

Chloride Abstraction from Ruthenium Alkyl  
*Bis*-diphosphine Dichlorides

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## Abstract

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Despite their early discovery, relatively few classes of ruthenium dinitrogen complexes are known. This work describes the successful coordination of dinitrogen to the electron-rich alkylphosphine cores  $[\text{RuCl}(\text{dmpe})_2]^+$  and  $[\text{RuCl}(\text{depe})_2]^+$  by chloride abstraction from both the *cis* and *trans* dichloro derivatives. One such complex, *trans*- $[\text{RuCl}(\text{N}_2)(\text{dmpe})_2](\text{BArF}_{24})$ , possesses the most activated ruthenium  $\nu_{\text{NN}}$  reported to date.

A variety of chloride abstraction agents were tested on the *cis* and *trans* isomers of  $[\text{RuCl}_2(\text{P-P})_2]$  (P-P = dmpe, depe) with the choice of abstracting agent, anion and solvent all found to significantly affect the outcome. Reaction with silver triflate and trimethylsilyl triflate was found to give dichlororuthenium(III) products, which could be readily reduced to the ruthenium(II) starting materials with common reducing agents, as well as by alcohols and hydrazine.

The use of thallium triflate avoided oxidation and led to the formation of the crystallographically characterised polymeric incorporation product,  $[\{\text{trans}-[\text{RuCl}_2(\text{dmpe})_2]\cdot\text{Tl}(\text{OTf})\}_n]$  from *trans*- $[\text{RuCl}_2(\text{dmpe})_2]$  and the interesting chloride-bridged ruthenium dimer *cis*- $[\{\text{Ru}(\text{depe})_2\}_2(\mu\text{-Cl})_2](\text{OTf})_2$  from *trans*- $[\text{RuCl}_2(\text{depe})_2]$ . Anion exchange of the complex  $[\{\text{trans}-[\text{RuCl}_2(\text{dmpe})_2]\cdot\text{Tl}(\text{OTf})\}_n]$  with the non-coordinating anion *tetrakis*(3,5-bis(trifluoromethyl)phenyl)borate resulted in removal of thallium from the system and coordination of dinitrogen to give *trans*- $[\text{RuCl}(\text{N}_2)(\text{dmpe})_2](\text{BArF}_{24})$ . *Cis*- $[\{\text{Ru}(\text{depe})_2\}_2(\mu\text{-Cl})_2](\text{OTf})_2$  was found to readily react with a variety of small ligands and gave products such as *cis*- $[\text{RuCl}(\text{CO})(\text{depe})_2](\text{OTf})$ , *cis*- $[\text{RuCl}(\text{NCMe})(\text{depe})_2](\text{OTf})$ , *cis*- $[\text{RuCl}(\text{CN}^t\text{Bu})(\text{depe})_2](\text{OTf})$ , *cis*- $[\text{RuCl}(\text{NH}_3)(\text{depe})_2](\text{OTf})$ , *cis*- $[\text{RuCl}(\text{N}_3)(\text{depe})_2]$ , and *trans*- $[\text{RuCl}(\eta^2\text{-H}_2)(\text{depe})_2](\text{OTf})$ . A preliminary X-ray single crystal structure analysis was conducted on the complex *cis*- $[\text{RuCl}(\text{CN}^t\text{Bu})(\text{depe})_2](\text{OTf})$ .

The thallium(I) salt  $\text{Tl}(\text{BArF}_{24})$  was found to be an efficient chloride abstraction agent under mild conditions. Reactions with *cis*- and *trans*- $[\text{RuCl}_2(\text{depe})_2]$  and *cis*- $[\text{RuCl}_2(\text{dmpe})_2]$  furnished dinitrogen complexes of the form *cis*- $[\{\text{RuCl}(\text{P-P})_2\}_2(\mu\text{-N}_2)](\text{BArF}_{24})_2$ , whilst reaction of *trans*- $[\text{RuCl}_2(\text{dmpe})_2]$  with  $\text{Tl}(\text{BArF}_{24})$  led to the stable five-coordinate complex *trans*- $[\text{RuCl}(\text{dmpe})_2](\text{BArF}_{24})$ . Vapour diffusion techniques applied to a solution of *cis*- $[\{\text{RuCl}(\text{depe})_2\}_2(\mu\text{-N}_2)](\text{BArF}_{24})_2$  gave rise to crystals of

*trans*-[RuCl(N<sub>2</sub>)(depe)<sub>2</sub>](BArF<sub>24</sub>), on which preliminary X-ray molecular structure analysis was performed.

Reactions of both *cis*-[Ru(depe)<sub>2</sub>]<sub>2</sub>(μ-Cl)<sub>2</sub>(OTf)<sub>2</sub> and *trans*-[RuCl<sub>2</sub>(dmpe)<sub>2</sub>] with high pressure (140 psi) dinitrogen at 140-150°C in methanol or tetrahydrofuran resulted in solvent carbonyl abstraction to afford *trans*-[RuCl(CO)(depe)<sub>2</sub>](OTf) and *trans*-[RuCl(CO)(dmpe)<sub>2</sub>](Cl) from the depe and dmpe complexes respectively. The molecular structure of *trans*-[RuCl(CO)(dmpe)<sub>2</sub>](Cl) was determined *via* single crystal X-ray structure analysis.

