| N1A—C3A—C2A—C1A | 0.4 (5) | C22—C21—C26—C25 | -0.1 (8) |
| N2C—N1C—C3C—C2C | 0.1 (5) | C22—C21—B1—C41 | -165.3 (4) |
| C1B—N1B—C2B—C3B | -0.1 (6) | C22—C21—B1—C31 | -45.2 (6) |
| C1B—N1B—C1—N1A | 55.9 (6) | C22—C21—B1—C11 | 77.2 (5) |
| C1B—N2B—C2—N2C | -57.6 (5) | C22—C23—C24—C25 | 0.5 (9) |
| C1B—N2B—C3B—C2B | -1.4 (6) | C12—C11—C16—C15 | 0.2 (7) |
| C21—C26—C25—C24 | 0.3 (10) | C12—C11—B1—C21 | -177.9 (4) |
| C15—C14—C13—C12 | -0.9 (8) | C12—C11—B1—C41 | 63.0 (6) |
| C42—C41—C46—C45 | -0.8 (7) | C12—C11—B1—C31 | -60.1 (6) |
| C42—C41—B1—C21 | 93.8 (5) | C36—C31—C32—C33 | -1.5 (7) |
| C42—C41—B1—C31 | -22.5 (6) | C36—C31—B1—C21 | -51.0 (6) |
| C42—C41—B1—C11 | -146.6 (4) | C36—C31—B1—C41 | 67.7 (5) |
| C42—C43—C44—C45 | -0.4 (7) | C36—C31—B1—C11 | -171.6 (4) |
| C3C—N1C—N2C—C2 | 177.5 (4) | C36—C35—C34—C33 | -0.1 (8) |
| C3C—N1C—N2C—C1C | 0.1 (5) | C46—C41—B1—C21 | -83.1 (5) |
| C3C—C2C—C1C—N2C | 0.3 (5) | C46—C41—B1—C31 | 160.6 (4) |
| C1A—N2A—N1A—C3A | 0.4 (5) | C46—C41—B1—C11 | 36.5 (6) |
| C1A—N2A—N1A—C1 | 179.0 (4) | C14—C15—C16—C11 | 1.0 (7) |
| C2B—N1B—C1B—Ru01 | 159.5 (3) | C32—C31—C36—C35 | 2.7 (7) |

| | | | |
|---|---|---|---|
| C2B—N1B—C1B—N2B | -0.7 (5) | C32—C31—B1—C21 | 126.3 (5) |
| C2B—N1B—C1—N1A | -104.9 (5) | C32—C31—B1—C41 | -115.0 (5) |
| C41—C42—C43—C44 | -0.5 (7) | C32—C31—B1—C11 | 5.6 (6) |
| C41—C46—C45—C44 | 0.0 (8) | C32—C33—C34—C35 | 1.2 (8) |
| C31—C36—C35—C34 | -2.0 (8) | C26—C21—C22—C23 | 0.1 (7) |
| C31—C32—C33—C34 | -0.4 (8) | C26—C21—B1—C41 | 15.7 (7) |
| C2—N2C—C1C—C2C | -177.5 (4) | C26—C21—B1—C31 | 135.7 (5) |
| C2—N2B—C1B—Ru01 | 7.9 (6) | C26—C21—B1—C11 | -101.9 (6) |
| C2—N2B—C1B—N1B | 168.6 (4) | B1—C21—C22—C23 | -179.0 (4) |
| C2—N2B—C3B—C2B | -167.6 (5) | B1—C21—C26—C25 | 179.0 (6) |
| C11—C12—C13—C14 | 2.1 (8) | B1—C41—C46—C45 | 176.3 (4) |
| C1C—N2C—C2—N2B | -126.2 (5) | B1—C31—C36—C35 | -179.8 (4) |
| C1C—C2C—C3C—N1C | -0.3 (6) | B1—C31—C32—C33 | -178.9 (4) |
| C3B—N2B—C1B—Ru01 | -159.4 (3) | B1—C11—C16—C15 | 176.5 (4) |
| C3B—N2B—C1B—N1B | 1.2 (5) | B1—C11—C12—C13 | -178.1 (5) |
| C3B—N2B—C2—N2C | 107.6 (5) | C24—C23—C22—C21 | -0.3 (8) |
| C23—C24—C25—C26 | -0.5 (10) | | |

### 7.1.8. Crystal data for complex 6

#### Selected geometric parameters (Å)

| | | | |
|---|---|---|---|
| P3—C16 | 1.824 (2) | C18—C40 | 1.392 (3) |
| P3—C18 | 1.825 (2) | C21—C52 | 1.387 (4) |
| P3—C29 | 1.8158 (18) | C23—C4aa | 1.390 (3) |
| P3—Ru2 | 2.3819 (6) | C24—C25 | 1.379 (3) |
| P5—C8 | 1.816 (2) | C24—C32 | 1.386 (3) |
| P5—C17 | 1.824 (2) | C25—C38 | 1.391 (3) |

| | | | |
|---|---|---|---|
| P5—Ru1 | 2.3690 (6) | C29—C32 | 1.397 (3) |
| P5—C6 | 1.8170 (19) | C30—C42 | 1.380 (3) |
| C7—C29 | 1.396 (3) | C40—C50 | 1.379 (3) |
| C7—C38 | 1.391 (3) | C42—C49 | 1.383 (4) |
| C8—C43 | 1.393 (3) | C43—C5 | 1.373 (3) |
| C8—C52 | 1.401 (3) | C49—C50 | 1.394 (4) |
| C9—C11 | 1.396 (3) | Ru2—Cl2$^{i}$ | 2.7642 (7) |
| C9—C19 | 1.387 (3) | Ru2—Cl2 | 2.5367 (7) |
| C10—C22 | 1.386 (4) | Ru2—Ru1 | 3.3796 (5) |
| C10—C4aa | 1.395 (4) | Ru2—Cl3 | 2.6765 (7) |
| C11—C14 | 1.387 (3) | Cl2—Ru1 | 2.7182 (7) |
| C12—C21 | 1.391 (4) | Ru1—Cl3 | 2.6550 (7) |
| C12—C5 | 1.382 (4) | Ru1—Cl3$^{i}$ | 2.5620 (6) |
| C14—C20 | 1.384 (3) | C2aa—C3aa | 1.396 (3) |
| C15—C17 | 1.399 (3) | C2aa—C13 | 1.377 (4) |
| C15—C22 | 1.391 (3) | C6—C3aa | 1.402 (3) |
| C16—C19 | 1.387 (3) | C6—C0aa | 1.385 (3) |
| C16—C20 | 1.396 (3) | C1aa—C0aa | 1.394 (3) |
| C17—C23 | 1.398 (3) | C1aa—C13 | 1.390 (4) |
| C18—C30 | 1.398 (3) | | |

Symmetry code(s): (i) -*x*+2, *y*, -*z*+1/2.

## Selected geometric parameters (º)

| | | | |
|---|---|---|---|
| C18—P3—C16 | 105.20 (9) | C42—C30—C18 | 120.8 (2) |
| C29—P3—C16 | 102.94 (9) | C29—C32—C24 | 120.2 (2) |
| C29—P3—C18 | 105.60 (9) | C25—C38—C7 | 119.8 (2) |
| Ru2—P3—C16 | 112.15 (7) | C50—C40—C18 | 121.1 (2) |
| Ru2—P3—C18 | 109.79 (7) | C49—C42—C30 | 120.2 (2) |
| Ru2—P3—C29 | 119.97 (6) | C5—C43—C8 | 120.4 (2) |
| C17—P5—C8 | 104.23 (9) | C50—C49—C42 | 119.7 (2) |
| Ru1—P5—C8 | 112.64 (6) | C49—C50—C40 | 119.9 (2) |
| Ru1—P5—C17 | 114.89 (7) | C21—C52—C8 | 120.0 (2) |
| C6—P5—C8 | 103.92 (9) | Cl2$^{i}$—Ru2—P3 | 108.911 (15) |
| C6—P5—C17 | 103.46 (9) | Cl2—Ru2—P3 | 137.247 (16) |
| C6—P5—Ru1 | 116.31 (7) | Ru1—Ru2—P3 | 150.735 (13) |
| C38—C7—C29 | 120.33 (19) | Ru1—Ru2—Cl2 | 52.374 (11) |
| C43—C8—P5 | 124.14 (16) | Ru1—Ru2—Cl2$^{i}$ | 96.988 (11) |
| C52—C8—P5 | 116.74 (16) | Cl3—Ru2—P3 | 116.611 (17) |
| C52—C8—C43 | 119.1 (2) | Cl3—Ru2—Cl2 | 101.589 (16) |
| C19—C9—C11 | 120.3 (2) | Cl3—Ru2—Cl2$^{i}$ | 86.218 (13) |

| | | | |
|---|---|---|---|
| C4aa—C10—C22 | 120.1 (2) | Cl3—Ru2—Ru1 | 50.382 (12) |
| C14—C11—C9 | 119.3 (2) | Ru1—Cl2—Ru2 | 79.969 (14) |
| C5—C12—C21 | 119.7 (2) | Ru1—Cl2—Ru2$^{i}$ | 88.262 (13) |
| C20—C14—C11 | 120.28 (19) | Ru2—Ru1—P5 | 122.809 (14) |
| C22—C15—C17 | 120.1 (2) | Cl2—Ru1—P5 | 112.062 (15) |
| C19—C16—P3 | 123.13 (14) | Cl2—Ru1—Ru2 | 47.657 (11) |
| C20—C16—P3 | 117.70 (16) | Cl3$^{i}$—Ru1—P5 | 139.652 (18) |
| C20—C16—C19 | 119.16 (19) | Cl3—Ru1—P5 | 119.728 (17) |
| C15—C17—P5 | 118.19 (16) | Cl3$^{i}$—Ru1—Ru2 | 97.101 (11) |
| C23—C17—P5 | 122.80 (15) | Cl3—Ru1—Ru2 | 50.944 (10) |
| C23—C17—C15 | 119.0 (2) | Cl3$^{i}$—Ru1—Cl2 | 89.490 (14) |
| C30—C18—P3 | 117.67 (16) | Cl3—Ru1—Cl2 | 97.518 (15) |
| C40—C18—P3 | 123.93 (16) | Ru1$^{i}$—Cl3—Ru2 | 93.537 (14) |
| C40—C18—C30 | 118.32 (19) | Ru1—Cl3—Ru2 | 78.674 (14) |
| C16—C19—C9 | 120.4 (2) | C13—C2aa—C3aa | 120.3 (2) |
| C16—C20—C14 | 120.5 (2) | C3aa—C6—P5 | 121.64 (16) |
| C52—C21—C12 | 120.1 (2) | C0aa—C6—P5 | 118.62 (15) |
| C15—C22—C10 | 120.4 (2) | C0aa—C6—C3aa | 119.62 (18) |
| C4aa—C23—C17 | 120.9 (2) | C13—C1aa—C0aa | 119.5 (2) |
| C32—C24—C25 | 120.4 (2) | C6—C3aa—C2aa | 119.5 (2) |
| C38—C25—C24 | 120.11 (19) | C1aa—C0aa—C6 | 120.5 (2) |
| C7—C29—P3 | 123.94 (14) | C43—C5—C12 | 120.7 (2) |
| C32—C29—P3 | 116.75 (14) | C1aa—C13—C2aa | 120.5 (2) |
| C32—C29—C7 | 119.13 (17) | C23—C4aa—C10 | 119.4 (2) |

Symmetry code(s): (i) -*x*+2, *y*, -*z*+1/2.

### 7.1.9. Crystal data for complex 8

#### Selected geometric parameters (Å)

| | | | |
|---|---|---|---|
| Ni1—Cl1 | 2.2001 (12) | C12B—H12B | 0.9500 |
| Ni1—N1A | 1.887 (3) | C12B—C13B | 1.398 (6) |
| Ni1—N1C | 1.907 (3) | C13B—H13B | 0.9500 |
| Ni1—C1B | 1.848 (4) | C13B—C14B | 1.376 (7) |
| N1A—N2A | 1.368 (4) | C14B—H14B | 0.9500 |
| N1A—C3A | 1.338 (5) | C14B—C15B | 1.379 (7) |
| N1B—C0AA | 1.454 (5) | C15B—H15B | 0.9500 |
| N1B—C1B | 1.337 (5) | C15B—C16B | 1.384 (6) |

| | | | |
|---|---|---|---|
| N1B—C3B | 1.377 (5) | C16B—H16B | 0.9500 |
| N1C—N2C | 1.362 (5) | C21B—C22B | 1.389 (6) |
| N1C—C3C | 1.342 (5) | C21B—C26B | 1.407 (6) |
| N2A—C0AA | 1.450 (5) | C21B—B1B | 1.656 (6) |
| N2A—C1A | 1.329 (5) | C22B—H22B | 0.9500 |
| N2B—C1B | 1.348 (5) | C22B—C23B | 1.394 (5) |
| N2B—C2 | 1.457 (5) | C23B—H23B | 0.9500 |
| N2B—C2B | 1.391 (5) | C23B—C24B | 1.384 (6) |
| N2C—C1C | 1.348 (5) | C24B—H24B | 0.9500 |
| N2C—C2 | 1.452 (5) | C24B—C25B | 1.383 (6) |
| C0AA—H0AA | 0.9900 | C25B—H25B | 0.9500 |
| C0AA—H0AB | 0.9900 | C25B—C26B | 1.401 (5) |
| C1A—H1A | 0.9500 | C26B—H26B | 0.9500 |
| C1A—C2A | 1.367 (6) | C31B—C32B | 1.409 (5) |
| C1C—H1C | 0.9500 | C31B—C36B | 1.406 (5) |
| C1C—C2C | 1.361 (6) | C31B—B1B | 1.629 (6) |
| C2—H2A | 0.9900 | C32B—H32B | 0.9500 |
| C2—H2B | 0.9900 | C32B—C33B | 1.383 (6) |
| C2A—H2AA | 0.9500 | C33B—H33B | 0.9500 |
| C2A—C3A | 1.391 (6) | C33B—C34B | 1.383 (6) |
| C2B—H2BA | 0.9500 | C34B—H34B | 0.9500 |
| C2B—C3B | 1.347 (6) | C34B—C35B | 1.391 (6) |
| C2C—H2C | 0.9500 | C35B—H35B | 0.9500 |
| C2C—C3C | 1.389 (6) | C35B—C36B | 1.395 (6) |
| C3A—H3A | 0.9500 | C36B—H36B | 0.9500 |
| C3B—H3B | 0.9500 | C41B—C42B | 1.411 (5) |
| C3C—H3C | 0.9500 | C41B—C46B | 1.410 (5) |
| O1AC—C2AC | 1.190 (7) | C41B—B1B | 1.639 (6) |
| C1AC—H1AA | 0.9800 | C42B—H42B | 0.9500 |
| C1AC—H1AB | 0.9800 | C42B—C43B | 1.391 (6) |
| C1AC—H1AC | 0.9800 | C43B—H43B | 0.9500 |
| C1AC—C2AC | 1.439 (8) | C43B—C44B | 1.376 (6) |
| C2AC—C3AC | 1.493 (11) | C44B—H44B | 0.9500 |
| C2AC—C1 | 1.644 (17) | C44B—C45B | 1.380 (6) |
| C2AC—O2 | 1.26 (2) | C45B—H45B | 0.9500 |
| C3AC—H3AA | 0.9800 | C45B—C46B | 1.386 (6) |
| C3AC—H3AB | 0.9800 | C46B—H46B | 0.9500 |
| C3AC—H3AC | 0.9800 | C1—H1B | 0.9800 |
| C11B—C12B | 1.398 (6) | C1—H1D | 0.9800 |
| C11B—C16B | 1.397 (6) | C1—H1E | 0.9800 |
| C11B—B1B | 1.651 (6) | | |

Selected geometric parameters (º)

| | | | |
|---|---|---|---|
| N1A—Ni1—Cl1 | 90.93 (11) | C16B—C11B—B1B | 120.0 (4) |
| N1A—Ni1—N1C | 177.07 (15) | C11B—C12B—H12B | 119.0 |
| N1C—Ni1—Cl1 | 91.48 (11) | C13B—C12B—C11B | 122.1 (5) |
| C1B—Ni1—Cl1 | 176.03 (13) | C13B—C12B—H12B | 119.0 |
| C1B—Ni1—N1A | 88.11 (16) | C12B—C13B—H13B | 119.8 |
| C1B—Ni1—N1C | 89.59 (16) | C14B—C13B—C12B | 120.4 (5) |
| N2A—N1A—Ni1 | 125.2 (3) | C14B—C13B—H13B | 119.8 |
| C3A—N1A—Ni1 | 129.3 (3) | C13B—C14B—H14B | 120.5 |
| C3A—N1A—N2A | 105.0 (3) | C13B—C14B—C15B | 118.9 (4) |
| C1B—N1B—C0AA | 120.9 (3) | C15B—C14B—H14B | 120.5 |
| C1B—N1B—C3B | 111.2 (3) | C14B—C15B—H15B | 119.9 |
| C3B—N1B—C0AA | 127.8 (4) | C14B—C15B—C16B | 120.2 (5) |
| N2C—N1C—Ni1 | 124.3 (3) | C16B—C15B—H15B | 119.9 |
| C3C—N1C—Ni1 | 129.4 (3) | C11B—C16B—H16B | 118.5 |
| C3C—N1C—N2C | 105.7 (3) | C15B—C16B—C11B | 123.0 (4) |
| N1A—N2A—C0AA | 120.3 (3) | C15B—C16B—H16B | 118.5 |
| C1A—N2A—N1A | 110.9 (4) | C22B—C21B—C26B | 114.9 (4) |
| C1A—N2A—C0AA | 128.6 (4) | C22B—C21B—B1B | 124.8 (4) |
| C1B—N2B—C2 | 120.4 (3) | C26B—C21B—B1B | 120.1 (4) |
| C1B—N2B—C2B | 111.1 (3) | C21B—C22B—H22B | 118.1 |
| C2B—N2B—C2 | 128.4 (4) | C21B—C22B—C23B | 123.8 (4) |
| N1C—N2C—C2 | 121.2 (3) | C23B—C22B—H22B | 118.1 |
| C1C—N2C—N1C | 110.6 (4) | C22B—C23B—H23B | 120.2 |
| C1C—N2C—C2 | 127.7 (4) | C24B—C23B—C22B | 119.5 (4) |
| N1B—C0AA—H0AA | 110.0 | C24B—C23B—H23B | 120.2 |
| N1B—C0AA—H0AB | 110.0 | C23B—C24B—H24B | 120.5 |
| N2A—C0AA—N1B | 108.5 (3) | C25B—C24B—C23B | 119.1 (4) |
| N2A—C0AA—H0AA | 110.0 | C25B—C24B—H24B | 120.5 |
| N2A—C0AA—H0AB | 110.0 | C24B—C25B—H25B | 119.9 |
| H0AA—C0AA—H0AB | 108.4 | C24B—C25B—C26B | 120.2 (4) |
| N2A—C1A—H1A | 125.9 | C26B—C25B—H25B | 119.9 |
| N2A—C1A—C2A | 108.3 (4) | C21B—C26B—H26B | 118.8 |
| C2A—C1A—H1A | 125.9 | C25B—C26B—C21B | 122.3 (4) |
| N1B—C1B—Ni1 | 127.4 (3) | C25B—C26B—H26B | 118.8 |
| N1B—C1B—N2B | 104.9 (3) | C32B—C31B—B1B | 122.4 (3) |
| N2B—C1B—Ni1 | 127.6 (3) | C36B—C31B—C32B | 115.1 (4) |
| N2C—C1C—H1C | 126.2 | C36B—C31B—B1B | 122.2 (4) |
| N2C—C1C—C2C | 107.5 (4) | C31B—C32B—H32B | 118.6 |

| | | | |
|---|---|---|---|
| C2C—C1C—H1C | 126.2 | C33B—C32B—C31B | 122.8 (4) |
| N2B—C2—H2A | 110.2 | C33B—C32B—H32B | 118.6 |
| N2B—C2—H2B | 110.2 | C32B—C33B—H33B | 119.7 |
| N2C—C2—N2B | 107.8 (3) | C34B—C33B—C32B | 120.6 (4) |
| N2C—C2—H2A | 110.2 | C34B—C33B—H33B | 119.7 |
| N2C—C2—H2B | 110.2 | C33B—C34B—H34B | 120.6 |
| H2A—C2—H2B | 108.5 | C33B—C34B—C35B | 118.7 (4) |
| C1A—C2A—H2AA | 127.5 | C35B—C34B—H34B | 120.6 |
| C1A—C2A—C3A | 105.0 (4) | C34B—C35B—H35B | 119.9 |
| C3A—C2A—H2AA | 127.5 | C34B—C35B—C36B | 120.2 (4) |
| N2B—C2B—H2BA | 127.2 | C36B—C35B—H35B | 119.9 |
| C3B—C2B—N2B | 105.6 (4) | C31B—C36B—H36B | 118.8 |
| C3B—C2B—H2BA | 127.2 | C35B—C36B—C31B | 122.5 (4) |
| C1C—C2C—H2C | 126.9 | C35B—C36B—H36B | 118.8 |
| C1C—C2C—C3C | 106.1 (4) | C42B—C41B—B1B | 124.3 (4) |
| C3C—C2C—H2C | 126.9 | C46B—C41B—C42B | 114.4 (4) |
| N1A—C3A—C2A | 110.8 (4) | C46B—C41B—B1B | 121.0 (4) |
| N1A—C3A—H3A | 124.6 | C41B—C42B—H42B | 118.6 |
| C2A—C3A—H3A | 124.6 | C43B—C42B—C41B | 122.8 (4) |
| N1B—C3B—H3B | 126.4 | C43B—C42B—H42B | 118.6 |
| C2B—C3B—N1B | 107.2 (4) | C42B—C43B—H43B | 119.7 |
| C2B—C3B—H3B | 126.4 | C44B—C43B—C42B | 120.6 (4) |
| N1C—C3C—C2C | 110.0 (4) | C44B—C43B—H43B | 119.7 |
| N1C—C3C—H3C | 125.0 | C43B—C44B—H44B | 120.7 |
| C2C—C3C—H3C | 125.0 | C43B—C44B—C45B | 118.6 (4) |
| H1AA—C1AC—H1AB | 109.5 | C45B—C44B—H44B | 120.7 |
| H1AA—C1AC—H1AC | 109.5 | C44B—C45B—H45B | 119.6 |
| H1AB—C1AC—H1AC | 109.5 | C44B—C45B—C46B | 120.8 (4) |
| C2AC—C1AC—H1AA | 109.5 | C46B—C45B—H45B | 119.6 |
| C2AC—C1AC—H1AB | 109.5 | C41B—C46B—H46B | 118.6 |
| C2AC—C1AC—H1AC | 109.5 | C45B—C46B—C41B | 122.8 (4) |
| O1AC—C2AC—C1AC | 124.2 (7) | C45B—C46B—H46B | 118.6 |
| O1AC—C2AC—C3AC | 118.3 (8) | C11B—B1B—C21B | 104.6 (3) |
| C1AC—C2AC—C3AC | 111.1 (6) | C31B—B1B—C11B | 111.9 (3) |
| C1AC—C2AC—C1 | 100.6 (9) | C31B—B1B—C21B | 111.4 (3) |

| | | | |
|---|---|---|---|
| O2—C2AC—C1AC | 147.3 (13) | C31B—B1B—C41B | 104.4 (3) |
| O2—C2AC—C1 | 109.4 (13) | C41B—B1B—C11B | 112.4 (3) |
| C2AC—C3AC—H3AA | 109.5 | C41B—B1B—C21B | 112.3 (3) |
| C2AC—C3AC—H3AB | 109.5 | C2AC—C1—H1B | 109.5 |
| C2AC—C3AC—H3AC | 109.5 | C2AC—C1—H1D | 109.5 |
| H3AA—C3AC—H3AB | 109.5 | C2AC—C1—H1E | 109.5 |
| H3AA—C3AC—H3AC | 109.5 | H1B—C1—H1D | 109.5 |
| H3AB—C3AC—H3AC | 109.5 | H1B—C1—H1E | 109.5 |
| C12B—C11B—B1B | 124.3 (4) | H1D—C1—H1E | 109.5 |
| C16B—C11B—C12B | 115.4 (4) | | |

Selected geometric parameters (º)

| | | | |
|---|---|---|---|
| Ni1—N1A—N2A—C0AA | -11.2 (5) | C12B—C11B—B1B—C41B | 23.8 (5) |
| Ni1—N1A—N2A—C1A | 172.8 (3) | C12B—C13B—C14B—C15B | -0.9 (7) |
| Ni1—N1A—C3A—C2A | -172.5 (3) | C13B—C14B—C15B—C16B | 1.0 (7) |
| Ni1—N1C—N2C—C1C | 172.9 (3) | C14B—C15B—C16B—C11B | -0.2 (7) |
| Ni1—N1C—N2C—C2 | -14.4 (5) | C16B—C11B—C12B—C13B | 0.8 (6) |
| Ni1—N1C—C3C—C2C | -172.3 (3) | C16B—C11B—B1B—C21B | 75.5 (4) |
| Cl1—Ni1—N1A—N2A | 149.3 (3) | C16B—C11B—B1B—C31B | -45.2 (5) |
| Cl1—Ni1—N1A—C3A | -40.5 (4) | C16B—C11B—B1B—C41B | -162.4 (4) |
| N1A—Ni1—C1B—N1B | 33.0 (3) | C21B—C22B—C23B—C24B | 2.4 (6) |
| N1A—Ni1—C1B—N2B | -151.7 (3) | C22B—C21B—C26B—C25B | 1.7 (6) |
| N1A—N2A—C0AA—N1B | 52.4 (4) | C22B—C21B—B1B—C11B | 94.5 (4) |
| N1A—N2A—C1A—C2A | -0.2 (5) | C22B—C21B—B1B—C31B | -144.5 (4) |
| N1C—Ni1—C1B—N1B | -148.8 (3) | C22B—C21B—B1B—C41B | -27.7 (5) |
| N1C—Ni1—C1B— | 26.5 (3) | C22B—C23B— | 0.2 (6) |

| | | | |
|---|---|---|---|
| N2B | | C24B—C25B | |
| N1C—N2C—C1C—C2C | -1.0 (5) | C23B—C24B—C25B—C26B | -1.6 (6) |
| N1C—N2C—C2—N2B | 54.7 (5) | C24B—C25B—C26B—C21B | 0.6 (6) |
| N2A—N1A—C3A—C2A | -0.8 (5) | C26B—C21B—C22B—C23B | -3.2 (6) |
| N2A—C1A—C2A—C3A | -0.3 (5) | C26B—C21B—B1B—C11B | -80.9 (4) |
| N2B—C2B—C3B—N1B | -0.1 (4) | C26B—C21B—B1B—C31B | 40.1 (5) |
| N2C—N1C—C3C—C2C | -1.6 (5) | C26B—C21B—B1B—C41B | 156.8 (4) |
| N2C—C1C—C2C—C3C | 0.0 (6) | C31B—C32B—C33B—C34B | -1.6 (6) |
| C0AA—N1B—C1B—Ni1 | -0.2 (5) | C32B—C31B—C36B—C35B | -1.1 (6) |
| C0AA—N1B—C1B—N2B | -176.3 (3) | C32B—C31B—B1B—C11B | 149.3 (4) |
| C0AA—N1B—C3B—C2B | 175.7 (4) | C32B—C31B—B1B—C21B | 32.7 (5) |
| C0AA—N2A—C1A—C2A | -175.8 (4) | C32B—C31B—B1B—C41B | -88.8 (4) |
| C1A—N2A—C0AA—N1B | -132.4 (4) | C32B—C33B—C34B—C35B | 0.9 (6) |
| C1A—C2A—C3A—N1A | 0.7 (5) | C33B—C34B—C35B—C36B | -0.3 (6) |
| C1B—Ni1—N1A—N2A | -26.8 (3) | C34B—C35B—C36B—C31B | 0.5 (6) |
| C1B—Ni1—N1A—C3A | 143.4 (4) | C36B—C31B—C32B—C33B | 1.7 (6) |
| C1B—N1B—C0AA—N2A | -47.1 (5) | C36B—C31B—B1B—C11B | -36.6 (5) |
| C1B—N1B—C3B—C2B | 0.6 (4) | C36B—C31B—B1B—C21B | -153.2 (4) |
| C1B—N2B—C2—N2C | -51.2 (5) | C36B—C31B—B1B—C41B | 85.3 (4) |
| C1B—N2B—C2B—C3B | -0.4 (4) | C41B—C42B—C43B—C44B | -0.1 (7) |
| C1C—N2C—C2—N2B | -134.1 (4) | C42B—C41B—C46B—C45B | 2.2 (6) |
| C1C—C2C—C3C—N1C | 1.1 (6) | C42B—C41B—B1B—C11B | -145.6 (4) |
| C2—N2B—C1B—Ni1 | 7.5 (5) | C42B—C41B—B1B—C21B | -27.9 (6) |
| C2—N2B—C1B—N1B | -176.4 (3) | C42B—C41B—B1B—C31B | 92.9 (4) |
| C2—N2B—C2B— | 176.5 (4) | C42B—C43B— | 2.1 (7) |

| | | | |
|---|---|---|---|
| C3B | | C44B—C45B | |
| C2—N2C—C1C—C2C | -173.0 (4) | C43B—C44B—C45B—C46B | -1.8 (7) |
| C2B—N2B—C1B—Ni1 | -175.3 (3) | C44B—C45B—C46B—C41B | -0.4 (7) |
| C2B—N2B—C1B—N1B | 0.8 (4) | C46B—C41B—C42B—C43B | -2.0 (6) |
| C2B—N2B—C2—N2C | 132.1 (4) | C46B—C41B—B1B—C11B | 41.0 (5) |
| C3A—N1A—N2A—C0AA | 176.7 (3) | C46B—C41B—B1B—C21B | 158.6 (4) |
| C3A—N1A—N2A—C1A | 0.7 (5) | C46B—C41B—B1B—C31B | -80.5 (5) |
| C3B—N1B—C0AA—N2A | 138.2 (4) | B1B—C11B—C12B—C13B | 174.9 (4) |
| C3B—N1B—C1B—Ni1 | 175.3 (3) | B1B—C11B—C16B—C15B | -175.1 (4) |
| C3B—N1B—C1B—N2B | -0.9 (4) | B1B—C21B—C22B—C23B | -178.9 (4) |
| C3C—N1C—N2C—C1C | 1.6 (5) | B1B—C21B—C26B—C25B | 177.6 (4) |
| C3C—N1C—N2C—C2 | 174.3 (4) | B1B—C31B—C32B—C33B | 176.1 (4) |
| C11B—C12B—C13B—C14B | 0.0 (6) | B1B—C31B—C36B—C35B | -175.6 (4) |
| C12B—C11B—C16B—C15B | -0.7 (6) | B1B—C41B—C42B—C43B | -175.8 (4) |
| C12B—C11B—B1B—C21B | -98.4 (4) | B1B—C41B—C46B—C45B | 176.3 (4) |
| C12B—C11B—B1B—C31B | 140.9 (4) | | |

### 7.1.10. Crystal data for complex 9

#### Selected geometric parameters (Å)

| | | | |
|---|---|---|---|
| Ni01—Cl01 | 2.2199 (9) | N04—C01 | 1.347 (2) |
| Ni01—N06 | 1.9016 (19) | N04—C03 | 1.391 (3) |
| Ni01—N01 | 1.8996 (18) | N04—C04 | 1.455 (3) |
| Ni01—C01 | 1.847 (2) | C02—H02 | 0.9500 |
| P01—F02 | 1.6073 (16) | C02—C03 | 1.355 (3) |
| P01—F01 | 1.5993 (15) | C11—H11 | 0.9500 |
| P01—F03 | 1.5974 (17) | C11—C10 | 1.395 (3) |
| P01—F05 | 1.6032 (17) | C08—H08 | 0.9500 |
| P01—F06 | 1.6023 (15) | C08—C07 | 1.400 (3) |

| | | | |
|---|---|---|---|
| P01—F04 | 1.6017 (17) | C05—H05A | 0.9900 |
| N06—N05 | 1.364 (2) | C05—H05B | 0.9900 |
| N06—C08 | 1.333 (3) | C03—H03 | 0.9500 |
| N03—C02 | 1.390 (2) | C09—H09 | 0.9500 |
| N03—C01 | 1.344 (3) | C09—C10 | 1.380 (3) |
| N03—C05 | 1.453 (3) | C04—H04A | 0.9900 |
| N01—N02 | 1.365 (2) | C04—H04B | 0.9900 |
| N01—C11 | 1.344 (3) | C10—H10 | 0.9500 |
| N02—C05 | 1.451 (2) | C07—H07 | 0.9500 |
| N02—C09 | 1.347 (3) | C07—C06 | 1.370 (4) |
| N05—C04 | 1.446 (3) | C06—H06 | 0.9500 |
| N05—C06 | 1.351 (3) | | |

Selected geometric parameters (º)

| | | | |
|---|---|---|---|
| N06—Ni01—Cl01 | 90.68 (6) | N03—C02—H02 | 126.9 |
| N01—Ni01—Cl01 | 92.31 (6) | C03—C02—N03 | 106.29 (18) |
| N01—Ni01—N06 | 175.68 (7) | C03—C02—H02 | 126.9 |
| C01—Ni01—Cl01 | 178.86 (6) | N01—C11—H11 | 124.5 |
| C01—Ni01—N06 | 88.40 (9) | N01—C11—C10 | 110.98 (18) |
| C01—Ni01—N01 | 88.64 (9) | C10—C11—H11 | 124.5 |
| F01—P01—F02 | 90.07 (9) | N03—C01—Ni01 | 128.01 (15) |
| F01—P01—F05 | 89.28 (10) | N03—C01—N04 | 104.72 (16) |
| F01—P01—F06 | 179.19 (10) | N04—C01—Ni01 | 127.27 (15) |
| F01—P01—F04 | 90.11 (9) | N06—C08—H08 | 124.8 |
| F03—P01—F02 | 89.48 (9) | N06—C08—C07 | 110.4 (2) |
| F03—P01—F01 | 90.45 (10) | C07—C08—H08 | 124.8 |
| F03—P01—F05 | 179.13 (10) | N03—C05—H05A | 110.1 |
| F03—P01—F06 | 90.34 (10) | N03—C05—H05B | 110.1 |
| F03—P01—F04 | 89.93 (10) | N02—C05—N03 | 108.05 (15) |
| F05—P01—F02 | 89.69 (9) | N02—C05—H05A | 110.1 |
| F06—P01—F02 | 89.78 (8) | N02—C05—H05B | 110.1 |
| F06—P01—F05 | 89.92 (10) | H05A—C05—H05B | 108.4 |
| F04—P01—F02 | 179.38 (9) | N04—C03—H03 | 126.9 |
| F04—P01—F05 | 90.91 (10) | C02—C03—N04 | 106.10 (18) |
| F04—P01—F06 | 90.05 (9) | C02—C03—H03 | 126.9 |
| N05—N06—Ni01 | 124.19 (15) | N02—C09—H09 | 126.3 |
| C08—N06—Ni01 | 129.52 (16) | N02—C09—C10 | 107.33 (18) |
| C08—N06—N05 | 105.91 (18) | C10—C09—H09 | 126.3 |
| C02—N03—C05 | 128.28 (17) | N05—C04—N04 | 108.45 (17) |
| C01—N03—C02 | 111.48 (17) | N05—C04—H04A | 110.0 |
| C01—N03—C05 | 120.13 (16) | N05—C04—H04B | 110.0 |

| | | | |
|---|---|---|---|
| N02—N01—Ni01 | 124.85 (13) | N04—C04—H04A | 110.0 |
| C11—N01—Ni01 | 129.10 (14) | N04—C04—H04B | 110.0 |
| C11—N01—N02 | 105.00 (17) | H04A—C04—H04B | 108.4 |
| N01—N02—C05 | 120.12 (17) | C11—C10—H10 | 127.4 |
| C09—N02—N01 | 111.42 (16) | C09—C10—C11 | 105.26 (18) |
| C09—N02—C05 | 128.07 (17) | C09—C10—H10 | 127.4 |
| N06—N05—C04 | 121.40 (18) | C08—C07—H07 | 127.2 |
| C06—N05—N06 | 110.6 (2) | C06—C07—C08 | 105.5 (2) |
| C06—N05—C04 | 127.8 (2) | C06—C07—H07 | 127.2 |
| C01—N04—C03 | 111.41 (17) | N05—C06—C07 | 107.6 (2) |
| C01—N04—C04 | 120.60 (17) | N05—C06—H06 | 126.2 |
| C03—N04—C04 | 127.99 (17) | C07—C06—H06 | 126.2 |

### 7.1.11. Crystal data for complex 10

#### Selected geometric parameters (Å)

| | | | |
|---|---|---|---|
| Ni1D—C2D | 1.885 (11) | C41A—B1A | 1.681 (12) |
| Ni1D—C2D$^{i}$ | 1.885 (10) | C46A—H46A | 0.9500 |
| Ni1D—C8D | 1.928 (9) | C46A—C45A | 1.3900 |
| Ni1D—C8D$^{i}$ | 1.928 (9) | C45A—H45A | 0.9500 |
| N1D—C2D | 1.344 (12) | C45A—C44A | 1.3900 |
| N1D—C3D | 1.410 (15) | C44A—H44A | 0.9500 |
| N1D—C1AA | 1.373 (15) | C44A—C43A | 1.3900 |
| C2D—C1D | 1.292 (13) | C43A—H43A | 0.9500 |
| N3D—C5D | 1.500 (15) | C43A—C42A | 1.3900 |
| N3D—C6D | 1.395 (15) | C42A—H42A | 0.9500 |
| N3D—C8D | 1.358 (11) | C11B—C12B | 1.3900 |
| C4D—C7D | 1.372 (15) | C11B—C15B | 1.3900 |
| C4D—C8D | 1.333 (13) | C11B—B1B | 1.697 (12) |
| C4D—C9D | 1.462 (16) | C12B—H12B | 0.9500 |
| C1D—C0AA | 1.394 (14) | C12B—C13B | 1.3900 |
| C1D—C6 | 1.446 (15) | C13B—H13B | 0.9500 |
| C0AA—H0AA | 0.9500 | C13B—C14B | 1.3900 |
| C0AA—C3D | 1.336 (17) | C14B—H14B | 0.9500 |
| C3D—H3D | 0.9500 | C14B—C16B | 1.3900 |
| C1AA—H1AA | 0.9900 | C16B—H16B | 0.9500 |
| C1AA—H1AB | 0.9900 | C16B—C15B | 1.3900 |
| C1AA—C5D | 1.360 (18) | C15B—H15B | 0.9500 |
| C5D—H5DA | 0.9900 | C21B—C26B | 1.3900 |
| C5D—H5DB | 0.9900 | C21B—C22B | 1.3900 |
| C6D—H6D | 0.9500 | C21B—B1B | 1.671 (13) |