# Table of Contents

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<i>Abstract</i> .....	<i>iii</i>
<i>List of Figures</i> .....	<i>xii</i>
<i>List of Tables</i> .....	<i>xvi</i>
<i>List of Abbreviations</i> .....	<i>xvii</i>

## Chapter 1 – Introduction

<b>1.1 Nitrogen fixation</b> .....	<b>1</b>
1.1.1 Biological nitrogen fixation.....	2
1.1.2 Industrial nitrogen fixation.....	6
1.1.3 Laboratory nitrogen fixation .....	9
<b>1.2 Ruthenium dinitrogen chemistry</b> .....	<b>15</b>
1.2.1 Ruthenium dinitrogen complexes with pincer co-ligands .....	17
1.2.2 Ruthenium dinitrogen complexes with sulfur co-ligands.....	23
1.2.3 Ruthenium dinitrogen complexes with nitrogen co-ligand .....	30
1.2.4 Ruthenium dinitrogen complexes of phosphine ligands .....	45
1.2.5 Ruthenium dinitrogen complexes of other ligands .....	54
1.2.6 Overall trends in ruthenium dinitrogen complexes .....	61

## Chapter 2 – Reactions of $[\text{Ru}(\text{L}^1)(\text{L}^2)(\text{dmpe})_2]$ ( $\text{L}^1 = \text{Cl}; \text{L}^2 = \text{Cl}, \text{H}$ )

<b>2.1 Introduction</b> .....	<b>81</b>
<b>2.2 Xray crystal structure of <math>\text{trans}-[\text{RuCl}_2(\text{dmpe})_2]</math></b> .....	<b>84</b>
<b>2.3 Direct reactions of <math>\text{trans}-[\text{RuCl}_2(\text{dmpe})_2]</math></b> .....	<b>86</b>
<b>2.4 Direct reactions with <math>\text{trans}-[\text{RuCl}(\text{H})(\text{dmpe})_2]</math></b> .....	<b>87</b>
<b>2.5 Reaction of <math>\text{trans}-[\text{RuCl}_2(\text{dmpe})_2]</math> with chloride abstraction agents..</b>	<b>87</b>
2.5.1 Treatment of $\text{trans}-[\text{RuCl}_2(\text{dmpe})_2]$ with $\text{Ag}(\text{OTf})$ in dcm.....	88

2.5.2	Treatment of <i>trans</i> -[RuCl <sub>2</sub> (dmpe) <sub>2</sub> ] with TMS(OTf) in toluene.....	91
2.5.3	Treatment of <i>trans</i> -[RuCl <sub>2</sub> (dmpe) <sub>2</sub> ] with Tl(OTf) in thf.....	92
2.5.4	Treatment of <i>trans</i> -[RuCl <sub>2</sub> (dmpe) <sub>2</sub> ]·Tl(OTf) with Na(BPh <sub>4</sub> )/Na(BF <sub>4</sub> )	100
2.5.5	Treatment of <i>trans</i> -[RuCl <sub>2</sub> (dmpe) <sub>2</sub> ]·Tl(OTf) with Na(BArF <sub>24</sub> ).....	100
2.5.6	Treatment of <i>trans</i> -[RuCl <sub>2</sub> (dmpe) <sub>2</sub> ] with Na(BArF <sub>24</sub> ) in MeOH.....	103
2.5.7	Treatment of <i>trans</i> -[RuCl <sub>2</sub> (dmpe) <sub>2</sub> ] with Ag(OTf) in MeOH.....	106
2.5.8	Treatment of <i>trans</i> -[RuCl <sub>2</sub> (dmpe) <sub>2</sub> ] with TMS(OTf) in MeOH.....	109
2.5.9	Treatment of <i>trans</i> -[RuCl <sub>2</sub> (dmpe) <sub>2</sub> ] with Tl(BArF <sub>24</sub> ) in MeOH.....	111
2.5.10	Treatment of <i>trans</i> -[RuCl <sub>2</sub> (dmpe) <sub>2</sub> ] with Tl(BF <sub>4</sub> ) in MeOH.....	114
2.5.11	Treatment of <i>trans</i> -[RuCl <sub>2</sub> (dmpe) <sub>2</sub> ] with Na(BPh <sub>4</sub> ) under 140 psi N <sub>2</sub>	115
<b>2.6</b>	<b>Reactions of <i>cis</i>-[RuCl<sub>2</sub>(dmpe)<sub>2</sub>] .....</b>	<b>121</b>
2.6.1	Treatment of <i>cis</i> -[RuCl <sub>2</sub> (dmpe) <sub>2</sub> ] with TMS(OTf) in MeOH.....	122
2.6.2	Treatment of <i>cis</i> -[RuCl <sub>2</sub> (dmpe) <sub>2</sub> ] with Tl(BArF <sub>24</sub> ) in MeOH.....	124
2.6.3	Treatment of <i>cis</i> -[RuCl <sub>2</sub> (dmpe) <sub>2</sub> ] with Tl(BF <sub>4</sub> ) in MeOH.....	126
<b>2.7</b>	<b>Reactions of <i>trans</i>-[RuCl<sub>2</sub>(dmpe)<sub>2</sub>](OTf) .....</b>	<b>128</b>
<b>2.8</b>	<b>Conclusions .....</b>	<b>129</b>

## Chapter 3 – Reactions of [RuCl<sub>2</sub>(depe)<sub>2</sub>]

<b>3.1</b>	<b>Introduction .....</b>	<b>137</b>
<b>3.2</b>	<b>Reactions of <i>trans</i>-[RuCl<sub>2</sub>(depe)<sub>2</sub>].....</b>	<b>138</b>
3.2.1	Treatment of <i>trans</i> -[RuCl <sub>2</sub> (depe) <sub>2</sub> ] with Ag(OTf) in dcm.....	138
3.2.2	Treatment of <i>trans</i> -[RuCl <sub>2</sub> (depe) <sub>2</sub> ] with TMS(OTf) in toluene.....	138
3.2.3	Treatment of <i>trans</i> -[RuCl <sub>2</sub> (depe) <sub>2</sub> ] with Tl(OTf) in thf.....	140
3.2.4	Reactions of <i>cis</i> -[{Ru(depe) <sub>2</sub> } <sub>2</sub> (μ-Cl) <sub>2</sub> ](OTf) <sub>2</sub> .....	147
3.2.5	Treatment of <i>trans</i> -[RuCl <sub>2</sub> (depe) <sub>2</sub> ] with TMS(OTf) in MeOH.....	148
3.2.6	Treatment of <i>trans</i> -[RuCl <sub>2</sub> (depe) <sub>2</sub> ] with Ag(OTf) in MeOH.....	149
3.2.7	Treatment of <i>trans</i> -[RuCl <sub>2</sub> (depe) <sub>2</sub> ] with Tl(BArF <sub>24</sub> ) in MeOH.....	152
3.2.8	Treatment of <i>trans</i> -[RuCl <sub>2</sub> (depe) <sub>2</sub> ] with Tl(BF <sub>4</sub> ) in MeOH.....	156

<b>3.3</b>	<b><i>Reactions of cis-[RuCl<sub>2</sub>(depe)<sub>2</sub>]</i></b> .....	<b>159</b>
3.3.1	Treatment of <i>cis</i> -[RuCl <sub>2</sub> (depe) <sub>2</sub> ] with TMS(OTf) in methanol.....	159
3.3.2	Treatment of <i>cis</i> -[RuCl <sub>2</sub> (depe) <sub>2</sub> ] with Tl(BArF <sub>24</sub> ) in methanol .....	160
3.3.3	Treatment of <i>cis</i> -[RuCl <sub>2</sub> (depe) <sub>2</sub> ] with Tl(BF <sub>4</sub> ) in methanol.....	161
<b>3.4</b>	<b><i>Conclusions</i></b> .....	<b>163</b>

## Chapter 4 – Reactions of [Ru<sub>2</sub>Cl<sub>2</sub>(depe)<sub>4</sub>](OTf)<sub>2</sub>

<b>4.1</b>	<b><i>Introduction</i></b> .....	<b>166</b>
<b>4.2</b>	<b><i>Reactions with neutral ligands</i></b> .....	<b>168</b>
4.2.1	Reaction with carbon monoxide .....	168
4.2.2	Reaction with acetonitrile.....	171
4.2.3	Reaction with <i>tert</i> -butyl isonitrile.....	173
4.2.4	Reaction with <sup>15</sup> N-ammonia .....	179
4.2.5	Reaction with hydrazine .....	180
4.2.6	Reaction with hydrogen .....	181
4.2.7	Reaction with high pressure dinitrogen .....	186
4.2.8	Reactions with CO <sub>2</sub> , H <sub>2</sub> CCH <sub>2</sub> , and N <sub>2</sub> O .....	188
<b>4.3</b>	<b><i>Reactions with anionic ligands</i></b> .....	<b>188</b>
4.3.1	Reaction with sodium tetraphenylborate.....	188
4.3.2	Reaction with sodium azide .....	188
<b>4.4</b>	<b><sup>31</sup>P{<sup>1</sup>H} simulation of unsymmetrical <i>cis</i>-[RuXY(P-P)<sub>2</sub>] complexes..</b>	<b>190</b>
<b>4.5</b>	<b><i>Conclusions</i></b> .....	<b>195</b>

## Chapter 5 – Tripodal phosphine ligands

<b>5.1</b>	<b><i>Introduction</i></b> .....	<b>201</b>
<b>5.2</b>	<b><i>Synthesis of tripodal phosphine ligands</i></b> .....	<b>205</b>
5.2.1	Preparation of <i>tris</i> (2-dimethylphosphinoethyl)phosphine.....	205
5.2.2	Preparation of <i>tris</i> (2-diphenylphosphinoethyl)phosphine.....	207
5.2.3	Attempted preparation of <i>tris</i> (3-dimethylphosphinopropyl)- phosphine .....	208
<b>5.3</b>	<b><i>Conclusions</i></b> .....	<b>213</b>