| | | | |
|---|---|---|---|
| C6D—C7D | 1.343 (15) | C26B—H26B | 0.9500 |
| C7D—H7D | 0.9500 | C26B—C25B | 1.3900 |
| C9D—H9DA | 0.9900 | C25B—H25B | 0.9500 |
| C9D—H9DB | 0.9900 | C25B—C1 | 1.3900 |
| C9D—C8 | 1.485 (18) | C1—H1 | 0.9500 |
| Ni1C—C2C$^{ii}$ | 1.884 (11) | C1—C24B | 1.3900 |
| Ni1C—C2C | 1.884 (11) | C24B—H24B | 0.9500 |
| Ni1C—N8C$^{ii}$ | 1.922 (12) | C24B—C22B | 1.3900 |
| Ni1C—N8C | 1.922 (12) | C22B—H22B | 0.9500 |
| N0AA—C2C | 1.315 (13) | C31B—C36B | 1.3900 |
| N0AA—C3C | 1.374 (15) | C31B—C32B | 1.3900 |
| N0AA—C4C | 1.509 (16) | C31B—B1B | 1.646 (13) |
| C2C—N1C | 1.483 (19) | C36B—H36B | 0.9500 |
| N3C—C5C | 1.47 (2) | C36B—C35B | 1.3900 |
| N3C—N8C | 1.392 (15) | C35B—H35B | 0.9500 |
| N3C—C10 | 1.454 (19) | C35B—C34B | 1.3900 |
| N1C—C8AA | 1.32 (2) | C34B—H34B | 0.9500 |
| C8AA—H8AA | 0.9500 | C34B—C33B | 1.3900 |
| C8AA—C3C | 1.30 (2) | C33B—H33B | 0.9500 |
| C3C—H3C | 0.9500 | C33B—C32B | 1.3900 |
| C4C—H4CA | 0.9900 | C32B—H32B | 0.9500 |
| C4C—H4CB | 0.9900 | C41B—C42B | 1.3900 |
| C4C—C5C | 1.373 (18) | C41B—C46B | 1.3900 |
| C5C—H5CA | 0.9900 | C41B—B1B | 1.704 (13) |
| C5C—H5CB | 0.9900 | C42B—H42B | 0.9500 |
| C7C—N8C | 1.42 (2) | C42B—C43B | 1.3900 |
| C7C—C12 | 1.40 (2) | C43B—C44B | 1.3900 |
| C11A—C12A | 1.3900 | C44B—H44B | 0.9500 |
| C11A—C16A | 1.3900 | C44B—C45B | 1.3900 |
| C11A—B1A | 1.693 (13) | C45B—H45B | 0.9500 |
| C12A—H12A | 0.9500 | C45B—C46B | 1.3900 |
| C12A—C13A | 1.3900 | C46B—H46B | 0.9500 |
| C13A—H13A | 0.9500 | C6—H6A | 0.9900 |
| C13A—C14A | 1.3900 | C6—H6B | 0.9900 |
| C14A—H14A | 0.9500 | C6—C4AA | 1.497 (17) |
| C14A—C15A | 1.3900 | C8—H8A | 0.9900 |
| C15A—H15A | 0.9500 | C8—H8B | 0.9900 |
| C15A—C16A | 1.3900 | C8—N9AA | 1.51 (3) |
| C16A—H16A | 0.9500 | N4—N2 | 1.4200 |
| C21A—C22A | 1.3900 | N4—C7 | 1.4200 |
| C21A—C26A | 1.3900 | N4—C4AA | 1.58 (3) |

| | | | |
|---|---|---|---|
| C21A—B1A | 1.686 (12) | N2—C3AA | 1.4200 |
| C22A—C23A | 1.3900 | C3AA—H3AA | 0.9500 |
| C23A—C24A | 1.3900 | C3AA—C2AA | 1.4200 |
| C24A—C25A | 1.3900 | C2AA—H2AA | 0.9500 |
| C25A—C26A | 1.3900 | C2AA—C7 | 1.4200 |
| C31A—C32A | 1.3900 | C7—H7 | 0.9500 |
| C31A—C36A | 1.3900 | C4AA—H4AA | 0.9900 |
| C31A—B1A | 1.675 (12) | C4AA—H4AB | 0.9900 |
| C32A—H32A | 0.9500 | C10—H10 | 0.9500 |
| C32A—C33A | 1.3900 | C10—C12 | 1.56 (3) |
| C33A—H33A | 0.9500 | N9AA—N4CA | 1.4200 |
| C33A—C34A | 1.3900 | N9AA—C1BA | 1.4200 |
| C34A—H34A | 0.9500 | N4CA—C3CA | 1.4200 |
| C34A—C35A | 1.3900 | C3CA—H3CA | 0.9500 |
| C35A—H35A | 0.9500 | C3CA—C2CA | 1.4200 |
| C35A—C36A | 1.3900 | C2CA—H2CA | 0.9500 |
| C36A—H36A | 0.9500 | C2CA—C1BA | 1.4200 |
| C41A—C46A | 1.3900 | C1BA—H1BA | 0.9500 |
| C41A—C42A | 1.3900 | C12—H12 | 0.9500 |

Symmetry code(s): (i) -*x*-2, -*y*, -*z*-2; (ii) -*x*-2, -*y*+1, -*z*-3.

## Selected geometric parameters (º)

| | | | |
|---|---|---|---|
| C2D—Ni1D—C2D$^{i}$ | 180.0 | C46A—C45A—C44A | 120.0 |
| C2D$^{i}$—Ni1D—C8D$^{i}$ | 92.5 (4) | C44A—C45A—H45A | 120.0 |
| C2D—Ni1D—C8D$^{i}$ | 87.5 (4) | C45A—C44A—H44A | 120.0 |
| C2D$^{i}$—Ni1D—C8D | 87.5 (4) | C43A—C44A—C45A | 120.0 |
| C2D—Ni1D—C8D | 92.5 (4) | C43A—C44A—H44A | 120.0 |
| C8D—Ni1D—C8D$^{i}$ | 180.0 | C44A—C43A—H43A | 120.0 |
| C2D—N1D—C3D | 109.5 (11) | C44A—C43A—C42A | 120.0 |
| C2D—N1D—C1AA | 124.3 (11) | C42A—C43A—H43A | 120.0 |
| C1AA—N1D—C3D | 126.1 (11) | C41A—C42A—H42A | 120.0 |
| N1D—C2D—Ni1D | 122.7 (9) | C43A—C42A—C41A | 120.0 |
| C1D—C2D—Ni1D | 131.4 (8) | C43A—C42A—H42A | 120.0 |
| C1D—C2D—N1D | 105.8 (10) | C11A—B1A—C41A | 109.6 (7) |
| C6D—N3D—C5D | 122.3 (11) | C21A—B1A—C11A | 110.0 (7) |
| C8D—N3D—C5D | 128.8 (11) | C21A—B1A—C41A | 108.1 (7) |
| C8D—N3D—C6D | 108.9 (10) | C31A—B1A—C11A | 112.5 (7) |
| C7D—C4D—C9D | 123.9 (14) | C31A—B1A—C21A | 107.6 (7) |
| C8D—C4D—C7D | 110.7 (10) | C31A—B1A—C41A | 109.0 (7) |

| | | | |
|---|---|---|---|
| C8D—C4D—C9D | 124.7 (13) | C12B—C11B—C15B | 120.0 |
| C2D—C1D—C0AA | 112.9 (10) | C12B—C11B—B1B | 119.8 (6) |
| C2D—C1D—C6 | 119.2 (12) | C15B—C11B—B1B | 120.1 (6) |
| C0AA—C1D—C6 | 127.7 (13) | C11B—C12B—H12B | 120.0 |
| C1D—C0AA—H0AA | 127.4 | C11B—C12B—C13B | 120.0 |
| C3D—C0AA—C1D | 105.2 (12) | C13B—C12B—H12B | 120.0 |
| C3D—C0AA—H0AA | 127.4 | C12B—C13B—H13B | 120.0 |
| N1D—C3D—H3D | 126.7 | C14B—C13B—C12B | 120.0 |
| C0AA—C3D—N1D | 106.5 (11) | C14B—C13B—H13B | 120.0 |
| C0AA—C3D—H3D | 126.7 | C13B—C14B—H14B | 120.0 |
| N1D—C1AA—H1AA | 107.1 | C13B—C14B—C16B | 120.0 |
| N1D—C1AA—H1AB | 107.1 | C16B—C14B—H14B | 120.0 |
| H1AA—C1AA—H1AB | 106.8 | C14B—C16B—H16B | 120.0 |
| C5D—C1AA—N1D | 120.8 (15) | C15B—C16B—C14B | 120.0 |
| C5D—C1AA—H1AA | 107.1 | C15B—C16B—H16B | 120.0 |
| C5D—C1AA—H1AB | 107.1 | C11B—C15B—H15B | 120.0 |
| N3D—C5D—H5DA | 106.7 | C16B—C15B—C11B | 120.0 |
| N3D—C5D—H5DB | 106.7 | C16B—C15B—H15B | 120.0 |
| C1AA—C5D—N3D | 122.4 (12) | C26B—C21B—C22B | 120.0 |
| C1AA—C5D—H5DA | 106.7 | C26B—C21B—B1B | 117.5 (6) |
| C1AA—C5D—H5DB | 106.7 | C22B—C21B—B1B | 122.4 (7) |
| H5DA—C5D—H5DB | 106.6 | C21B—C26B—H26B | 120.0 |
| N3D—C6D—H6D | 126.5 | C25B—C26B—C21B | 120.0 |
| C7D—C6D—N3D | 106.9 (11) | C25B—C26B—H26B | 120.0 |
| C7D—C6D—H6D | 126.5 | C26B—C25B—H25B | 120.0 |
| C4D—C7D—H7D | 126.4 | C26B—C25B—C1 | 120.0 |
| C6D—C7D—C4D | 107.1 (12) | C1—C25B—H25B | 120.0 |
| C6D—C7D—H7D | 126.4 | C25B—C1—H1 | 120.0 |
| N3D—C8D—Ni1D | 125.8 (7) | C24B—C1—C25B | 120.0 |
| C4D—C8D—Ni1D | 127.9 (8) | C24B—C1—H1 | 120.0 |
| C4D—C8D—N3D | 106.3 (9) | C1—C24B—H24B | 120.0 |
| C4D—C9D—H9DA | 108.0 | C1—C24B—C22B | 120.0 |
| C4D—C9D—H9DB | 108.0 | C22B—C24B—H24B | 120.0 |
| C4D—C9D—C8 | 117 (2) | C21B—C22B—H22B | 120.0 |
| H9DA—C9D—H9DB | 107.2 | C24B—C22B—C21B | 120.0 |
| C8—C9D—H9DA | 108.0 | C24B—C22B—H22B | 120.0 |
| C8—C9D—H9DB | 108.0 | C36B—C31B—C32B | 120.0 |
| C2C$^{ii}$—Ni1C—C2C | 180.0 | C36B—C31B—B1B | 122.7 (5) |
| C2C$^{ii}$—Ni1C—N8C | 91.6 (5) | C32B—C31B—B1B | 117.3 (5) |
| C2C$^{ii}$—Ni1C—N8C$^{ii}$ | 88.4 (5) | C31B—C36B—H36B | 120.0 |

| | | | |
|---|---|---|---|
| C2C—Ni1C—N8C$^{ii}$ | 91.6 (5) | C31B—C36B—C35B | 120.0 |
| C2C—Ni1C—N8C | 88.4 (5) | C35B—C36B—H36B | 120.0 |
| N8C$^{ii}$—Ni1C—N8C | 180.0 (8) | C36B—C35B—H35B | 120.0 |
| C2C—N0AA—C3C | 112.5 (12) | C34B—C35B—C36B | 120.0 |
| C2C—N0AA—C4C | 125.1 (11) | C34B—C35B—H35B | 120.0 |
| C3C—N0AA—C4C | 121.5 (11) | C35B—C34B—H34B | 120.0 |
| N0AA—C2C—Ni1C | 133.1 (9) | C35B—C34B—C33B | 120.0 |
| N0AA—C2C—N1C | 100.4 (11) | C33B—C34B—H34B | 120.0 |
| N1C—C2C—Ni1C | 123.2 (10) | C34B—C33B—H33B | 120.0 |
| N8C—N3C—C5C | 122.1 (13) | C32B—C33B—C34B | 120.0 |
| N8C—N3C—C10 | 102.6 (14) | C32B—C33B—H33B | 120.0 |
| C10—N3C—C5C | 135.1 (13) | C31B—C32B—H32B | 120.0 |
| C8AA—N1C—C2C | 109.0 (15) | C33B—C32B—C31B | 120.0 |
| N1C—C8AA—H8AA | 125.5 | C33B—C32B—H32B | 120.0 |
| C3C—C8AA—N1C | 109.0 (17) | C42B—C41B—C46B | 120.0 |
| C3C—C8AA—H8AA | 125.5 | C42B—C41B—B1B | 120.5 (5) |
| N0AA—C3C—H3C | 126.1 | C46B—C41B—B1B | 119.4 (5) |
| C8AA—C3C—N0AA | 107.8 (14) | C41B—C42B—H42B | 120.0 |
| C8AA—C3C—H3C | 126.1 | C41B—C42B—C43B | 120.0 |
| N0AA—C4C—H4CA | 108.1 | C43B—C42B—H42B | 120.0 |
| N0AA—C4C—H4CB | 108.1 | C44B—C43B—C42B | 120.0 |
| H4CA—C4C—H4CB | 107.3 | C43B—C44B—H44B | 120.0 |
| C5C—C4C—N0AA | 116.7 (12) | C43B—C44B—C45B | 120.0 |
| C5C—C4C—H4CA | 108.1 | C45B—C44B—H44B | 120.0 |
| C5C—C4C—H4CB | 108.1 | C44B—C45B—H45B | 120.0 |
| N3C—C5C—H5CA | 108.1 | C44B—C45B—C46B | 120.0 |
| N3C—C5C—H5CB | 108.1 | C46B—C45B—H45B | 120.0 |
| C4C—C5C—N3C | 116.9 (16) | C41B—C46B—H46B | 120.0 |
| C4C—C5C—H5CA | 108.1 | C45B—C46B—C41B | 120.0 |
| C4C—C5C—H5CB | 108.1 | C45B—C46B—H46B | 120.0 |
| H5CA—C5C—H5CB | 107.3 | C11B—B1B—C41B | 108.0 (7) |
| N8C—C7C—C12 | 112.0 (18) | C21B—B1B—C11B | 110.8 (7) |
| N3C—N8C—Ni1C | 118.4 (11) | C21B—B1B—C41B | 108.8 (7) |
| N3C—N8C—C7C | 112.8 (13) | C31B—B1B—C11B | 106.9 (7) |
| C7C—N8C—Ni1C | 128.6 (11) | C31B—B1B—C21B | 110.2 (8) |
| C12A—C11A—C16A | 120.0 | C31B—B1B—C41B | 112.2 (7) |
| C12A—C11A—B1A | 120.6 (5) | C1D—C6—H6A | 108.9 |
| C16A—C11A—B1A | 119.3 (5) | C1D—C6—H6B | 108.9 |
| C11A—C12A—H12A | 120.0 | C1D—C6—C4AA | 113.2 (18) |
| C11A—C12A—C13A | 120.0 | H6A—C6—H6B | 107.7 |
| C13A—C12A—H12A | 120.0 | C4AA—C6—H6A | 108.9 |

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|---|---|---|---|
| C12A—C13A—H13A | 120.0 | C4AA—C6—H6B | 108.9 |
| C12A—C13A—C14A | 120.0 | C9D—C8—H8A | 110.1 |
| C14A—C13A—H13A | 120.0 | C9D—C8—H8B | 110.1 |
| C13A—C14A—H14A | 120.0 | H8A—C8—H8B | 108.4 |
| C15A—C14A—C13A | 120.0 | N9AA—C8—C9D | 108 (2) |
| C15A—C14A—H14A | 120.0 | N9AA—C8—H8A | 110.1 |
| C14A—C15A—H15A | 120.0 | N9AA—C8—H8B | 110.1 |
| C14A—C15A—C16A | 120.0 | N2—N4—C7 | 108.0 |
| C16A—C15A—H15A | 120.0 | N2—N4—C4AA | 121.1 (17) |
| C11A—C16A—H16A | 120.0 | C7—N4—C4AA | 130.6 (17) |
| C15A—C16A—C11A | 120.0 | C3AA—N2—N4 | 108.0 |
| C15A—C16A—H16A | 120.0 | N2—C3AA—H3AA | 126.0 |
| C22A—C21A—C26A | 120.0 | N2—C3AA—C2AA | 108.0 |
| C22A—C21A—B1A | 121.6 (6) | C2AA—C3AA—H3AA | 126.0 |
| C26A—C21A—B1A | 118.4 (6) | C3AA—C2AA—H2AA | 126.0 |
| C23A—C22A—C21A | 120.0 | C7—C2AA—C3AA | 108.0 |
| C22A—C23A—C24A | 120.0 | C7—C2AA—H2AA | 126.0 |
| C23A—C24A—C25A | 120.0 | N4—C7—H7 | 126.0 |
| C24A—C25A—C26A | 120.0 | C2AA—C7—N4 | 108.0 |
| C25A—C26A—C21A | 120.0 | C2AA—C7—H7 | 126.0 |
| C32A—C31A—C36A | 120.0 | C6—C4AA—N4 | 108.4 (18) |
| C32A—C31A—B1A | 122.5 (6) | C6—C4AA—H4AA | 110.0 |
| C36A—C31A—B1A | 117.3 (6) | C6—C4AA—H4AB | 110.0 |
| C31A—C32A—H32A | 120.0 | N4—C4AA—H4AA | 110.0 |
| C31A—C32A—C33A | 120.0 | N4—C4AA—H4AB | 110.0 |
| C33A—C32A—H32A | 120.0 | H4AA—C4AA—H4AB | 108.4 |
| C32A—C33A—H33A | 120.0 | N3C—C10—H10 | 124.1 |
| C34A—C33A—C32A | 120.0 | C12—C10—N3C | 111.7 (14) |
| C34A—C33A—H33A | 120.0 | C12—C10—H10 | 124.1 |
| C33A—C34A—H34A | 120.0 | N4CA—N9AA—C8 | 133 (2) |
| C33A—C34A—C35A | 120.0 | C1BA—N9AA—C8 | 119 (2) |
| C35A—C34A—H34A | 120.0 | C1BA—N9AA—N4CA | 108.0 |
| C34A—C35A—H35A | 120.0 | N9AA—N4CA—C3CA | 108.0 |
| C34A—C35A—C36A | 120.0 | N4CA—C3CA—H3CA | 126.0 |
| C36A—C35A—H35A | 120.0 | C2CA—C3CA—N4CA | 108.0 |
| C31A—C36A—H36A | 120.0 | C2CA—C3CA— | 126.0 |

| | | | |
|---|---|---|---|
| | | H3CA | |
| C35A—C36A—C31A | 120.0 | C3CA—C2CA—H2CA | 126.0 |
| C35A—C36A—H36A | 120.0 | C3CA—C2CA—C1BA | 108.0 |
| C46A—C41A—C42A | 120.0 | C1BA—C2CA—H2CA | 126.0 |
| C46A—C41A—B1A | 122.1 (6) | N9AA—C1BA—C2CA | 108.0 |
| C42A—C41A—B1A | 117.8 (5) | N9AA—C1BA—H1BA | 126.0 |
| C41A—C46A—H46A | 120.0 | C2CA—C1BA—H1BA | 126.0 |
| C41A—C46A—C45A | 120.0 | C7C—C12—H12 | 130.2 |
| C45A—C46A—H46A | 120.0 | C10—C12—C7C | 100 (2) |
| C46A—C45A—H45A | 120.0 | C10—C12—H12 | 130.2 |

Symmetry code(s): (i) -*x*-2, -*y*, -*z*-2; (ii) -*x*-2, -*y*+1, -*z*-3.

## Selected geometric parameters, torsion angles (º)

| | | | |
|---|---|---|---|
| Ni1D—C2D—C1D—C0AA | -177.2 (9) | C36A—C31A—B1A—C21A | -76.4 (7) |
| Ni1D—C2D—C1D—C6 | -1.0 (18) | C36A—C31A—B1A—C41A | 40.6 (9) |
| N1D—C2D—C1D—C0AA | -0.3 (14) | C41A—C46A—C45A—C44A | 0.0 |
| N1D—C2D—C1D—C6 | 175.9 (12) | C46A—C41A—C42A—C43A | 0.0 |
| N1D—C1AA—C5D—N3D | 44 (3) | C46A—C41A—B1A—C11A | 95.0 (8) |
| C2D—N1D—C3D—C0AA | 2.7 (17) | C46A—C41A—B1A—C21A | -24.8 (9) |
| C2D—N1D—C1AA—C5D | -73 (2) | C46A—C41A—B1A—C31A | -141.5 (6) |
| C2D—C1D—C0AA—C3D | 2.0 (16) | C46A—C45A—C44A—C43A | 0.0 |
| C2D—C1D—C6—C4AA | 119.6 (18) | C45A—C44A—C43A—C42A | 0.0 |
| N3D—C6D—C7D—C4D | 1.3 (16) | C44A—C43A—C42A—C41A | 0.0 |
| C4D—C9D—C8—N9AA | 76 (3) | C42A—C41A—C46A—C45A | 0.0 |
| C1D—C0AA—C3D—N1D | -2.7 (16) | C42A—C41A—B1A—C11A | -82.1 (7) |
| C1D—C6—C4AA— | -70 (2) | C42A—C41A— | 158.1 (5) |

| | | | |
|---|---|---|---|
| N4 | | B1A—C21A | |
| C0AA—C1D—C6—C4AA | -65 (2) | C42A—C41A—B1A—C31A | 41.4 (9) |
| C3D—N1D—C2D—Ni1D | 175.8 (9) | B1A—C11A—C12A—C13A | 175.5 (6) |
| C3D—N1D—C2D—C1D | -1.4 (14) | B1A—C11A—C16A—C15A | -175.5 (6) |
| C3D—N1D—C1AA—C5D | 111.8 (18) | B1A—C21A—C22A—C23A | 179.2 (7) |
| C1AA—N1D—C2D—Ni1D | 0.1 (18) | B1A—C21A—C26A—C25A | -179.2 (6) |
| C1AA—N1D—C2D—C1D | -177.1 (13) | B1A—C31A—C32A—C33A | -175.0 (7) |
| C1AA—N1D—C3D—C0AA | 178.2 (14) | B1A—C31A—C36A—C35A | 175.2 (7) |
| C5D—N3D—C6D—C7D | 178.0 (14) | B1A—C41A—C46A—C45A | -177.1 (7) |
| C5D—N3D—C8D—Ni1D | 2 (2) | B1A—C41A—C42A—C43A | 177.2 (7) |
| C5D—N3D—C8D—C4D | -178.0 (14) | C11B—C12B—C13B—C14B | 0.0 |
| C6D—N3D—C5D—C1AA | -163.9 (17) | C12B—C11B—C15B—C16B | 0.0 |
| C6D—N3D—C8D—Ni1D | -178.2 (9) | C12B—C11B—B1B—C21B | -151.2 (6) |
| C6D—N3D—C8D—C4D | 2.1 (14) | C12B—C11B—B1B—C31B | 88.7 (8) |
| C7D—C4D—C8D—Ni1D | 179.0 (9) | C12B—C11B—B1B—C41B | -32.2 (9) |
| C7D—C4D—C8D—N3D | -1.3 (14) | C12B—C13B—C14B—C16B | 0.0 |
| C7D—C4D—C9D—C8 | 60 (3) | C13B—C14B—C16B—C15B | 0.0 |
| C8D—Ni1D—C2D—N1D | 60.7 (10) | C14B—C16B—C15B—C11B | 0.0 |
| C8D$^{i}$—Ni1D—C2D—N1D | -119.3 (10) | C15B—C11B—C12B—C13B | 0.0 |
| C8D—Ni1D—C2D—C1D | -122.8 (11) | C15B—C11B—B1B—C21B | 32.6 (10) |
| C8D$^{i}$—Ni1D—C2D—C1D | 57.2 (11) | C15B—C11B—B1B—C31B | -87.5 (8) |
| C8D—N3D—C5D—C1AA | 16 (3) | C15B—C11B—B1B—C41B | 151.6 (5) |
| C8D—N3D—C6D—C7D | -2.1 (16) | C21B—C26B—C25B—C1 | 0.0 |
| C8D—C4D—C7D—C6D | 0.0 (16) | C26B—C21B—C22B—C24B | 0.0 |
| C8D—C4D—C9D— | -110 (2) | C26B—C21B— | -90.6 (8) |

| | | | |
|---|---|---|---|
| C8 | | B1B—C11B | |
| C9D—C4D—C7D—C6D | -171.6 (16) | C26B—C21B—B1B—C31B | 27.5 (9) |
| C9D—C4D—C8D—Ni1D | -9 (2) | C26B—C21B—B1B—C41B | 150.8 (6) |
| C9D—C4D—C8D—N3D | 170.2 (15) | C26B—C25B—C1—C24B | 0.0 |
| C9D—C8—N9AA—N4CA | -122 (3) | C25B—C1—C24B—C22B | 0.0 |
| C9D—C8—N9AA—C1BA | 66 (3) | C1—C24B—C22B—C21B | 0.0 |
| Ni1C—C2C—N1C—C8AA | -172.3 (15) | C22B—C21B—C26B—C25B | 0.0 |
| N0AA—C2C—N1C—C8AA | -10 (2) | C22B—C21B—B1B—C11B | 86.1 (9) |
| N0AA—C4C—C5C—N3C | 49 (2) | C22B—C21B—B1B—C31B | -155.8 (6) |
| C2C—N0AA—C3C—C8AA | -9 (2) | C22B—C21B—B1B—C41B | -32.5 (9) |
| C2C—N0AA—C4C—C5C | 27 (2) | C31B—C36B—C35B—C34B | 0.0 |
| C2C—N1C—C8AA—C3C | 6 (3) | C36B—C31B—C32B—C33B | 0.0 |
| N3C—C10—C12—C7C | -11 (2) | C36B—C31B—B1B—C11B | -5.1 (9) |
| N1C—C8AA—C3C—N0AA | 1 (2) | C36B—C31B—B1B—C21B | -125.6 (6) |
| C3C—N0AA—C2C—Ni1C | 170.4 (14) | C36B—C31B—B1B—C41B | 113.1 (6) |
| C3C—N0AA—C2C—N1C | 11.3 (17) | C36B—C35B—C34B—C33B | 0.0 |
| C3C—N0AA—C4C—C5C | -165.1 (15) | C35B—C34B—C33B—C32B | 0.0 |
| C4C—N0AA—C2C—Ni1C | -21 (2) | C34B—C33B—C32B—C31B | 0.0 |
| C4C—N0AA—C2C—N1C | -179.8 (12) | C32B—C31B—C36B—C35B | 0.0 |
| C4C—N0AA—C3C—C8AA | -178.3 (16) | C32B—C31B—B1B—C11B | 173.6 (5) |
| C5C—N3C—N8C—Ni1C | -8.1 (17) | C32B—C31B—B1B—C21B | 53.2 (8) |
| C5C—N3C—N8C—C7C | 177.6 (16) | C32B—C31B—B1B—C41B | -68.2 (8) |
| C5C—N3C—C10—C12 | -169.6 (18) | C41B—C42B—C43B—C44B | 0.0 |
| N8C$^{ii}$—Ni1C—C2C—N0AA | 136.3 (17) | C42B—C41B—C46B—C45B | 0.0 |
| N8C—Ni1C—C2C— | -43.7 (17) | C42B—C41B— | 130.4 (6) |

| | | | |
|---|---|---|---|
| N0AA | | B1B—C11B | |
| N8C$^{ii}$—Ni1C—C2C—N1C | -68.5 (15) | C42B—C41B—B1B—C21B | -109.3 (7) |
| N8C—Ni1C—C2C—N1C | 111.5 (15) | C42B—C41B—B1B—C31B | 12.9 (10) |
| N8C—N3C—C5C—C4C | -77.4 (19) | C42B—C43B—C44B—C45B | 0.0 |
| N8C—N3C—C10—C12 | 5.9 (18) | C43B—C44B—C45B—C46B | 0.0 |
| N8C—C7C—C12—C10 | 11 (3) | C44B—C45B—C46B—C41B | 0.0 |
| C11A—C12A—C13A—C14A | 0.0 | C46B—C41B—C42B—C43B | 0.0 |
| C12A—C11A—C16A—C15A | 0.0 | C46B—C41B—B1B—C11B | -52.6 (9) |
| C12A—C11A—B1A—C21A | 125.6 (6) | C46B—C41B—B1B—C21B | 67.7 (8) |
| C12A—C11A—B1A—C31A | -114.6 (6) | C46B—C41B—B1B—C31B | -170.1 (6) |
| C12A—C11A—B1A—C41A | 6.9 (9) | B1B—C11B—C12B—C13B | -176.2 (8) |
| C12A—C13A—C14A—C15A | 0.0 | B1B—C11B—C15B—C16B | 176.2 (7) |
| C13A—C14A—C15A—C16A | 0.0 | B1B—C21B—C26B—C25B | 176.8 (7) |
| C14A—C15A—C16A—C11A | 0.0 | B1B—C21B—C22B—C24B | -176.6 (7) |
| C16A—C11A—C12A—C13A | 0.0 | B1B—C31B—C36B—C35B | 178.7 (7) |
| C16A—C11A—B1A—C21A | -58.9 (8) | B1B—C31B—C32B—C33B | -178.8 (6) |
| C16A—C11A—B1A—C31A | 60.9 (8) | B1B—C41B—C42B—C43B | 176.9 (7) |
| C16A—C11A—B1A—C41A | -177.6 (5) | B1B—C41B—C46B—C45B | -177.0 (7) |
| C21A—C22A—C23A—C24A | 0.0 | C6—C1D—C0AA—C3D | -173.8 (15) |
| C22A—C21A—C26A—C25A | 0.0 | C8—N9AA—N4CA—C3CA | -173 (3) |
| C22A—C21A—B1A—C11A | -6.1 (9) | C8—N9AA—C1BA—C2CA | 174 (2) |
| C22A—C21A—B1A—C31A | -128.8 (6) | N4—N2—C3AA—C2AA | 0.0 |
| C22A—C21A—B1A—C41A | 113.5 (7) | N2—N4—C7—C2AA | 0.0 |
| C22A—C23A—C24A—C25A | 0.0 | N2—N4—C4AA—C6 | -73 (2) |
| C23A—C24A— | 0.0 | N2—C3AA—C2AA— | 0.0 |

| | | | |
|---|---|---|---|
| C25A—C26A | | C7 | |
| C24A—C25A—C26A—C21A | 0.0 | C3AA—C2AA—C7—N4 | 0.0 |
| C26A—C21A—C22A—C23A | 0.0 | C7—N4—N2—C3AA | 0.0 |
| C26A—C21A—B1A—C11A | 173.1 (5) | C7—N4—C4AA—C6 | 101 (2) |
| C26A—C21A—B1A—C31A | 50.4 (8) | C4AA—N4—N2—C3AA | 174.9 (18) |
| C26A—C21A—B1A—C41A | -67.3 (8) | C4AA—N4—C7—C2AA | -174 (2) |
| C31A—C32A—C33A—C34A | 0.0 | C10—N3C—C5C—C4C | 97.4 (19) |
| C32A—C31A—C36A—C35A | 0.0 | C10—N3C—N8C—Ni1C | 175.7 (9) |
| C32A—C31A—B1A—C11A | -22.5 (9) | C10—N3C—N8C—C7C | 1.3 (18) |
| C32A—C31A—B1A—C21A | 98.7 (7) | N9AA—N4CA—C3CA—C2CA | 0.0 |
| C32A—C31A—B1A—C41A | -144.3 (6) | N4CA—N9AA—C1BA—C2CA | 0.0 |
| C32A—C33A—C34A—C35A | 0.0 | N4CA—C3CA—C2CA—C1BA | 0.0 |
| C33A—C34A—C35A—C36A | 0.0 | C3CA—C2CA—C1BA—N9AA | 0.0 |
| C34A—C35A—C36A—C31A | 0.0 | C1BA—N9AA—N4CA—C3CA | 0.0 |
| C36A—C31A—C32A—C33A | 0.0 | C12—C7C—N8C—Ni1C | 177.5 (15) |
| C36A—C31A—B1A—C11A | 162.4 (5) | C12—C7C—N8C—N3C | -9 (3) |

Symmetry code(s): (i) -*x*-2, -*y*, -*z*-2; (ii) -*x*-2, -*y*+1, -*z*-3.

## 7.1.12. Crystal data for complex 11

### Table 2. Selected geometric parameters (Å, º)

| | | | |
|---|---|---|---|
| Au1—Cl2 | 2.2854 (11) | C11—C12 | 1.331 (6) |
| Au1—C3 | 1.973 (4) | C11—H111 | 0.922 |
| C3—N4 | 1.359 (5) | C12—N13 | 1.389 (6) |
| C3—N13 | 1.349 (5) | C12—H121 | 0.934 |
| N4—C5 | 1.463 (6) | N13—C14 | 1.458 (5) |
| N4—C11 | 1.390 (6) | C14—N15 | 1.428 (6) |
| C5—N6 | 1.445 (5) | C14—H142 | 0.977 |

| | | | |
|---|---|---|---|
| C5—H52 | 0.976 | C14—H141 | 0.983 |
| C5—H51 | 0.988 | N15—N16 | 1.358 (5) |
| N6—N7 | 1.355 (5) | N15—C19 | 1.349 (5) |
| N6—C10 | 1.360 (5) | N16—C17 | 1.332 (6) |
| N7—C8 | 1.331 (6) | C17—C18 | 1.398 (8) |
| C8—C9 | 1.390 (7) | C17—H171 | 0.927 |
| C8—H81 | 0.935 | C18—C19 | 1.354 (7) |
| C9—C10 | 1.348 (6) | C18—H181 | 0.947 |
| C9—H91 | 0.922 | C19—H191 | 0.942 |
| C10—H101 | 0.944 | | |

| | | | |
|---|---|---|---|
| Cl2—Au1—C3 | 177.16 (11) | N6—C10—C9 | 106.6 (4) |
| Au1—C3—N4 | 126.9 (3) | N4—C11—C12 | 106.8 (4) |
| Au1—C3—N13 | 128.4 (3) | C11—C12—N13 | 107.1 (4) |
| N4—C3—N13 | 104.5 (4) | C12—N13—C3 | 110.9 (3) |
| C3—N4—C5 | 124.7 (4) | C12—N13—C14 | 123.9 (4) |
| C3—N4—C11 | 110.7 (3) | C3—N13—C14 | 125.2 (4) |
| C5—N4—C11 | 124.6 (4) | N13—C14—N15 | 111.7 (3) |
| N4—C5—N6 | 112.4 (3) | C14—N15—N16 | 119.2 (3) |
| C5—N6—N7 | 120.0 (4) | C14—N15—C19 | 128.7 (4) |
| C5—N6—C10 | 127.9 (4) | N16—N15—C19 | 111.9 (3) |
| N7—N6—C10 | 112.1 (4) | N15—N16—C17 | 103.6 (4) |
| N6—N7—C8 | 103.8 (4) | N16—C17—C18 | 112.4 (4) |
| N7—C8—C9 | 111.8 (4) | C17—C18—C19 | 104.3 (4) |
| C8—C9—C10 | 105.7 (4) | C18—C19—N15 | 107.8 (4) |

### Selected hydrogen-bond parameters

| *D*—H···*A* | *D*—H (Å) | H···*A* (Å) | *D*···*A* (Å) | *D*—H···*A* (°) |
|---|---|---|---|---|
| C5—H52···N16$^{i}$ | 0.976 | 2.433 | 3.297 (7) | 147.31 (14) |

Symmetry code(s): (i) $x$+1/2, -$y$+1/2, $z$+1/2.

## 7.1.13. Crystal data for complex 12

### Selected geometric parameters (Å, º)

| | | | |
|---|---|---|---|
| Au1—Cl2 | 2.2807 (7) | N12—C13 | 1.331 (4) |
| Au1—Cl3 | 2.3116 (7) | C13—C14 | 1.389 (5) |
| Au1—Cl4 | 2.2780 (7) | C13—H131 | 0.897 |
| Au1—C5 | 2.007 (2) | C14—C15 | 1.361 (4) |

| | | | |
|---|---|---|---|
| C5—N6 | 1.346 (3) | C14—H141 | 0.944 |
| C5—N9 | 1.342 (3) | C15—H151 | 0.972 |
| N6—C7 | 1.388 (3) | C16—N17 | 1.432 (3) |
| N6—C16 | 1.468 (3) | C16—H162 | 1.024 |
| C7—C8 | 1.342 (3) | C16—H161 | 0.984 |
| C7—H71 | 0.914 | N17—N18 | 1.354 (3) |
| C8—N9 | 1.387 (3) | N17—C21 | 1.356 (3) |
| C8—H81 | 0.981 | N18—C19 | 1.325 (3) |
| N9—C10 | 1.470 (3) | C19—C20 | 1.390 (4) |
| C10—N11 | 1.435 (3) | C19—H191 | 0.997 |
| C10—H101 | 0.947 | C20—C21 | 1.364 (4) |
| C10—H102 | 0.900 | C20—H201 | 0.969 |
| N11—N12 | 1.346 (3) | C21—H211 | 0.906 |
| N11—C15 | 1.357 (3) | | |

| | | | |
|---|---|---|---|
| Cl2—Au1—Cl3 | 91.47 (3) | N9—C10—N11 | 111.30 (18) |
| Cl2—Au1—Cl4 | 177.44 (2) | C10—N11—N12 | 119.9 (2) |
| Cl3—Au1—Cl4 | 90.13 (3) | C10—N11—C15 | 127.8 (2) |
| Cl2—Au1—C5 | 89.37 (7) | N12—N11—C15 | 112.4 (2) |
| Cl3—Au1—C5 | 179.11 (6) | N11—N12—C13 | 103.8 (2) |
| Cl4—Au1—C5 | 89.02 (6) | N12—C13—C14 | 112.3 (3) |
| Au1—C5—N6 | 127.06 (16) | C13—C14—C15 | 104.9 (3) |
| Au1—C5—N9 | 127.00 (17) | C14—C15—N11 | 106.6 (3) |
| N6—C5—N9 | 105.91 (19) | N6—C16—N17 | 111.26 (18) |
| C5—N6—C7 | 110.20 (19) | C16—N17—N18 | 119.37 (19) |
| C5—N6—C16 | 125.97 (19) | C16—N17—C21 | 127.7 (2) |
| C7—N6—C16 | 123.8 (2) | N18—N17—C21 | 112.7 (2) |
| N6—C7—C8 | 106.7 (2) | N17—N18—C19 | 103.6 (2) |
| C7—C8—N9 | 106.9 (2) | N18—C19—C20 | 112.4 (2) |
| C8—N9—C5 | 110.23 (19) | C19—C20—C21 | 105.2 (2) |
| C8—N9—C10 | 123.84 (19) | C20—C21—N17 | 106.1 (2) |
| C5—N9—C10 | 125.9 (2) | | |

## Selected hydrogen-bond parameters

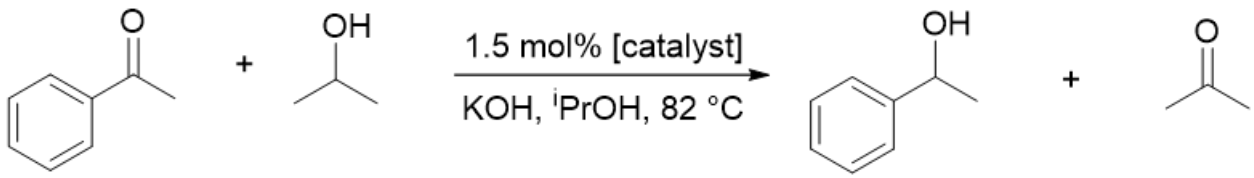
| *D*—H···*A* | *D*—H (Å) | H···*A* (Å) | *D*···*A* (Å) | *D*—H···*A* (°) |
|---|---|---|---|---|
| C8—H81···N18$^{i}$ | 0.981 | 2.581 | 3.495 (4) | 155.06 (7) |
| C16—H162···N12$^{ii}$ | 1.024 | 2.545 | 3.504 (4) | 155.78 (7) |

Symmetry code(s): (i) *x*-1, *y*, *z*; (ii) -*x*+1, -*y*+1, -*z*+2.