## Chapter 6 – Conclusions and future work

<b>6.1</b>	<b><i>Conclusions</i></b> .....	<b>216</b>
<b>6.2</b>	<b><i>Future work</i></b> .....	<b>218</b>

## Chapter 7 – Experimental

<b>7.1</b>	<b><i>General Procedures</i></b> .....	<b>221</b>
<b>7.2</b>	<b><i>Ligand synthesis</i></b> .....	<b>226</b>
7.2.1	Trichlorophosphine sulfide .....	226
7.2.2	Methylmagnesium iodide .....	226
7.2.3	Tetramethyldiphosphine disulfide.....	227
7.2.4	Dimethylphosphine .....	228
7.2.5	Diphenylphosphine .....	229
7.2.6	Vinylmagnesium bromide .....	229
7.2.7	Trivinylphosphine.....	230
7.2.8	Lithium diisopropylamide .....	230
7.2.9	Titration of lithium diisopropylamide .....	231
7.2.10	<i>Tris</i> ((dimethylphosphino)ethyl)phosphine .....	231
7.2.11	<i>Tris</i> ((diphenylphosphino)ethyl)phosphine.....	232
7.2.12	<i>Tris</i> ( <i>sec</i> (dimethylphosphino)propyl)phosphine .....	233
7.2.13	Reaction of triallylphosphine with lithium diisopropylamide .....	234



7.2.14	<i>Tris</i> (3-hydroxypropyl)amine .....	234
7.2.15	<i>Tris</i> (3-bromopropyl)amine .....	235
7.2.16	<i>Tris</i> (3-(diphenylphosphino)propyl)amine .....	236
7.2.17	(2-bromophenyl)diphenylphosphine .....	237
7.2.18	1-(phenyl(2-(diphenylphosphino)phenyl)phosphino)-2-(diphenylphosphino)benzene .....	238
<b>7.3</b>	<b><i>Metal Complex Precursors</i></b> .....	<b>239</b>
7.3.1	Dichloro <i>tris</i> (triphenylphosphine)ruthenium(II) .....	239
7.3.2	Chlorohydrido <i>tris</i> (triphenylphosphine)ruthenium(II) .....	240
7.3.3	<i>Trans</i> -dichloro <i>bis</i> (1,2- <i>bis</i> (dimethylphosphino)ethane)ruthenium(II) .....	241
7.3.4	<i>Trans</i> -dichloro <i>bis</i> (1,2- <i>bis</i> (diethylphosphino)ethane)ruthenium(II)....	242
7.3.5	<i>Trans</i> -chlorohydrido <i>bis</i> (1,2- <i>bis</i> (dimethylphosphino)ethane)-ruthenium(II) .....	243
7.3.6	<i>Cis</i> -dihydrido <i>bis</i> (1,2- <i>bis</i> (dimethylphosphino)ethane)ruthenium(II) .	243
7.3.7	<i>Cis</i> -dihydrido <i>bis</i> (1,2- <i>bis</i> (diethylphosphino)ethane)ruthenium(II) ....	244
7.3.8	<i>Tri-μ</i> -chloro- <i>hexakis</i> (dimethylphenylphosphine)diruthenium(II) chloride .....	245
7.3.9	<i>Cis</i> -dichloro <i>bis</i> (1,2- <i>bis</i> (dimethylphosphino)ethane)ruthenium(II) ...	246
7.3.10	<i>Cis</i> -dichloro <i>bis</i> (1,2- <i>bis</i> (diethylphosphino)ethane)ruthenium(II) .....	247
<b>7.4</b>	<b><i>Ruthenium Complexes of Triphos**</i></b> .....	<b>247</b>
7.4.1	Reaction of [RuCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>3</sub> ] with triphos** in acetone .....	247
<b>7.5</b>	<b><i>Direct Reaction with Ruthenium Dichlorides</i></b> .....	<b>248</b>
7.5.1	Reaction of <i>trans</i> -[RuCl <sub>2</sub> (dmpe) <sub>2</sub> ] with hydrazine .....	248
7.5.2	Reaction of <i>trans</i> -[RuCl(H)(dmpe) <sub>2</sub> ] with hydrazine.....	249
7.5.3	Reaction of <i>cis</i> -[Ru(H) <sub>2</sub> (dmpe) <sub>2</sub> ] with hydrazine .....	249
7.5.4	Reaction of <i>cis</i> -[Ru(H) <sub>2</sub> (depe) <sub>2</sub> ] with triflic acid.....	249