## 7.2. Catalysis data

### 7.2.1. Catalysis data for chapter 2

#### 7.2.1.1. Catalysed transfer hydrogenation of acetophenone using Ru(II) complexes 3-6.



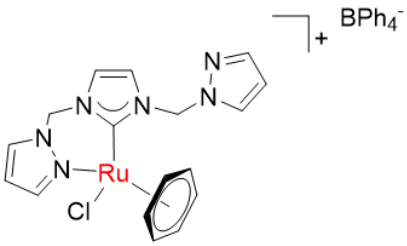




**Table 7.1** Catalysed transfer hydrogenation of acetophenone using **3**.

| Time (h) | % conversion |
|---|---|
| 0.5 | 80 |
| 4 | 84 |

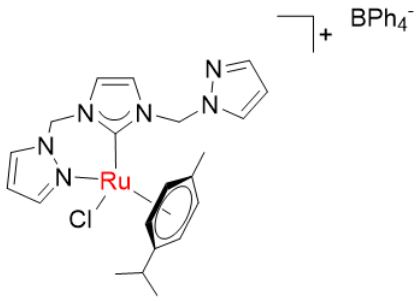



**Table 7.2** Catalysed transfer hydrogenation of acetophenone using **4**

| Time (h) | % conversion |
|---|---|
| 0.5 | 39 |
| 1 | 55 |
| 1.5 | 67 |
| 2 | 82 |
| 2.5 | 88 |
| 3 | 92 |
| 3.5 | 94 |
| 4 | 100 |

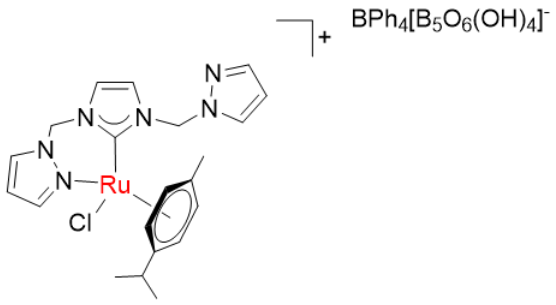



**Table 7.3** Catalysed transfer hydrogenation of acetophenone using **4a**

| Time (h) | % conversion |
|---|---|
| 0.5 | 91 |
| 1 | 96 |
| 1.5 | 96 |
| 2 | 96 |
| 2.5 | 97 |
| 4 | 100 |

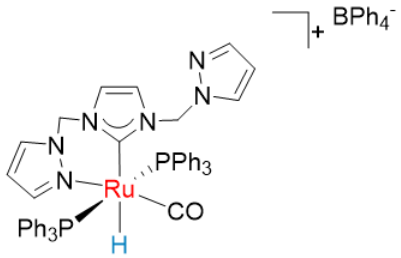



**Table 7.4** Catalysed transfer hydrogenation of acetophenone using **5**

| Time (h) | % conversion |
|---|---|
| 3.5 | 24 |
| 4 | 35 |
| 27 | 100 |

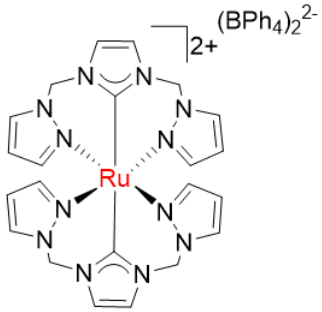
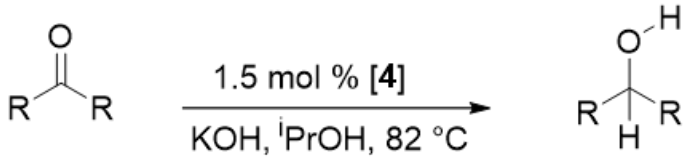



**Table 7.5** Catalysed transfer hydrogenation of acetophenone using **7**

| Time (h) | % conversion |
|---|---|
| 0.5 | 6 |
| 4 | 14 |
| 22.5 | 25 |

### 7.2.1.2. Catalysed transfer hydrogenation of a range of ketone substrates using complex 4.




Substrate = Benzophenone

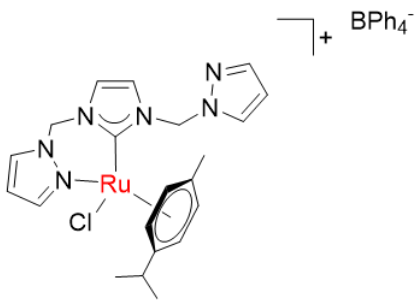



**Table 7.6** Catalysed transfer hydrogenation of benzophenone using **4**

| Time (h) | % conversion |
|---|---|
| 0.16 | 49 |
| 0.33 | 59 |
| 0.5 | 69 |
| 1 | 80 |
| 1.5 | 90 |
| 2 | 97 |
| 2.5 | 99 |
| 3 | 100 |

Substrate = 4- nitro-acetophenone

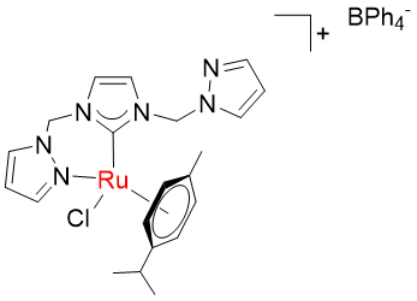



**Table 7.7** Catalysed transfer hydrogenation of 4-nitro-acetophenone using **4**

| Time (h) | % conversion |
|---|---|
| 0.5 | 0 |
| 4 | 0 |

Substrate = Cyclohexanone

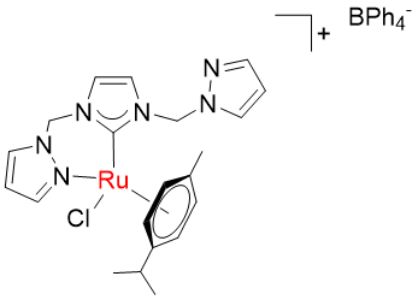



**Table 7.8** Catalysed transfer hydrogenation of cyclohexanone using **4**

| Time (h) | % conversion |
|---|---|
| 0.16 | 51 |
| 0.33 | 63 |
| 0.5 | 72 |
| 1 | 86 |
| 1.5 | 96 |
| 2 | 100 |

Substrate = 2-hexanone

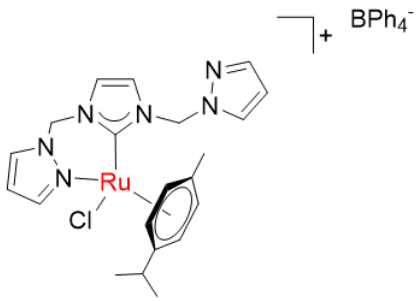
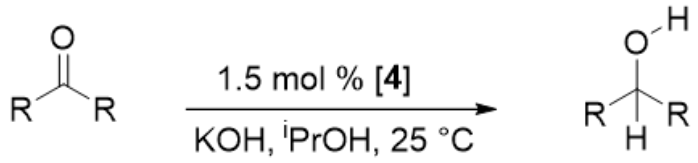



**Table 7.9** Catalysed transfer hydrogenation of 2-hexanone using **4**

| Time (h) | % conversion |
|---|---|
| 0.16 | 22 |
| 0.33 | 34 |
| 0.5 | 44 |
| 1 | 66 |
| 1.5 | 76 |
| 2 | 78 |
| 2.5 | 86 |
| 3 | 92 |
| 3.5 | 100 |

### 7.2.1.3. Catalysed transfer hydrogenation of a range of ketone substrates using complex 4 at room temperature conditions.




Substrate = Benzophenone

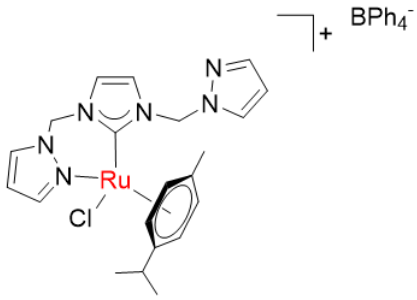
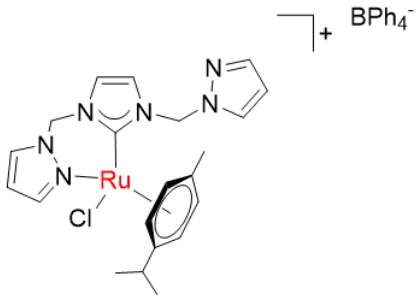



**Table 7.10** Catalysed transfer hydrogenation of benzophenone at r.t. using **4**

| Time (h) | % conversion |
|---|---|
| 0.5 | 0 |
| 4 | 0 |




Substrate = 4- nitro-acetophenone

**Table 7.11** Catalysed transfer hydrogenation of 4-nitro-acetophenone at r.t. using **4**

| Time (h) | % conversion |
|---|---|
| 0.5 | 0 |
| 4 | 0 |

Substrate = Cyclohexanone

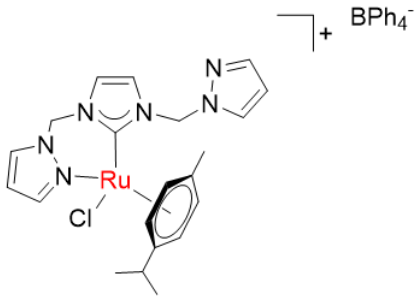



**Table 7.12** Catalysed transfer hydrogenation of cyclohexanone at r.t. using **4**

| Time (h) | % conversion |
|---|---|
| 0.5 | 0 |
| 4 | 0 |

Substrate = 2-hexanone

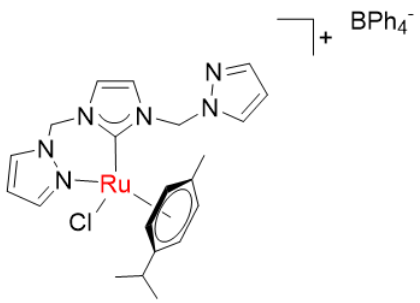
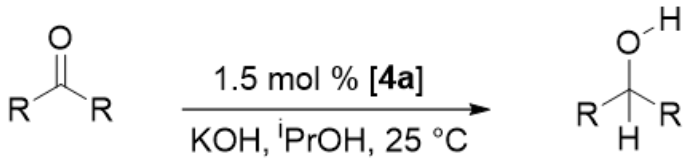



**Table 7.13** Catalysed transfer hydrogenation of 2-hexanone at r.t. using **4**

| Time (h) | % conversion |
|---|---|
| 0.5 | 0 |
| 4 | 0 |

### 7.2.1.4. Catalysed transfer hydrogenation of a range of ketone substrates using 4a at room temperature conditions




Substrate = acetophenone

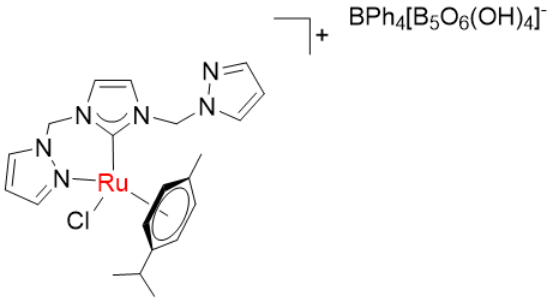
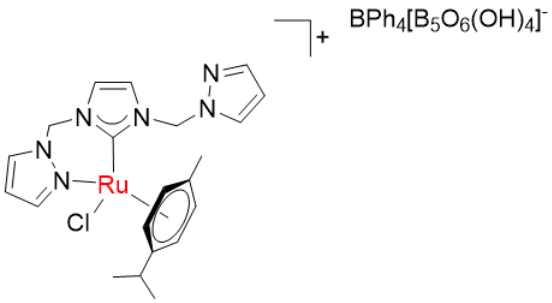



**Table 7.14** Catalysed transfer hydrogenation of acetophenone at r.t. using **4a**

| Time (h) | % conversion |
|---|---|
| 0.5 | 3 |
| 1 | 5 |
| 1.5 | 8 |
| 2 | 8 |
| 2.5 | 10 |
| 3 | 12 |
| 24 | 51 |

Substrate = Benzophenone

**Table 7.15** Catalysed transfer hydrogenation of benzophenone at r.t. using **4a**




| Time (h) | % conversion |
|---|---|
| 4 | 12 |
| 24 | 41 |

Substrate = 4-nitro-acetophenone

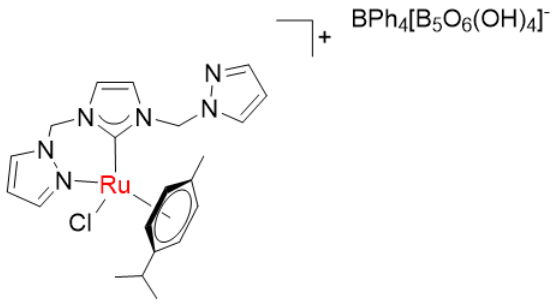



**Table 7.16** Catalysed transfer hydrogenation of 4-nitro-acetophenone at r.t. using **4a**

| Time (h) | % conversion |
|---|---|
| 0.5 | 0 |
| 4 | 0 |

Substrate = Cyclohexanone

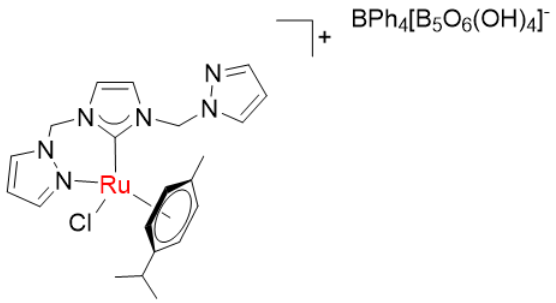



**Table 7.17** Catalysed transfer hydrogenation of cyclohexanone at r.t. using **4a**

| Time (h) | % conversion |
|---|---|
| 0.5 | 3 |
| 1 | 7 |
| 1.5 | 8 |
| 4 | 10 |
| 24 | 59 |

Substrate = 2-hexanone

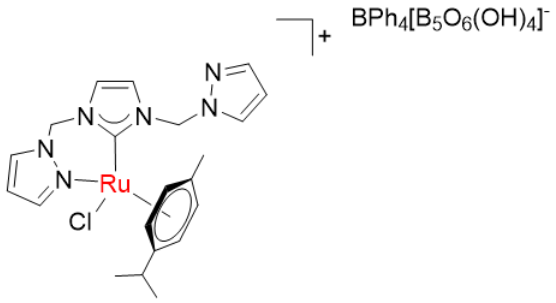
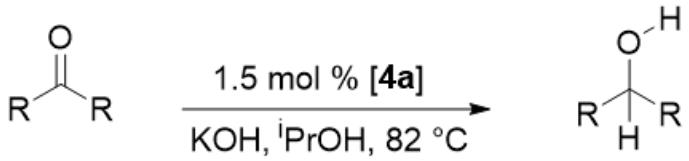



**Table 7.18** Catalysed transfer hydrogenation of 2-hexanone at r.t. using **4a**

| Time (h) | % conversion |
|---|---|
| 0.5 | 0 |
| 4 | 0 |

### 7.2.1.5. Catalysed transfer hydrogenation of a range of ketone substrates using 4a.




Substrate = Benzophenone

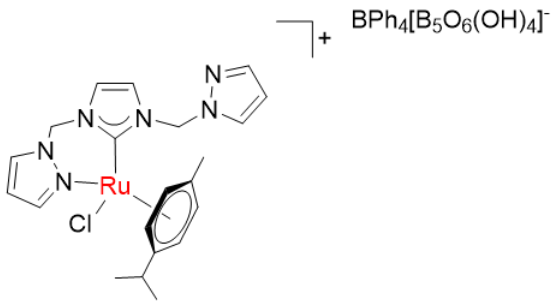



**Table 7.19** Catalysed transfer hydrogenation of benzophenone using **4a**

| Time (h) | % conversion |
|---|---|
| 0.16 | 66 |
| 0.33 | 83 |
| 0.5 | 91 |
| 1 | 91 |
| 1.5 | 91 |
| 2 | 100 |

Substrate = 4-nitro-acetophenone

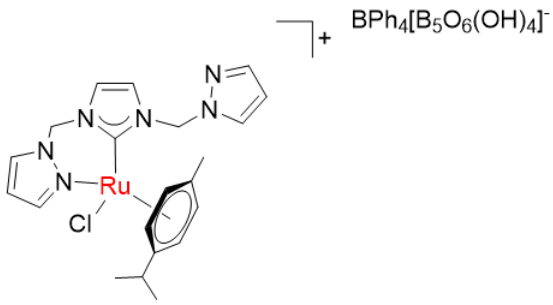



**Table 7.20** Catalysed transfer hydrogenation of 4-nitro-acetophenone at using **4a**

| Time (h) | % conversion |
|---|---|
| 0.5 | 0 |
| 4 | 0 |

Substrate = Cyclohexanone

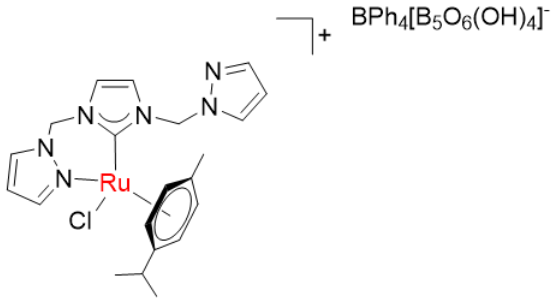



**Table 7.21** Catalysed transfer hydrogenation of cyclohexanone at using **4a**

| Time (h) | % conversion |
|---|---|
| 0.16 | 58 |
| 0.33 | 82 |
| 0.5 | 92 |
| 1 | 100 |

Substrate = 2-hexanone

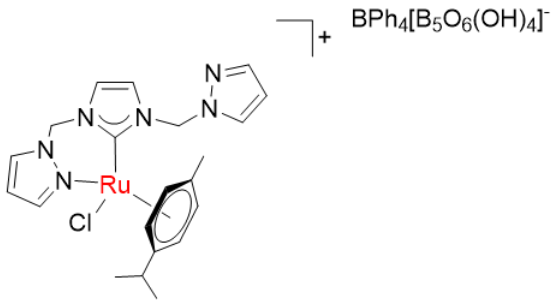
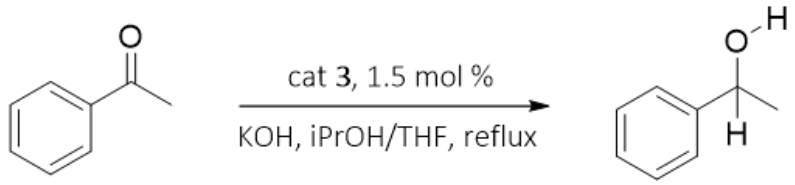



**Table 7.22** Catalysed transfer hydrogenation of 2-hexanone at using **4a**

| Time (h) | % conversion |
|---|---|
| 0.5 | 0 |
| 4 | 0 |

### 7.2.1.6. Catalysed transfer hydrogenation of acetophenone using 3 with THF/iPrOH solvent mix.




Substrate = acetophenone

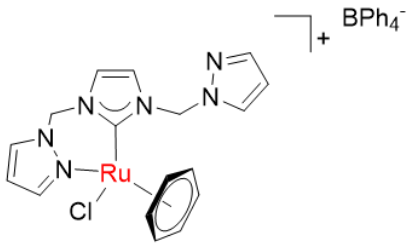
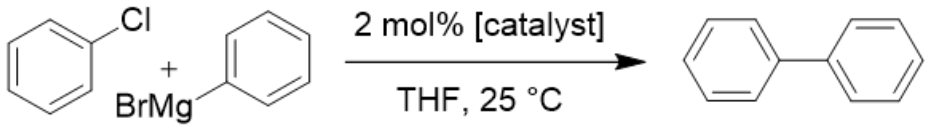



**Table 7.23** Catalysed transfer hydrogenation of acetophenone with THF/iPrOH using **4**

| Time (h) | % conversion |
|---|---|
| 0.16 | 47 |
| 0.33 | 61 |
| 0.5 | 87 |
| 1 | 91 |
| 1.5 | 97 |
| 2 | 100 |

### 7.2.2. Catalysis data for chapter 3

#### 7.2.2.1. Catalysed Kumada Cross Coupling of chlorobenzene with phenylmagnesium bromide using complexes 8, 9 and 10.



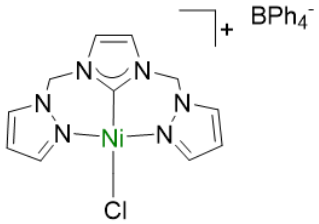




**Table 7.24** Catalysed Kumada Cross Coupling of chlorobenzene using **8**

| Time (h) | % conversion |
|---|---|
| 0.25 | 17 |
| 0.5 | 20 |
| 0.75 | 23 |
| 1 | 28 |
| 1.25 | 39 |
| 1.75 | 58 |
| 2.25 | 60 |
| 2.75 | 66 |
| 3.25 | 74 |
| 4 | 89 |
| 6 | 99 |

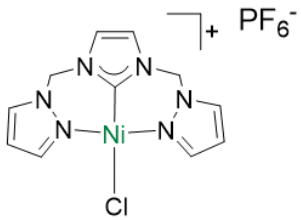
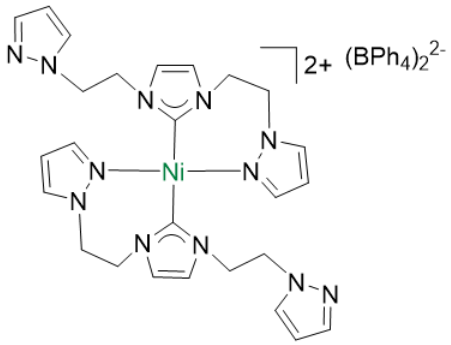



**Table 7.25** Catalysed Kumada Cross Coupling of chlorobenzene using **9**

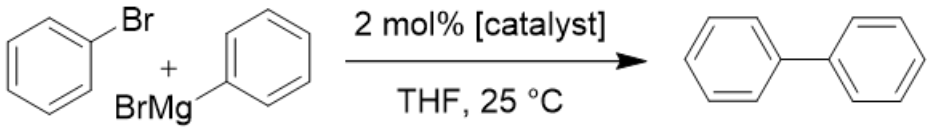
| Time (h) | % conversion |
|---|---|
| 0.25 | 9 |
| 0.5 | 9 |
| 0.75 | 9 |
| 1.75 | 15 |
| 6 | 40 |
| 20 | 40 |

**Table 7.26** Catalysed Kumada Cross Coupling of chlorobenzene using **10**




| Time (h) | % conversion |
|---|---|
| 0.25 | 40 |
| 0.5 | 40 |
| 4 | 40 |

### 7.2.2.2. Catalysed Kumada Cross Coupling of bromobenzene and phenylmagnesium bromide using complexes 8, 9 and 10.



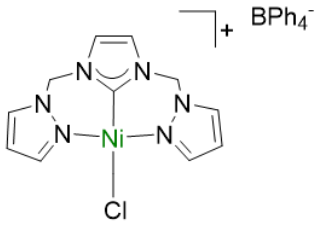




**Table 7.27** Catalysed Kumada Cross Coupling of bromobenzene using **8**

| Time (h) | % conversion |
|---|---|
| 0.25 | 50 |
| 0.5 | 50 |
| 0.75 | 65 |
| 1 | 69 |
| 1.25 | 72 |
| 1.75 | 74 |
| 2.25 | 80 |
| 2.75 | 87 |
| 3.25 | 87 |

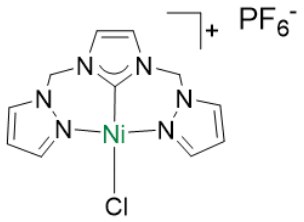



**Table 7.28** Catalysed Kumada Cross Coupling of bromobenzene using **9**

| Time (h) | % conversion |
|---|---|
| 0.25 | 10 |
| 0.5 | 18 |
| 0.75 | 25 |
| 1 | 27 |
| 1.25 | 27 |
| 1.75 | 46 |
| 2.25 | 68 |
| 2.75 | 80 |
| 3.25 | 84 |
| 4 | 87 |
| 5.75 | 89 |
| 24 | 100 |

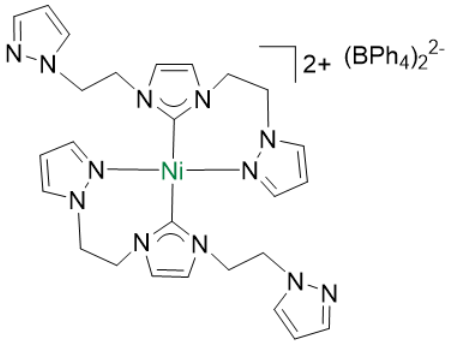
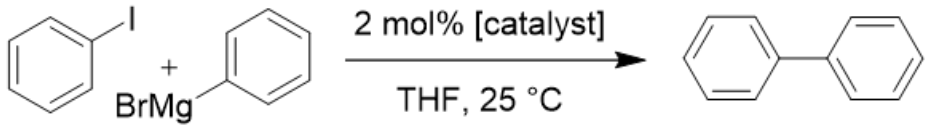



**Table 7.29** Catalysed Kumada Cross Coupling of bromobenzene using **10**

| Time (h) | % conversion |
|---|---|
| 0.25 | 17 |
| 0.5 | 28 |
| 1 | 40 |
| 4 | 40 |

### 7.2.2.3. Catalysed Kumada Cross Coupling reaction of iodobenzene with phenylmagnesium bromide using 8.



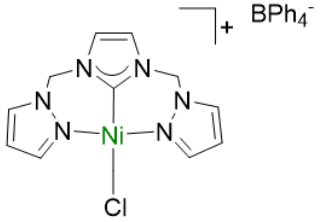
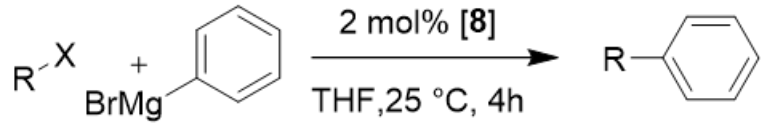



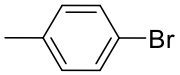

**Table 7.30** Catalysed Kumada Cross Coupling of iodobenzene using **8**

| Time (h) | % conversion |
|---|---|
| 0.16 | 57 |
| 0.5 | 74 |
| 1.25 | 97 |
| 1.75 | 100 |

### 7.2.2.4. Catalysed Kumada Cross Coupling of a range of halogenated substrates with phenylmagnesium bromide using 8.




X = Cl, Br



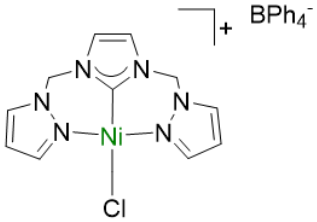
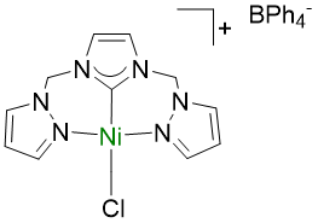




**Table 7.31** Catalysed Kumada Cross Coupling of tolylbromide using **8**

| Time (h) | % conversion |
|---|---|
| 0.5 | 39 |
| 0.75 | 58 |
| 1 | 60 |
| 1.25 | 63 |
| 1.5 | 70 |
| 2 | 73 |
| 2.25 | 78 |
| 4 | 78 |


**Table 7.32** Catalysed Kumada Cross Coupling of 4-methoxy-phenylbromide using **8**




| Time (h) | % conversion |
|---|---|
| 0.25 | 17 |
| 3 | 50 |

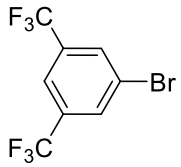
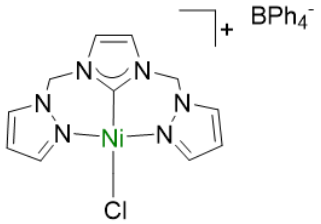



**Table 7.33** Catalysed Kumada Cross Coupling of 1,3-difluoromethyl-phenylbromide using **8**




| Time (h) | % conversion |
|---|---|
| 0.25 | 2 |
| 1.25 | 29 |
| 3 | 68 |

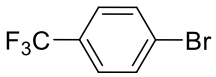
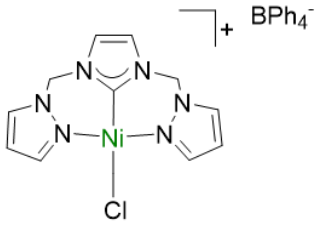



**Table 7.34** Catalysed Kumada Cross Coupling of 4-fluoromethyl-phenylbromide using **8**




| Time (h) | % conversion |
|---|---|
| 1.25 | 13 |
| 3 | 16 |

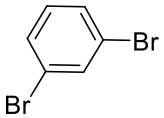
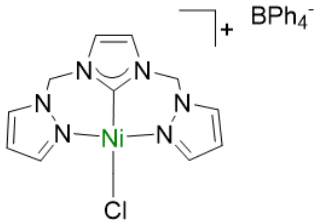



**Table 7.35** Catalysed Kumada Cross Coupling of 1,3-dibromobenzene using **8**




| Time (h) | % conversion |
|---|---|
| 3 | 67 |
| 6 | 67 |

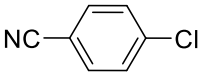
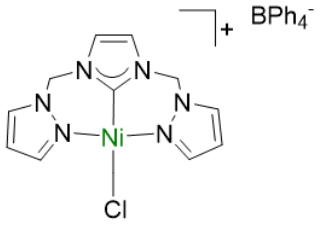
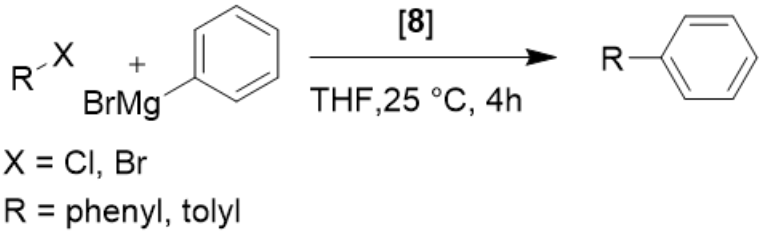



**Table 7.36** Catalysed Kumada Cross Coupling of 4-cyano-phenylchloride using **8**




| Time (h) | % conversion |
|---|---|
| 0.5 | 0 |
| 3 | 0 |
| 4 | 0 |

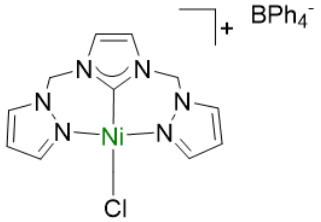
### 7.2.2.5. Catalysed Kumada Cross Coupling of a range of substrates with phenylmagnesium bromide using 8 at different catalyst loadings




1 mol% catalyst 8

**Table 7.37** Catalysed Kumada Cross Coupling of chlorobenzene using **8** at 1mol% catalyst loading

Substrate = Chlorobenzene




| Time (h) | % conversion |
|---|---|
| 0.25 | 35 |
| 1.25 | 39 |
| 4 | 43 |

5 mol% catalyst 8

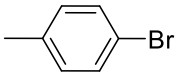
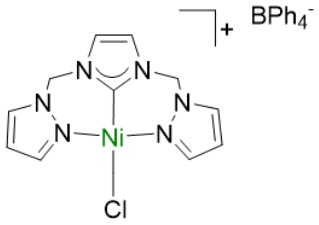


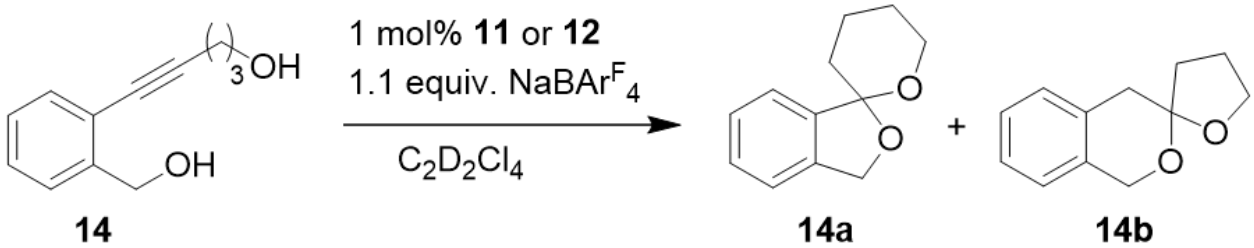

**Table 7.38** Catalysed Kumada Cross Coupling of tolylbromide using **8 at** 5 mol% catalyst loading




| Time (h) | % conversion |
|---|---|
| 0.5 | 34 |
| 0.75 | 56 |
| 1 | 60 |
| 1.25 | 63 |
| 1.5 | 71 |
| 1.75 | 72 |
| 2.25 | 75 |
| 4 | 75 |

### 7.2.3. Catalysis data for chapter 4

#### 7.2.3.1. Catalysed dihydroalkoxylation reactions of 14 using complexes 11 or 12.




80 °C

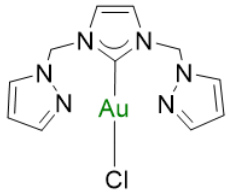



**Table 7.39** Catalysed dihydroalkoxylation of **14** using **11** at 80 °C.

| Time(h) | %conversion |
|---|---|
| 0 | 0 |
| 0.0225 | 91.24828467 |
| 0.033888889 | 98.17357504 |
| 0.041666667 | 99.28325695 |
| 0.049444444 | 99.69360836 |
| 0.057222222 | 99.76894767 |
| 0.065 | 99.9225853 |
| 0.0725 | 99.85434797 |

100 °C

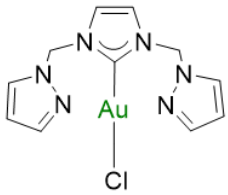



**Table 7.40** Catalysed dihydroalkoxylation of **14** using **11** at 100 °C.

| Time (h) | % conv. |
|---|---|
| 0 | 0 |
| 0.035833333 | 53.26479 |
| 0.045555556 | 59.42211 |
| 0.053055556 | 62.41782 |
| 0.060833333 | 65.21566 |
| 0.068611111 | 67.12119 |
| 0.076111111 | 70.3251 |
| 0.083888889 | 70.94524 |
| 0.091666667 | 73.025 |
| 0.099166667 | 74.26086 |
| 0.106944444 | 75.72667 |
| 0.114444444 | 74.42903 |
| 0.122222222 | 77.13883 |
| 0.131111111 | 78.45597 |
| 0.140277778 | 79.68174 |
| 0.149444444 | 79.73344 |
| 0.158611111 | 79.21114 |
| 0.167777778 | 80.63124 |
| 0.176666667 | 80.76303 |
| 0.185833333 | 80.94895 |
| 0.194722222 | 81.49323 |
| 0.203888889 | 80.64978 |
| 0.213055556 | 81.49763 |
| 0.2275 | 80.79814 |
| 0.242222222 | 81.53135 |
| 0.256944444 | 82.64867 |
| 0.271666667 | 82.33742 |
| 0.286388889 | 82.99134 |
| 0.300833333 | 84.21906 |
| 0.315555556 | 82.63602 |
| 0.330277778 | 81.30751 |
| 0.344722222 | 83.59704 |
| 0.359444444 | 84.07445 |
| 0.3825 | 85.27523 |
| 0.405555556 | 85.07555 |
| 0.428333333 | 83.45988 |
| 0.451388889 | 85.09716 |
| 0.474166667 | 85.33655 |
| 0.497222222 | 85.99142 |

| | |
|---|---|
| 0.520277778 | 86.34445 |
| 0.543333333 | 84.88706 |
| 0.566111111 | 85.81258 |
| 0.589166667 | 86.8089 |
| 0.628888889 | 87.00545 |
| 0.668333333 | 84.26898 |
| 0.708055556 | 86.46764 |
| 0.747777778 | 87.48134 |

70 ºC

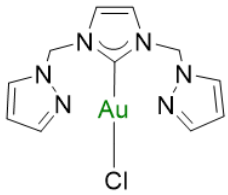



**Table 7.41** Catalysed dihydroalkoxylation of **14** using **11** at 70 ºC.

| Time(h) | %conversion |
|---|---|
| 0.006667 | 20.54232 |
| 0.013333 | 29.53276 |
| 0.02 | 37.0868 |
| 0.026667 | 44.50796 |
| 0.033056 | 51.54905 |
| 0.039722 | 58.42841 |
| 0.046667 | 64.63631 |
| 0.053056 | 70.28231 |
| 0.059722 | 75.21691 |
| 0.066389 | 79.65203 |
| 0.073056 | 83.3559 |
| 0.081111 | 86.86407 |
| 0.089167 | 89.90064 |
| 0.097222 | 92.17501 |
| 0.105278 | 93.95854 |
| 0.113333 | 95.36354 |
| 0.121389 | 96.40939 |
| 0.129444 | 97.24073 |
| 0.137222 | 97.79392 |
| 0.145278 | 98.30438 |
| 0.153333 | 98.63678 |
| 0.166944 | 99.09167 |
| 0.180556 | 99.33176 |
| 0.194167 | 99.47234 |
| 0.207778 | 99.5873 |
| 0.221389 | 99.67362 |
| 0.235 | 99.80683 |
| 0.248333 | 99.90566 |
| 0.261944 | 99.84319 |
| 0.275556 | 99.90628 |

25 °C

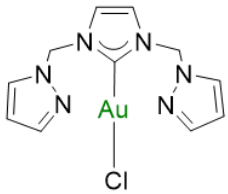



**Table 7.42** Catalysed dihydroalkoxylation of **14** using **11** at 25 °C.

| Time(h) | %conv |
|---|---|
| 0 | 0% |
| 0.017778 | 26% |
| 0.017778 | 31% |
| 0.024444 | 35% |
| 0.031111 | 38% |
| 0.037778 | 40% |
| 0.044167 | 43% |
| 0.050833 | 44% |
| 0.0575 | 47% |
| 0.064167 | 49% |
| 0.070556 | 52% |
| 0.077222 | 52% |
| 0.083889 | 55% |
| 0.091944 | 57% |
| 0.1 | 59% |
| 0.108056 | 60% |
| 0.115833 | 62% |
| 0.123889 | 63% |
| 0.131944 | 64% |
| 0.14 | 65% |
| 0.148056 | 67% |
| 0.156111 | 68% |
| 0.163889 | 69% |
| 0.1775 | 71% |
| 0.191111 | 73% |
| 0.204722 | 74% |
| 0.218333 | 75% |
| 0.231944 | 76% |
| 0.245556 | 77% |
| 0.258889 | 78% |
| 0.2725 | 79% |
| 0.286111 | 80% |
| 0.299722 | 82% |
| 0.338333 | 84% |
| 0.377222 | 86% |
| 0.415833 | 87% |
| 0.454444 | 88% |
| 0.493056 | 89% |
| 0.531667 | 90% |

| | |
|---|---|
| 0.570556 | 91% |
| 0.609167 | 92% |
| 0.647778 | 92% |
| 0.686389 | 93% |
| 0.775 | 95% |
| 0.863611 | 95% |
| 0.9525 | 96% |
| 1.041111 | 97% |
| 1.129722 | 98% |
| 1.218333 | 98% |
| 1.306944 | 98% |
| 1.395556 | 98% |

70 °C

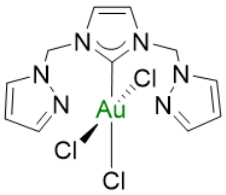



**Table 7.43** Catalysed dihydroalkoxylation of **14** using **12** at 70 °C.

| Time(h) | %conv |
|---|---|
| 0 | 0% |
| 0.017778 | 100% |

25 °C

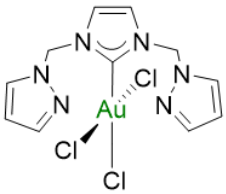
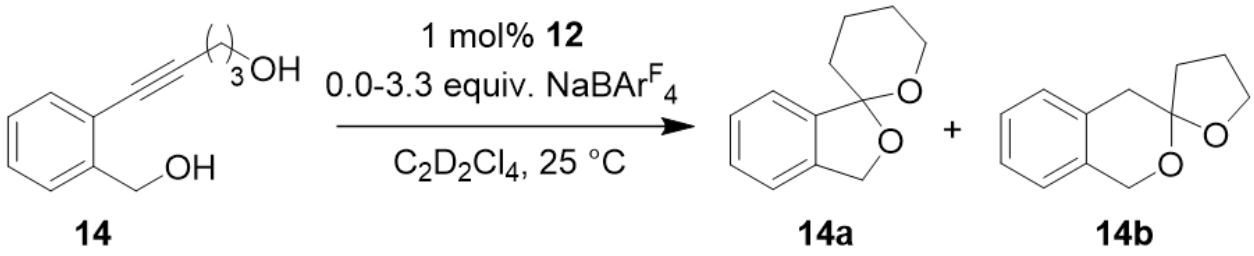