<b>7.6</b>	<b><i>Synthesis of Chloride Abstraction Reagents</i></b> .....	<b>250</b>
7.6.1	Thallium(I) triflate .....	250
7.6.2	Isopropylmagnesium(II) chloride .....	251
7.6.3	Sodium <i>tetrakis</i> (3,5- <i>bis</i> (trifluoromethyl)phenyl)borate.....	251
7.6.4	[H(OEt <sub>2</sub> ) <sub>2</sub> ][B(C <sub>6</sub> H <sub>3</sub> (CF <sub>3</sub> ) <sub>2</sub> ) <sub>4</sub> ].....	252
7.6.5	Thallium <i>tetrakis</i> (3,5- <i>bis</i> (trifluoromethyl)phenyl)borate.....	253
7.6.6	Thallium tetrafluoroborate .....	253
<b>7.7</b>	<b><i>Reaction of ruthenium dichlorides with chloride abstraction agents</i></b> .....	<b>254</b>
7.7.1	Reaction of <i>trans</i> -[RuCl <sub>2</sub> (dmpe) <sub>2</sub> ] with AgOTf in dcm.....	254
7.7.2	Reaction of <i>trans</i> -[RuCl <sub>2</sub> (dmpe) <sub>2</sub> ] with TMSOTf in toluene.....	255
7.7.3	Reaction of <i>trans</i> -[RuCl <sub>2</sub> (dmpe) <sub>2</sub> ] with Tl(OTf) in thf.....	256
7.7.4	Reaction of <i>trans</i> -[RuCl <sub>2</sub> (dmpe) <sub>2</sub> ] with Na(BArF <sub>24</sub> ) in MeOH .....	257
7.7.5	Reaction of <i>trans</i> -[RuCl <sub>2</sub> (dmpe) <sub>2</sub> ] with Ag(OTf) in MeOH.....	258
7.7.6	Reaction of <i>trans</i> -[RuCl <sub>2</sub> (dmpe) <sub>2</sub> ] with TMSOTf in MeOH .....	259
7.7.7	Reaction of <i>trans</i> -[RuCl <sub>2</sub> (dmpe) <sub>2</sub> ] with Tl(BArF <sub>24</sub> )in MeOH .....	260
7.7.8	Reaction of <i>trans</i> -[RuCl <sub>2</sub> (dmpe) <sub>2</sub> ] with Tl(BF <sub>4</sub> ) in MeOH.....	261
7.7.9	Reaction of <i>trans</i> -[RuCl <sub>2</sub> (dmpe) <sub>2</sub> ] with Na(BPh <sub>4</sub> ) under high pressure N <sub>2</sub> in MeOH .....	262
7.7.10	Reaction of <i>trans</i> -[RuCl <sub>2</sub> (dmpe) <sub>2</sub> ] with Na(BPh <sub>4</sub> ) under high pressure N <sub>2</sub> in thf.....	264
7.7.11	Reaction of <i>cis</i> -[RuCl <sub>2</sub> (dmpe) <sub>2</sub> ] with TMSOTf in MeOH .....	265
7.7.12	Reaction of <i>cis</i> -[RuCl <sub>2</sub> (dmpe) <sub>2</sub> ] with Tl(BArF <sub>24</sub> )in MeOH .....	266
7.7.13	Reaction of <i>cis</i> -[RuCl <sub>2</sub> (dmpe) <sub>2</sub> ] with Tl(BF <sub>4</sub> ) in MeOH.....	267
7.7.14	Reaction of <i>trans</i> -[RuCl <sub>2</sub> (depe) <sub>2</sub> ] with TMSOTf in toluene.....	268
7.7.15	Reaction of <i>trans</i> -[RuCl <sub>2</sub> (depe) <sub>2</sub> ] with Tl(OTf) in thf.....	269
7.7.16	Reaction of <i>trans</i> -[RuCl <sub>2</sub> (depe) <sub>2</sub> ] with TMSOTf in MeOH .....	270
7.7.17	Reaction of <i>trans</i> -[RuCl <sub>2</sub> (depe) <sub>2</sub> ] with Ag(OTf) in MeOH .....	271
7.7.18	Reaction of <i>trans</i> -[RuCl <sub>2</sub> (depe) <sub>2</sub> ] with Tl(BArF <sub>24</sub> ) in MeOH .....	272
7.7.19	Reaction of <i>trans</i> -[RuCl <sub>2</sub> (depe) <sub>2</sub> ] with Tl(BF <sub>4</sub> ) in MeOH.....	273
7.7.20	Reaction of <i>cis</i> -[RuCl <sub>2</sub> (depe) <sub>2</sub> ] with TMSOTf in MeOH .....	274