**Table 7.44** Catalysed dihydroalkoxylation of **14** using **12** at 25 °C.

| Time(h) | %conv |
|---|---|
| 0 | 0% |
| 0.014444 | 55% |
| 0.028889 | 66% |
| 0.040278 | 74% |
| 0.051667 | 81% |
| 0.062778 | 86% |
| 0.074167 | 90% |
| 0.085556 | 93% |
| 0.096667 | 95% |
| 0.108056 | 96% |
| 0.119444 | 97% |
| 0.130833 | 98% |
| 0.141944 | 99% |
| 0.154722 | 99% |
| 0.1675 | 100% |

| | |
|---|---|
| 0.18 | 100% |
| 0.192778 | 100% |

### 7.2.3.2. Catalysed dihydroalkoxylation of 14 using 12 with differing $NaBAr^F{}_4$ loadings




0.0 eq

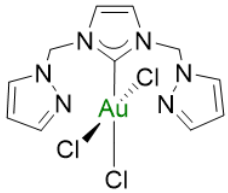



**Table 7.45** Catalysed dihydroalkoxylation of **14** using **12** and 0.0 eq $NaBAr^F{}_4$ at 25 °C.

| Time(h) | %conv |
|---|---|
| 0 | 0 |
| 0.017778 | 26% |
| 0.017778 | 31% |
| 0.024444 | 35% |
| 0.031111 | 38% |
| 0.037778 | 40% |
| 0.044167 | 43% |
| 0.050833 | 44% |
| 0.0575 | 47% |
| 0.064167 | 49% |
| 0.070556 | 52% |
| 0.077222 | 52% |
| 0.083889 | 55% |
| 0.091944 | 57% |
| 0.1 | 59% |
| 0.108056 | 60% |
| 0.115833 | 62% |
| 0.123889 | 63% |
| 0.131944 | 64% |
| 0.14 | 65% |
| 0.148056 | 67% |
| 0.156111 | 68% |
| 0.163889 | 69% |
| 0.1775 | 71% |

| | |
|---|---|
| 0.191111 | 73% |
| 0.204722 | 74% |
| 0.218333 | 75% |
| 0.231944 | 76% |
| 0.245556 | 77% |
| 0.258889 | 78% |
| 0.2725 | 79% |
| 0.286111 | 80% |
| 0.299722 | 82% |
| 0.338333 | 84% |
| 0.377222 | 86% |
| 0.415833 | 87% |
| 0.454444 | 88% |
| 0.493056 | 89% |
| 0.531667 | 90% |
| 0.570556 | 91% |
| 0.609167 | 92% |
| 0.647778 | 92% |
| 0.686389 | 93% |
| 0.775 | 95% |
| 0.863611 | 95% |
| 0.9525 | 96% |
| 1.041111 | 97% |
| 1.129722 | 98% |
| 1.218333 | 98% |
| 1.306944 | 98% |
| 1.395556 | 98% |

2.2 eq

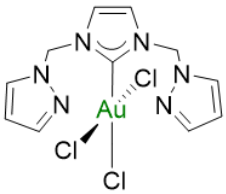



**Table 7.46** Catalysed dihydroalkoxylation of **14** using **12** and 2.2 eq $NaBAr^F{}_4$ at 25 °C.

| time(h) | %conv |
|---|---|
| 0 | 0% |
| 0.017778 | 58% |
| 0.024444 | 63% |
| 0.031111 | 68% |
| 0.037778 | 70% |
| 0.044167 | 73% |
| 0.050833 | 75% |
| 0.0575 | 77% |
| 0.064167 | 80% |

| | |
|---|---|
| 0.070556 | 81% |
| 0.077222 | 83% |
| 0.083889 | 85% |
| 0.091944 | 86% |
| 0.1 | 88% |
| 0.108056 | 89% |
| 0.115833 | 90% |
| 0.123889 | 92% |
| 0.131944 | 94% |
| 0.14 | 95% |
| 0.148056 | 96% |
| 0.156111 | 97% |
| 0.163889 | 98% |
| 0.1775 | 99% |

3.3 eq

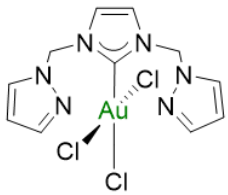
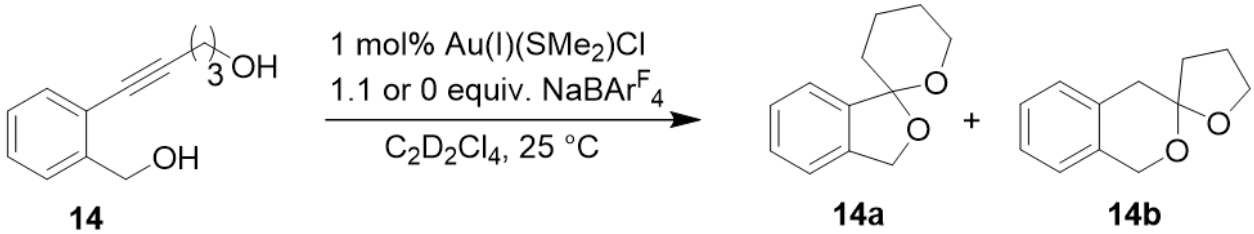


**Table 7.47** Catalysed dihydroalkoxylation of **14** using **12** and 3.3 eq $NaBAr^F{}_4$ at 25 °C.

| time(h) | %conv |
|---|---|
| 0 | 0% |
| 0.017222 | 67% |
| 0.023889 | 73% |
| 0.030556 | 78% |
| 0.037222 | 84% |
| 0.043611 | 86% |
| 0.050278 | 89% |
| 0.056944 | 93% |
| 0.063611 | 95% |
| 0.07 | 97% |
| 0.076667 | 99% |
| 0.083333 | 100% |

### 7.2.3.3. Catalysed dihydroalkoxylation of 14 using Au(I)(SMe$_2$)Cl



**0.0 eq $NaBAr^F{}_4$**

**Table 7.48** Catalysed dihydroalkoxylation of **14** using **Au(I)(SMe$_2$)Cl** and 0.0 eq $NaBAr^F{}_4$ at 25 $^oC$.

| Time(h) | %conv |
|---|---|
| 0 | 0% |
| 0.018056 | 16% |
| 0.024722 | 19% |
| 0.031111 | 21% |
| 0.037778 | 24% |
| 0.044444 | 26% |
| 0.051111 | 27% |
| 0.057778 | 29% |
| 0.064444 | 31% |
| 0.071111 | 32% |
| 0.077778 | 33% |
| 0.084167 | 34% |
| 0.092222 | 36% |
| 0.100278 | 37% |
| 0.108333 | 38% |
| 0.116389 | 39% |
| 0.124444 | 39% |
| 0.1325 | 40% |
| 0.140556 | 42% |
| 0.148611 | 42% |
| 0.156667 | 43% |
| 0.164444 | 43% |
| 0.178056 | 44% |
| 0.191667 | 45% |
| 0.205278 | 46% |
| 0.218889 | 47% |
| 0.2325 | 47% |
| 0.245833 | 48% |
| 0.259444 | 49% |
| 0.273056 | 49% |
| 0.286667 | 50% |
| 0.300278 | 50% |
| 0.338889 | 52% |
| 0.3775 | 54% |
| 0.416111 | 55% |
| 0.455 | 55% |
| 0.493611 | 57% |
| 0.532222 | 57% |

| | |
|---|---|
| 0.570833 | 58% |
| 0.609444 | 59% |
| 0.648056 | 59% |
| 0.686944 | 60% |
| 0.775556 | 61% |
| 0.864167 | 62% |
| 0.952778 | 64% |
| 1.041389 | 65% |
| 1.13 | 66% |
| 1.218611 | 67% |
| 1.3075 | 68% |
| 1.396111 | 68% |
| 1.484722 | 69% |
| 2.778611 | 70% |

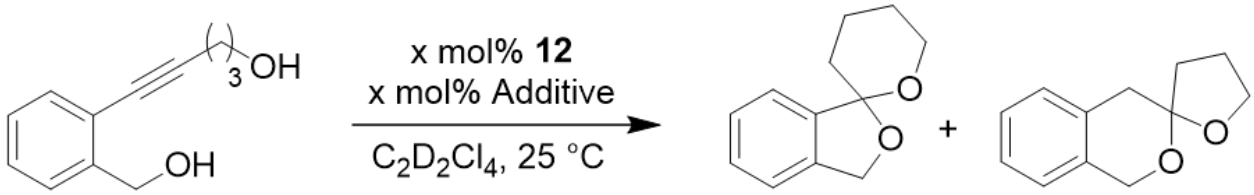
### 1.1 eq $NaBAr^F{}_4$

**Table 7.49** Catalysed dihydroalkoxylation of **14** using **Au(I)(SMe$_2$)Cl** and 1.1 eq $NaBAr^F{}_4$ at 25 $^oC$.

| Time(h) | %conv |
|---|---|
| 0 | 0% |
| 0.044722 | 15% |
| 0.051389 | 18% |
| 0.058333 | 22% |
| 0.064722 | 22% |
| 0.071389 | 23% |
| 0.078056 | 25% |
| 0.084722 | 27% |
| 0.091389 | 32% |
| 0.098056 | 31% |
| 0.104722 | 35% |
| 0.111389 | 37% |
| 0.119444 | 41% |
| 0.127222 | 45% |
| 0.135278 | 46% |
| 0.143333 | 48% |
| 0.151389 | 53% |
| 0.159444 | 56% |
| 0.167778 | 61% |
| 0.175556 | 65% |

| | |
|---|---|
| 0.183611 | 70% |
| 0.191667 | 75% |
| 0.205278 | 84% |
| 0.218889 | 92% |
| 0.2325 | 97% |
| 0.246111 | 98% |
| 0.259722 | 100% |

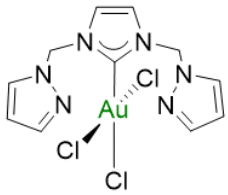
### 7.2.3.4. Catalysed dihydroalkoxylation of 14 using 12 at reduced catalytic loadings




**14** **14a** **14b**

0.1 mol% **12**, 0.11 mol% $NaBAr^F{}_4$

**Table 7.50** Catalysed dihydroalkoxylation of **14** using 0.1 mol% **12** and 1.1 eq $NaBAr^F{}_4$ at 25 °C.

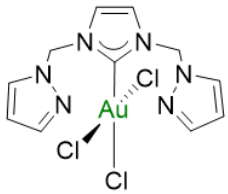



| Time(h) | %conv |
|---|---|
| 0 | 0% |
| 0.036667 | 30% |
| 0.043333 | 30% |
| 0.05 | 30% |
| 0.056667 | 30% |
| 0.063333 | 31% |
| 0.07 | 31% |
| 0.076389 | 31% |
| 0.083056 | 32% |
| 0.089722 | 31% |
| 0.096389 | 31% |
| 0.103056 | 31% |
| 0.111111 | 32% |
| 0.118889 | 32% |
| 0.126944 | 32% |
| 0.135 | 32% |
| 0.143056 | 32% |

| | |
|---|---|
| 0.151111 | 33% |
| 0.158611 | 32% |
| 0.166667 | 32% |
| 0.174722 | 32% |
| 0.182778 | 33% |
| 0.196111 | 32% |
| 0.209722 | 33% |
| 0.223333 | 33% |
| 0.236944 | 33% |
| 0.250556 | 33% |
| 0.264167 | 33% |
| 0.277778 | 33% |
| 0.291389 | 33% |
| 0.304722 | 33% |
| 0.318333 | 34% |
| 0.356944 | 33% |
| 0.395833 | 34% |
| 0.434444 | 34% |
| 0.473056 | 34% |
| 0.511667 | 34% |
| 0.550278 | 35% |
| 0.588889 | 35% |
| 0.6275 | 35% |

0.01mol% **12**, 0.011 mol% $NaBAr^F{}_4$

**Table 7.51** Catalysed dihydroalkoxylation of **14** using 0.01 mol% **12** and 1.1 eq $NaBAr^F{}_4$ at 25 °C.

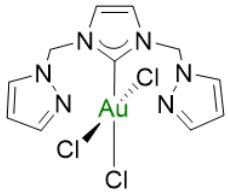



| Time(h) | %conv |
|---|---|
| 0 | 0% |
| 0.035 | 6% |
| 0.041667 | 9% |
| 0.048333 | 9% |

| | |
|---|---|
| 0.055 | 10% |
| | |
| 0.068333 | 10% |
| 0.075 | 10% |

1mol% **12**, 1.1 mol% $AgSbF_6$

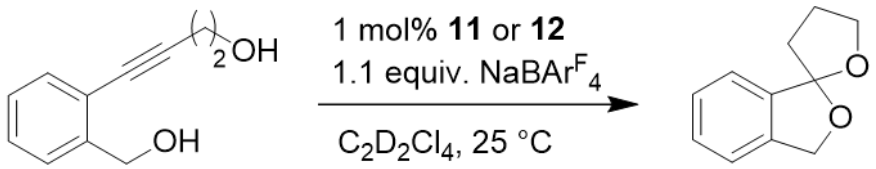
**Table 7.52** Catalysed dihydroalkoxylation of **14** using 1 mol% **12** and 1.1 eq $AgSbF_6$ at 25 °C.




| Time(h) | %conv |
|---|---|
| 0 | 0% |
| 0.035 | 69% |
| 0.041667 | 71% |
| 0.048333 | 73% |
| 0.055 | 75% |
| 0.061667 | 76% |
| 0.068333 | 77% |
| 0.075 | 79% |
| 0.081667 | 79% |
| 0.088333 | 81% |
| 0.095 | 81% |
| 0.101667 | 82% |
| 0.109722 | 83% |
| 0.117778 | 84% |
| 0.125833 | 84% |
| 0.133611 | 85% |
| 0.141667 | 85% |
| 0.149722 | 86% |
| 0.157778 | 86% |
| 0.165833 | 87% |
| 0.173889 | 87% |
| 0.181944 | 87% |
| 0.195556 | 88% |
| 0.208889 | 88% |
| 0.2225 | 89% |
| 0.236111 | 89% |
| 0.249722 | 89% |
| 0.263333 | 90% |
| 0.276944 | 90% |
| 0.290278 | 90% |
| 0.303889 | 90% |
| 0.3175 | 91% |
| 0.356389 | 91% |
| 0.395 | 91% |
| 0.433611 | 92% |
| 0.472222 | 92% |
| 0.510833 | 92% |
| 0.549722 | 92% |
| 0.588333 | 92% |

| | |
|---|---|
| 0.626944 | 92% |
| 0.665556 | 93% |
| 0.704167 | 93% |
| 0.792778 | 93% |
| 0.881389 | 93% |
| 0.97 | 93% |
| 1.058889 | 93% |
| 1.1475 | 93% |
| 1.236111 | 93% |
| 1.324722 | 93% |
| 1.413333 | 93% |
| 1.501944 | 93% |

### 7.2.3.5. Catalysed dihydroalkoxylation of 15 using 11 or 12




**15** **15a**

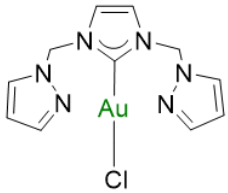
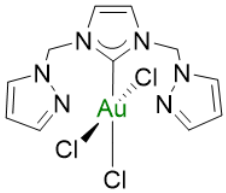



**Table 7.53** Catalysed dihydroalkoxylation of **15** using **11** and 1.1 eq NaBAr$^F_4$ at 25 °C.

| Time(h) | %conv |
|---|---|
| 0 | 0% |
| 0.034722 | 7% |
| 0.041389 | 7% |
| 0.048056 | 9% |
| 0.054722 | 11% |
| 0.061111 | 10% |
| 0.067778 | 12% |
| 0.074444 | 13% |
| 0.081111 | 14% |
| 0.087778 | 15% |
| 0.094444 | 15% |
| 0.101111 | 17% |
| 0.109167 | 17% |
| 0.116944 | 21% |

| | |
|---|---|
| 0.125 | 22% |
| 0.133056 | 23% |
| 0.141111 | 24% |
| 0.149167 | 22% |
| 0.157222 | 26% |
| 0.165278 | 26% |
| 0.173333 | 27% |
| 0.181111 | 29% |
| 0.194722 | 30% |
| 0.208333 | 30% |
| 0.221944 | 29% |
| 0.235556 | 34% |
| 0.249167 | 35% |
| 0.2625 | 36% |
| 0.276389 | 34% |
| 0.289722 | 38% |
| 0.303333 | 39% |
| 0.316944 | 40% |
| 0.355556 | 44% |
| 0.394167 | 47% |
| 0.432778 | 50% |
| 0.471389 | 52% |
| 0.510278 | 54% |
| 0.548889 | 57% |
| 0.5875 | 59% |
| 0.626111 | 62% |
| 0.664722 | 62% |
| 0.703611 | 64% |
| 0.792222 | 69% |
| 0.880833 | 74% |
| 0.969444 | 78% |
| 1.058056 | 81% |
| 1.146667 | 84% |
| 1.235556 | 87% |
| 1.324167 | 89% |
| 1.412778 | 90% |
| 1.501389 | 91% |
| 1.625556 | 93% |
| 1.953333 | 96% |

Table 7.54 Catalysed dihydroalkoxylation of **15** using **12** and 1.1 eq $NaBAr^F{}_4$ at 25 °C.




| time(h) | %conv |
|---|---|
| 0 | 0% |
| 0.035 | 44% |
| 0.041667 | 55% |
| 0.048333 | 63% |
| 0.055 | 69% |
| 0.061667 | 73% |
| 0.068333 | 76% |
| 0.075 | 79% |
| 0.081389 | 81% |
| 0.088056 | 83% |
| 0.094722 | 85% |
| 0.101389 | 86% |
| 0.109444 | 88% |
| 0.1175 | 89% |
| 0.125556 | 90% |
| 0.133611 | 91% |
| 0.141667 | 92% |
| 0.149722 | 93% |
| 0.1575 | 94% |
| 0.165556 | 95% |
| 0.173611 | 95% |
| 0.181667 | 96% |
| 0.195278 | 97% |
| 0.208889 | 97% |
| 0.2225 | 98% |
| 0.236111 | 98% |
| 0.249444 | 99% |
| 0.263056 | 99% |
| 0.276667 | 99% |

**1 mol% 12, 1.1 eq $AgSbF_6$**

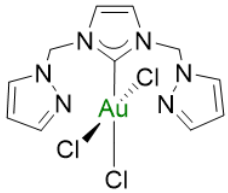
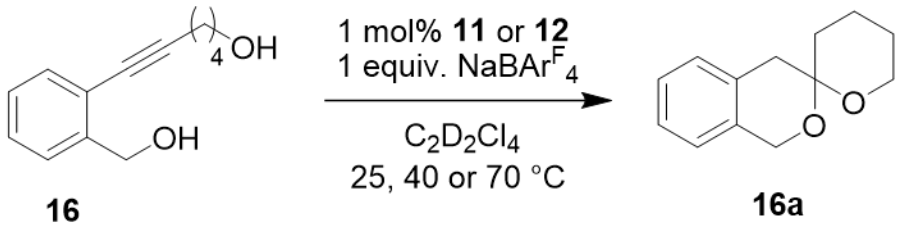



**Table 7.55** Catalysed dihydroalkoxylation of **15** using **12** and 1.1 eq $AgSbF_6$ at 25 °C.

| Time(h) | %conv |
|---|---|
| 0 | 0% |
| 0.033611 | 33% |
| 0.04 | 37% |
| 0.046667 | 41% |
| 0.053333 | 43% |
| 0.06 | 46% |
| 0.066667 | 49% |
| 0.073333 | 52% |
| 0.08 | 55% |
| 0.086667 | 56% |
| 0.093333 | 59% |
| 0.1 | 60% |
| 0.108056 | 63% |
| 0.116111 | 65% |
| 0.124167 | 66% |
| 0.132222 | 69% |
| 0.140278 | 70% |
| 0.148056 | 72% |
| 0.156111 | 73% |
| 0.164167 | 74% |
| 0.172222 | 75% |
| 0.180278 | 76% |
| 0.193889 | 78% |
| 0.2075 | 80% |
| 0.220833 | 81% |
| 0.234444 | 82% |
| 0.248056 | 83% |
| 0.261667 | 84% |
| 0.275278 | 86% |
| 0.288889 | 86% |
| 0.302222 | 87% |
| 0.315833 | 88% |
| 0.354444 | 90% |
| 0.393333 | 91% |
| 0.431944 | 92% |
| 0.470556 | 93% |

| | |
|---|---|
| 0.509167 | 94% |
| 0.547778 | 95% |
| 0.586389 | 95% |
| 0.625278 | 96% |
| 0.663889 | 96% |
| 0.7025 | 96% |
| 0.791111 | 97% |
| 0.879722 | 97% |
| 0.968333 | 98% |
| 1.056944 | 98% |
| 1.145833 | 98% |
| 1.234444 | 98% |
| 1.323056 | 98% |
| 1.411667 | 99% |
| 1.500278 | 99% |

### 7.2.3.6. Catalysed dihydroalkoxylation of 16 using 11 or 12.




70 °C

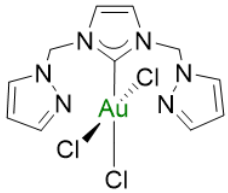



**Table 7.56** Catalysed dihydroalkoxylation of **16** using **11** and 1.1 eq NaBAr$^F_4$ at 70 °C.

| Time(h) | %conversion |
|---|---|
| 0.005556 | 0.246159 |
| 0.012222 | 0.29028 |
| 0.018889 | 2.157607 |
| 0.025556 | 1.091563 |
| 0.032222 | 2.284552 |
| 0.038889 | 3.334587 |
| 0.045556 | 2.10126 |
| 0.052222 | 4.277357 |
| 0.058889 | 5.451882 |

| | |
|---|---|
| 0.065556 | 5.072372 |
| 0.072222 | 8.117413 |
| 0.080278 | 9.904641 |
| 0.088333 | 10.83527 |
| 0.096111 | 13.86294 |
| 0.104167 | 14.65435 |
| 0.112222 | 17.11979 |
| 0.120278 | 18.36399 |
| 0.128333 | 18.50275 |
| 0.136389 | 19.99718 |
| 0.144444 | 20.66332 |
| 0.1525 | 20.55118 |
| 0.166111 | 21.83937 |
| 0.179722 | 22.29341 |
| 0.193333 | 21.06399 |
| 0.206944 | 22.9386 |
| 0.220556 | 21.92043 |
| 0.234167 | 23.34503 |
| 0.247778 | 23.48182 |
| 0.261389 | 23.5908 |
| 0.275 | 23.70938 |
| 0.288611 | 23.84087 |
| 0.327222 | 22.54701 |
| 0.365833 | 24.27542 |
| 0.404722 | 24.46038 |
| 0.443333 | 23.30172 |
| 0.481944 | 23.66627 |
| 0.520556 | 23.71367 |
| 0.559167 | 23.63021 |
| 0.598056 | 23.91652 |
| 0.636667 | 25.24997 |
| 0.675556 | 24.09889 |
| 0.764167 | 25.50791 |

40 °C

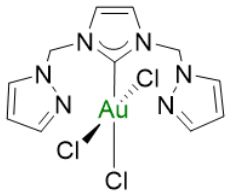
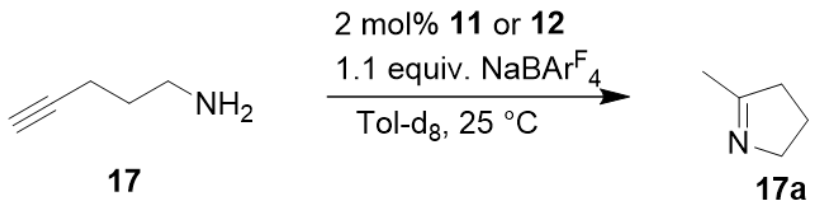



**Table 7.57** Catalysed dihydroalkoxylation of **16** using **12** and 1.1 eq $NaBAr^F{}_4$ at 40 °C.

| Time(h) | %conv |
|---|---|
| 0 | 0% |
| 0.051389 | 38% |
| 0.058056 | 38% |
| 0.064722 | 37% |
| 0.071389 | 38% |
| 0.078056 | 37% |
| 0.084722 | 37% |
| 0.091111 | 37% |
| 0.097778 | 36% |
| 0.104444 | 37% |
| 0.111111 | 36% |
| 0.117778 | 37% |
| 0.125833 | 36% |
| 0.133889 | 37% |
| 0.141944 | 36% |
| 0.15 | 36% |
| 0.158056 | 37% |
| 0.165833 | 37% |
| 0.173889 | 37% |
| 0.181944 | 37% |
| 0.19 | 37% |
| 0.198056 | 35% |
| 0.211667 | 36% |
| 0.225278 | 36% |
| 0.238889 | 36% |
| 0.2525 | 36% |
| 0.266111 | 36% |
| 0.279722 | 37% |
| 0.293333 | 36% |

### 7.2.3.7. Catalysed hydroamination of 17 using 11 or 12.



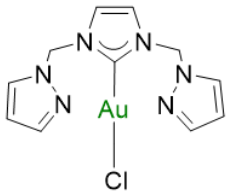




**Table 7.58** Catalysed hydroamination of **17** using **11** at 25 °C.

| Time(h) | %conv |
|---|---|
| 0 | 0% |
| 0.050556 | 3% |
| 0.056944 | 4% |
| 0.063611 | 4% |
| 0.070278 | 4% |
| 0.076944 | 5% |
| 0.083611 | 6% |
| 0.090278 | 5% |
| 0.096667 | 5% |
| 0.103333 | 5% |
| 0.11 | 5% |
| 0.116667 | 5% |
| 0.124722 | 6% |
| 0.132778 | 6% |
| 0.140833 | 7% |
| 0.148889 | 6% |
| 0.156944 | 6% |
| 0.164722 | 6% |
| 0.172778 | 6% |
| 0.180833 | 7% |
| 0.188889 | 7% |
| 0.196944 | 7% |
| 0.210278 | 7% |
| 0.223889 | 7% |
| 0.2375 | 8% |
| 0.251111 | 8% |
| 0.264722 | 8% |
| 0.278333 | 9% |

| | |
|---|---|
| 0.291667 | 9% |
| 0.305278 | 9% |
| 0.318889 | 9% |
| 0.3325 | 9% |
| 0.371111 | 9% |
| 0.41 | 10% |
| 0.448611 | 11% |
| 0.487222 | 11% |
| 0.525833 | 12% |
| 0.564444 | 12% |
| 0.603333 | 13% |
| 0.641944 | 13% |
| 0.680556 | 13% |
| 0.719167 | 13% |
| 0.808056 | 14% |
| 0.896667 | 15% |
| 0.985278 | 15% |
| 1.073889 | 16% |
| 1.1625 | 16% |
| 1.251111 | 17% |
| 1.339722 | 17% |
| 1.428611 | 18% |
| 1.517222 | 18% |

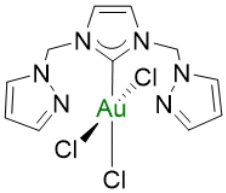
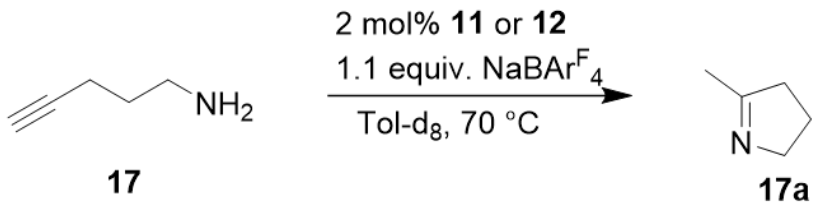



**Table 7.59** Catalysed hydroamination of **17** using **12** at 25 °C.

| Time(h) | %conv |
|---|---|
| 0 | 0% |
| 0.075556 | 3% |
| 0.082222 | 3% |
| 0.088889 | 4% |
| 0.095556 | 4% |
| 0.101944 | 4% |
| 0.108889 | 6% |
| 0.115556 | 6% |
| 0.122222 | 6% |
| 0.128611 | 6% |
| 0.135278 | 6% |
| 0.141944 | 6% |
| 0.15 | 6% |

| | |
|---|---|
| 0.158056 | 7% |
| 0.165833 | 7% |
| 0.173889 | 7% |
| 0.181944 | 8% |
| 0.19 | 8% |
| 0.197778 | 8% |
| 0.205833 | 9% |
| 0.213889 | 9% |
| 0.221944 | 9% |
| 0.235556 | 9% |
| 0.249167 | 10% |
| 0.262778 | 10% |
| 0.276111 | 10% |
| 0.289722 | 11% |
| 0.303333 | 11% |
| 0.316944 | 11% |
| 0.330556 | 12% |
| 0.343889 | 12% |
| 0.357778 | 12% |
| 0.396389 | 13% |
| 0.435 | 14% |
| 0.473611 | 15% |
| 0.512222 | 15% |
| 0.550833 | 16% |
| 0.589444 | 16% |
| 0.628333 | 17% |
| 0.666944 | 17% |
| 0.705556 | 18% |
| 0.744167 | 18% |
| 0.832778 | 19% |
| 0.921389 | 20% |
| 1.01 | 21% |
| 1.098611 | 22% |
| 1.187222 | 23% |
| 1.275833 | 23% |
| 1.364722 | 24% |
| 1.453056 | 24% |
| 1.541667 | 25% |




**17** **17a**

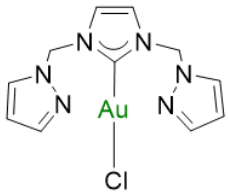



**Table 7.60** Catalysed hydroamination of **17** using **11** at 70 °C.

| Time(h) | %conv |
|---|---|
| 0 | 0% |
| 0.005 | 11% |
| 0.005 | 18% |
| 0.011667 | 22% |
| 0.018333 | 26% |
| 0.025 | 29% |
| 0.031667 | 31% |
| 0.038333 | 33% |
| 0.045 | 35% |
| 0.051667 | 37% |
| 0.058333 | 39% |
| 0.064722 | 40% |
| 0.071389 | 41% |
| 0.079444 | 43% |
| 0.0875 | 44% |
| 0.095556 | 45% |
| 0.103611 | 46% |
| 0.111389 | 47% |
| 0.119444 | 48% |
| 0.1275 | 49% |
| 0.135556 | 50% |
| 0.143611 | 51% |
| 0.151389 | 52% |
| 0.165 | 53% |
| 0.178611 | 54% |
| 0.192222 | 55% |
| 0.205833 | 56% |
| 0.219444 | 57% |
| 0.233056 | 59% |

| | |
|---|---|
| 0.246667 | 59% |
| 0.260278 | 60% |
| 0.273889 | 60% |
| 0.2875 | 62% |
| 0.326111 | 64% |
| 0.364722 | 66% |
| 0.403333 | 67% |
| 0.441944 | 68% |
| 0.480833 | 69% |

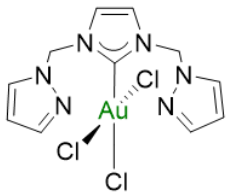
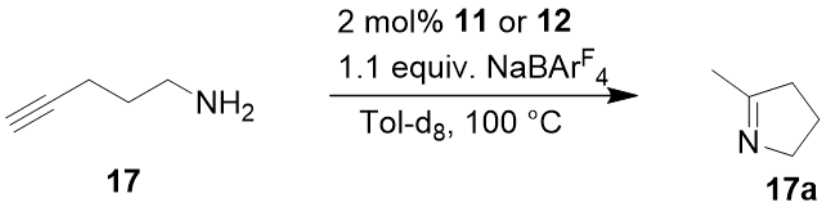



**Table 7.61** Catalysed hydroamination of **17** using **12** at 70 °C.

| Time(h) | %conv |
|---|---|
| 0 | 0% |
| 0.007222 | 7% |
| 0.013889 | 12% |
| 0.020556 | 17% |
| 0.027222 | 20% |
| 0.033889 | 22% |
| 0.040556 | 25% |
| 0.047222 | 26% |
| 0.053611 | 28% |
| 0.060556 | 29% |
| 0.066944 | 30% |
| 0.073611 | 31% |
| 0.081667 | 32% |
| 0.089722 | 34% |
| 0.097778 | 35% |
| 0.105556 | 36% |
| 0.113611 | 37% |
| 0.121667 | 38% |
| 0.129722 | 38% |
| 0.1375 | 39% |
| 0.145556 | 40% |
| 0.153611 | 41% |
| 0.167222 | 42% |
| 0.180833 | 43% |
| 0.194444 | 45% |
| 0.207778 | 46% |
| 0.221389 | 47% |
| 0.235 | 48% |
| 0.248611 | 49% |
| 0.262222 | 49% |

| | |
|---|---|
| 0.275556 | 50% |
| 0.289167 | 51% |
| 0.327778 | 53% |
| 0.366667 | 55% |
| 0.405278 | 57% |
| 0.443889 | 59% |
| 0.4825 | 60% |
| 0.521111 | 62% |
| 0.559722 | 63% |
| 0.598611 | 65% |
| 0.637222 | 66% |
| 0.675833 | 67% |
| 0.764444 | 70% |
| 0.853056 | 71% |
| 0.941944 | 73% |
| 1.030556 | 75% |
| 1.119167 | 76% |
| 1.207778 | 78% |
| 1.296389 | 79% |
| 1.385 | 81% |



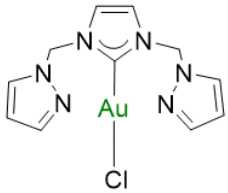




**Table 7.62** Catalysed hydroamination of **17** using **11** at 100 °C.

| time(h) | %conv |
|---|---|
| 0 | 0 |
| 0 | 0% |
| 0.015 | 58% |
| 0.022778 | 65% |
| 0.030833 | 70% |
| 0.038611 | 73% |
| 0.046944 | 76% |

| | |
|---|---|
| 0.055278 | 79% |
| 0.063056 | 81% |
| 0.070833 | 82% |
| 0.079167 | 83% |
| 0.086667 | 84% |
| 0.095833 | 86% |
| 0.105 | 86% |
| 0.114444 | 86% |
| 0.123611 | 88% |
| 0.132778 | 88% |
| 0.141944 | 89% |
| 0.151111 | 89% |
| 0.16 | 90% |
| 0.169167 | 90% |
| 0.178333 | 90% |
| 0.193333 | 91% |
| 0.208056 | 91% |
| 0.222778 | 91% |
| 0.237778 | 91% |
| 0.2525 | 92% |
| 0.2675 | 92% |
| 0.2825 | 92% |
| 0.296944 | 93% |
| 0.311944 | 91% |
| 0.326667 | 93% |
| 0.35 | 93% |

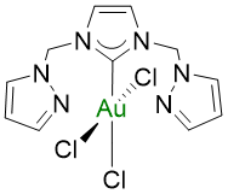
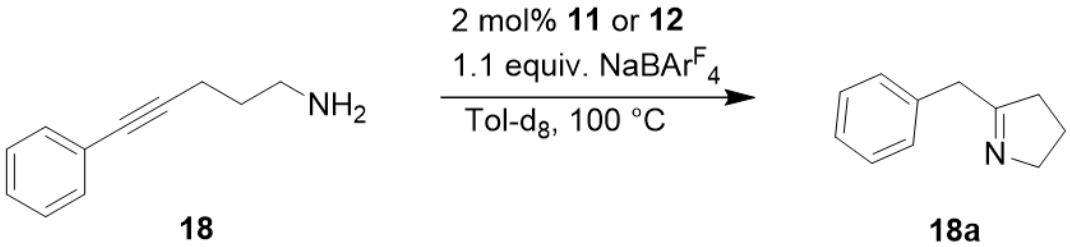



**Table 7.63** Catalysed hydroamination of **17** using **12** at 100 °C.

| Time(h) | %conv |
|---|---|
| 0 | 0% |
| 0.007778 | 39% |
| 0.015556 | 51% |
| 0.023333 | 60% |
| 0.031389 | 67% |
| 0.039167 | 71% |
| 0.046944 | 75% |
| 0.054722 | 78% |
| 0.0625 | 81% |
| 0.070278 | 82% |

| | |
|---|---|
| 0.078333 | 85% |
| 0.085833 | 86% |
| 0.095 | 87% |
| 0.104167 | 89% |
| 0.113611 | 89% |
| 0.122778 | 91% |
| 0.131667 | 92% |
| 0.140833 | 92% |
| 0.150278 | 94% |
| 0.159722 | 94% |
| 0.170278 | 94% |
| 0.179444 | 95% |
| 0.195 | 95% |
| 0.209722 | 96% |
| 0.224722 | 96% |
| 0.239444 | 96% |
| 0.254444 | 97% |

### 7.2.3.8. Catalysed hydroamination of 18 using 11 or 12.



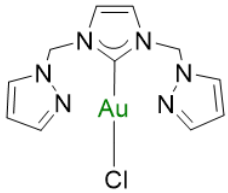
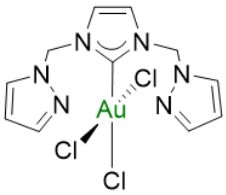




**Table 7.64** Catalysed hydroamination of **18** using **11** at 100 °C.

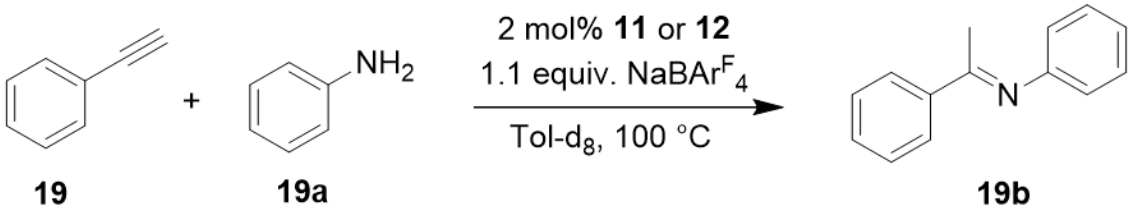
| Time(h) | %conv |
|---|---|
| 0 | 0% |
| 0.033333 | 50% |
| 0.066667 | 61% |
| 0.1 | 76% |
| 0.15 | 88% |
| 0.233333 | 94% |
| 0.4 | 98% |
| | 0.00% |

Table 7.65 Catalysed hydroamination of 18 using 12 at 100 °C.



| time(h) | %conv |
|---|---|
| 0 | 0% |
| 0.033333 | 69% |
| 0.066667 | 81% |
| 0.1 | 89% |
| 0.15 | 95% |
| 0.233333 | 98% |
| 0.4 | 100% |

### 7.2.3.9. Catalysed intermolecular hydroamination of 19 with 19a using 11 or 12



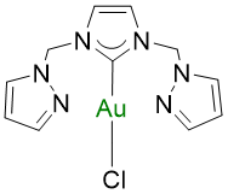



Table 7.66 Catalysed intermolecular hydroamination of 19 with 19a using 11 at 100 °C.

| Time(h) | %conv |
|---|---|
| 0 | 0 |
| 0.033 | 17 |
| 0.066 | 20 |
| 0.15 | 24 |
| 0.5 | 27 |
| 1 | 28 |
| 20 | 31 |

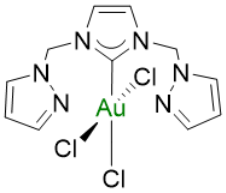
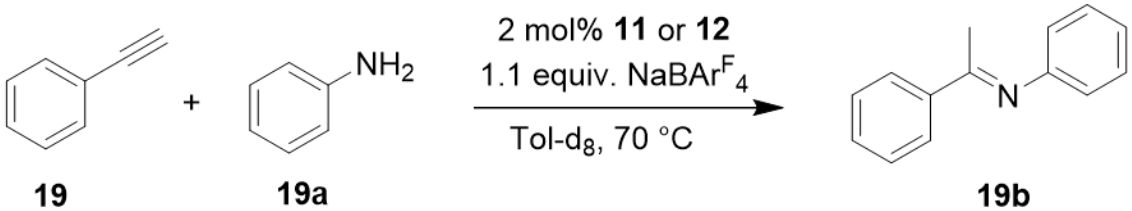


**Table 7.67** Catalysed intermolecular hydroamination of **19** with **19a** using **12** at 100 °C.

| Time(h) | %conv |
|---|---|
| 0 | 0 |
| 0.033 | 9 |
| 0.066 | 12 |
| 0.15 | 16 |
| 0.5 | 19 |
| 1 | 21 |
| 20 | 26 |



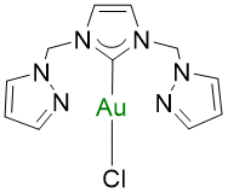



**Table 7.68** Catalysed intermolecular hydroamination of **19** with **19a** using **11** at 70 °C.

| Time(h) | %conv |
|---|---|
| 0 | 0 |
| 0.033 | 24 |
| 0.066 | 26 |
| 0.15 | 28 |
| 0.5 | 29 |
| 1 | 30 |
| 20 | 30 |

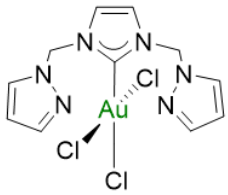



**Table 7.69** Catalysed intermolecular hydroamination of **19** with **19a** using **12** at 70 °C.

| Time(h) | %conv |
|---|---|
| 0 | 0 |
| 0.033 | 8 |
| 0.066 | 21 |
| 0.15 | 24 |
| 0.5 | 26 |
| 1 | 26 |
| 20 | 26 |

## 7.3. References:

(1) *Bruker, A., Bruker AXS Inc., Madison, WI,* 2007.

(2) Sheldrick, G. M. *Acta Crystallogr. Sect. A: Found. Crystallogr.* 2007, *64*, 112.

(3) Macrae, C. F.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Shields, G. P. *J. Appl. Crystallogr.* 2006, *39*, 453.