7.7.21	Reaction of <i>cis</i> -[RuCl <sub>2</sub> (depe) <sub>2</sub> ] with Tl(BArF <sub>24</sub> ) in MeOH .....	275
7.7.22	Reaction of <i>cis</i> -[RuCl <sub>2</sub> (depe) <sub>2</sub> ] with Tl(BF <sub>4</sub> ) in MeOH .....	276
<b>7.8 Reactions of <i>trans</i>-dichlorobis(1,2-bis(dimethylphosphino)ethane)</b>		
<b><i>ruthenium(II), Tl(OTf)</i> .....</b>		<b>277</b>
7.8.1	Reaction of <i>trans</i> -[RuCl <sub>2</sub> (dmpe) <sub>2</sub> ]·Tl(OTf) with Na(BPh <sub>4</sub> ) .....	277
7.8.2	Reaction of <i>trans</i> -[RuCl <sub>2</sub> (dmpe) <sub>2</sub> ]·Tl(OTf) with Na(BArF <sub>24</sub> ) .....	278
7.8.3	Reaction of <i>trans</i> -[RuCl <sub>2</sub> (dmpe) <sub>2</sub> ]·Tl(OTf) with hydrazine .....	279
7.8.4	Reaction of <i>trans</i> -[RuCl <sub>2</sub> (dmpe) <sub>2</sub> ]·Tl(OTf) with ammonia.....	280
<b>7.9 Reactions of <i>di-μ</i>-chlorotetrakis(1,2-bis(diethylphosphino)ethane)</b>		
<b><i>diruthenium(II) ditriflate</i> .....</b>		<b>281</b>
7.9.1	Reaction of [Ru <sub>2</sub> Cl <sub>2</sub> (depe) <sub>4</sub> ](OTf) <sub>2</sub> with carbon monoxide.....	281
7.9.2	Reaction of [Ru <sub>2</sub> Cl <sub>2</sub> (depe) <sub>4</sub> ](OTf) <sub>2</sub> with acetonitrile .....	282
7.9.3	Reaction of [Ru <sub>2</sub> Cl <sub>2</sub> (depe) <sub>4</sub> ](OTf) <sub>2</sub> with <i>tert</i> -butyl isonitrile .....	283
7.9.4	Reaction of [Ru <sub>2</sub> Cl <sub>2</sub> (depe) <sub>4</sub> ](OTf) <sub>2</sub> with <sup>15</sup> N-ammonia .....	284
7.9.5	Reaction of [Ru <sub>2</sub> Cl <sub>2</sub> (depe) <sub>4</sub> ](OTf) <sub>2</sub> with hydrazine.....	285
7.9.6	Reaction of [Ru <sub>2</sub> Cl <sub>2</sub> (depe) <sub>4</sub> ](OTf) <sub>2</sub> with hydrogen.....	286
7.9.7	Reaction of [Ru <sub>2</sub> Cl <sub>2</sub> (depe) <sub>4</sub> ](OTf) <sub>2</sub> with high pressure dinitrogen ...	286
7.9.8	Reaction of [Ru <sub>2</sub> Cl <sub>2</sub> (depe) <sub>4</sub> ](OTf) <sub>2</sub> with CO <sub>2</sub> , H <sub>2</sub> CCH <sub>2</sub> , and N <sub>2</sub> O ....	287
7.9.9	Reaction of [Ru <sub>2</sub> Cl <sub>2</sub> (depe) <sub>4</sub> ](OTf) <sub>2</sub> with sodium tetraphenylborate .	288
7.9.10	Reaction of [Ru <sub>2</sub> Cl <sub>2</sub> (depe) <sub>4</sub> ](OTf) <sub>2</sub> with sodium azide .....	288

## Chapter 8 – Appendixes

<b>8.1 Appendix 1 – crystal data .....</b>		<b>292</b>
8.1.1	Data for <i>trans</i> -[RuCl <sub>2</sub> (dmpe) <sub>2</sub> ].....	292
8.1.2	Data for <i>trans</i> -[RuCl <sub>2</sub> (dmpe) <sub>2</sub> ](OTf).....	304

## List of Figures

---

Figure 1.1 – Model of the FeMo-cofactor of nitrogenase .....	3
Figure 1.2 – Varying amino acid substitution in wild-type FeMo protein .....	5
Figure 1.3 – Simplified view of end-on dinitrogen bonding. ....	10
Figure 1.4 – Idealised Chatt cycle for nitrogen fixation on a Group 6 metal .....	13
Figure 1.5 – [Mo(N <sub>2</sub> )(HIPTN <sub>3</sub> N)], which catalytically reduces dinitrogen to ammonia in the presence of [lutidinium](BARF <sub>24</sub> ) and decamethylchromocene .....	14
Figure 1.6 – Formation of the 16e <sup>-</sup> cyclometalated [(PNP)Ru(N <sub>2</sub> )](OTf) .....	18
Figure 1.7 – Dinitrogen complexes of ruthenium bearing POP-based ligands .....	19
Figure 1.8 – The 16e <sup>-</sup> PCP complex [Ru(SiPhHCl)(N <sub>2</sub> )(PCP- <sup>t</sup> Bu)] .....	20
Figure 1.9 – Monomer-dimer equilibrium in the hydrido-dinitrogen complexes of Ru(PCP- <sup>t</sup> Bu) .....	21
Figure 1.10 – Formation of the 18e <sup>-</sup> per ruthenium centre bimetallic pincer complex [{RuCl <sub>2</sub> (NN'N)} <sub>2</sub> (μ-N <sub>2</sub> )] .....	21
Figure 1.11 – Reactivity of [{RuCl <sub>2</sub> (NN'N)} <sub>2</sub> (μ-N <sub>2</sub> )] with various small unsaturated molecules .....	22
Figure 1.12 – Reactivity of [{RuCl <sub>2</sub> (PNP- <sup>t</sup> Bu)} <sub>2</sub> (μ-N <sub>2</sub> )] .....	23
Figure 1.13 – Reactions of [Ru(py <sup>b</sup> uS <sub>4</sub> ) <sub>2</sub> ] .....	26
Figure 1.14 – Facile coordination of N <sub>2</sub> to the ruthenium thiolate fragment [Ru(P <sup>i</sup> Pr <sub>3</sub> )(N <sub>2</sub> Me <sub>2</sub> S <sub>2</sub> ') .....	27
Figure 1.15 – Dimerisation of [Ru(N <sub>2</sub> )(P <sup>i</sup> Pr <sub>3</sub> )(N <sub>2</sub> Me <sub>2</sub> S <sub>2</sub> ') .....	28
Figure 1.16 – Dinitrogen fixation targets coordinated by 'Ru(P <sup>i</sup> Pr <sub>3</sub> )(N <sub>2</sub> Me <sub>2</sub> S <sub>2</sub> ') .....	29
Figure 1.17 – Reversible loss of N <sub>2</sub> from [Ru(N <sub>2</sub> )(PCy <sub>3</sub> )(N <sub>2</sub> Me <sub>2</sub> S <sub>2</sub> ') .....	30
Figure 1.18 – Formation of [TpRu(L)(pn)] <sup>+</sup> (L = H <sub>2</sub> O, MeCN, acetone, vinylidene, CO, N <sub>2</sub> ) .....	32
Figure 1.19 – Formation of [TpRu(L)(P) <sub>2</sub> ] <sup>+</sup> (L = CO, <sup>t</sup> BuNC, N <sub>2</sub> ) .....	34
Figure 1.20 – [{RuCl(NNNN)} <sub>2</sub> (μ-N <sub>2</sub> )] <sup>2+</sup> .....	36
Figure 1.21 – The 14-electron ruthenium complex [Ru(TMP)] .....	38
Figure 1.22 – Ruthenium DPB and coordinated nitrogen substrates .....	40

Figure 1.23 – Formation of $[\text{Ru}(\text{N}_2)(\text{N}_3)(\text{en})_2]^+$ from a diazido intermediate .....	41
Figure 1.24 – Dinitrogen complexes of $[\text{Ru}(\kappa^5\text{-edta})]^{(2-)}$ .....	43
Figure 1.25 – The oxo-bridged ruthenium dimer $[(\text{bpy})_2(\text{NH}_3)\text{RuORu}(\text{NH}_3)(\text{bpy})_2]^{4+}$ ..	45
Figure 1.26 – Equilibrium of $[\{\text{RuH}_2(\text{N}_2)(\text{P}^i\text{Pr}_3)_2\}_2(\mu\text{-N}_2)]$ .....	46
Figure 1.27 – $[\text{Ru}(\text{H})_2(\text{N}_2)(\text{PPh}_3)_3]$ .....	47
Figure 1.28 – Formation of <i>trans</i> - $[\text{RuH}(\text{N}_2)(\text{P-P})_2](\text{BPh}_4)$ (P-P = depe, dppe) .....	48
Figure 1.29 – Dihydrogen / dinitrogen exchange in the complex $[\text{RuCl}(\text{A}_2)((\text{R,R})\text{-CHIRAPHOS})_2]^+$ ( $\text{A}_2 = \text{N}_2, \text{H}_2$ ) .....	49
Figure 1.30 – C-H activation in $[\{\text{Ru}(\text{H})(\text{SiMe}_3)(\text{PMe}_3)_3\}_2(\mu\text{-N}_2)]$ .....	49
Figure 1.31 – The thermolabile square-pyramidal species $[\text{Ru}(\text{H})_2(\text{CO})(\text{P}^t\text{Bu}_2\text{Me})_2]$ ..	50
Figure 1.32 – <i>trans</i> - $[\text{Ru}(\text{N}_2)(\text{H})(\text{R,R}'\text{-Me-DuPHOS})_2](\text{PF}_6)$ .....	51
Figure 1.33 – The chloride-bridged dimer $[(\text{N}_2)(\text{dppb})\text{Ru}(\mu\text{-Cl})_3\text{RuCl}(\text{dppb})]$ .....	52
Figure 1.34 – $[\{\text{RuH}(\text{P}^i\text{Pr}_3)_2\}_2(\mu\text{-Cl})_2]$ reaction with dinitrogen.....	53
Figure 1.35 – $[\text{Ru}(\text{H})(\text{N}_2)(\text{PP}_3)](\text{BPh}_4)$ , containing the rare <i>trans</i> P-Ru-N geometry....	54
Figure 1.36 – Reactions of $[\text{Ru}(\text{N}_2)(\text{H}_2\text{O})_5](\text{tos})_2$ .....	55
Figure 1.37 – Dinitrogen chemistry of $[\text{Ru}(\text{TPPTS})_2(\text{H}_2\text{O})_4](\text{tos})_2$ .....	56
Figure 1.38 – The efficient dinitrogen scavenger $[\text{Ru}(\text{acac})_2(\eta^2\text{-C}_2\text{H}_4)(\text{P}^i\text{Pr}_3)]$ .....	57
Figure 1.39 – $[\{(\text{C}_5\text{H}_5)\text{Ru}(\text{P})_2\}_2(\mu\text{-N}_2)]^{2+}$ spontaneously forms in the presence of even trace amounts of $\text{N}_2$ .....	59
Figure 1.40 – $[(\text{C}_5\text{Me}_5)\text{Ru}(\text{N}_2)(\text{PEt}_3)_2]^+$ .....	60
Figure 1.41 – $[(\text{C}_5\text{R}_5)\text{Ru}(\text{N}_2)(\text{dippe})](\text{BPh}_4)$ .....	61
Figure 2.1 – ORTEP diagram of one <i>trans</i> - $[\text{RuCl}_2(\text{dmpe})_2]$ molecule in the unit cell. ....	85
Figure 2.2 – $^1\text{H}\{^31\text{P}\}$ NMR spectrum of <i>trans</i> - $[\text{RuCl}_2(\text{dmpe})_2](\text{OTf})$ .....	89
Figure 2.3 – ORTEP diagram of <i>trans</i> - $[\text{RuCl}_2(\text{dmpe})_2](\text{OTf})$ .....	90
Figure 2.4 – VT $^31\text{P}\{^1\text{H}\}$ NMR spectra of " <i>trans</i> - $[\text{RuCl}_2(\text{dmpe})_2]\cdot\text{Tl}(\text{OTf})$ " .....	93
Figure 2.5 – Approx. repeating unit in a crystal of " <i>trans</i> - $[\text{RuCl}_2(\text{dmpe})_2]\cdot\text{Tl}(\text{OTf})$ " ..	94
Figure 2.6 – Selected atoms in an <i>isolated slice</i> through the crystal of " <i>trans</i> - $[\text{RuCl}_2(\text{dmpe})_2]\cdot\text{Tl}(\text{OTf})$ " .....	95
Figure 2.7 – ORTEP diagram of $\text{Tl}[\{\text{Ru}(\text{CCtBu})(\text{dcypb})\}_2(\mu\text{-Cl})_3]$ .....	97
Figure 2.8 – ORTEP diagram of $(\text{P}_2)\text{PdCl}_2\cdot\text{Tl}(\text{OTf})$ .....	98

Figure 2.9 – ORTEP diagram of $[\text{TlCl}_2\text{Ru}(\text{PPh}_3)(\text{I9})\text{aneS}_3]_2(\text{PF}_6)_2$ .....	99
Figure 2.10 – Experimental and simulated isotopic distributions of the molecular ion in the mass spectrum of $\text{trans-}[\text{RuCl}(\text{N}_2)(\text{dmpe})_2]^+$ .....	102
Figure 2.11 – $^{31}\text{P}\{^1\text{H}\}$ NMR of the $\text{R}_x^{\text{n}}$ mixture $\text{trans-}[\text{RuCl}_2(\text{dmpe})_2] + \text{Na}(\text{BARF}_{24})$ ..	104
Figure 2.12 – VT $^{31}\text{P}\{^1\text{H}\}$ NMR of the $\text{R}_x^{\text{n}}$ mixture $\text{trans-}[\text{RuCl}_2(\text{dmpe})_2] + \text{Ag}(\text{OTf})$ ..	108
Figure 2.13 – VT $^{31}\text{P}\{^1\text{H}\}$ NMR of the $\text{R}_x^{\text{n}}$ mixture $\text{trans-}[\text{RuCl}_2(\text{dmpe})_2] + \text{TMS}(\text{OTf})$ ..	110
Figure 2.14 – VT $^{31}\text{P}\{^1\text{H}\}$ NMR of the $\text{R}_x^{\text{n}}$ mixture $\text{trans-}[\text{RuCl}_2(\text{dmpe})_2] + \text{Tl}(\text{BARF}_{24})$ ..	113
Figure 2.15 – VT $^{31}\text{P}\{^1\text{H}\}$ NMR of the $\text{R}_x^{\text{n}}$ mixture $\text{trans-}[\text{RuCl}_2(\text{dmpe})_2] + \text{Tl}(\text{BF}_4)$ ..	114
Figure 2.16 – MALDI-MS of the product from the $\text{R}_x^{\text{n}}$ of $\text{trans-}[\text{RuCl}_2(\text{dmpe})_2]$ with $\text{Tl}(\text{BF}_4)$ .....	115
Figure 2.17 – $^{31}\text{P}\{^1\text{H}\}$ NMR of $\text{trans-}[\text{Ru}(\text{L})(\text{CO})(\text{dmpe})_2]^+$ (L = H, Cl) .....	116
Figure 2.18 – ORTEP diagram of $\text{trans-}[\text{RuCl}(\text{CO})(\text{dmpe})_2](\text{Cl})$ .....	119
Figure 2.19 – VT $^{31}\text{P}\{^1\text{H}\}$ NMR of the $\text{R}_x^{\text{n}}$ mixture $\text{cis-}[\text{RuCl}_2(\text{dmpe})_2] + \text{TMS}(\text{OTf})$ ..	123
Figure 2.20 – VT $^{31}\text{P}\{^1\text{H}\}$ NMR of the $\text{R}_x^{\text{n}}$ mixture $\text{cis-}[\text{RuCl}_2(\text{dmpe})_2] + \text{Tl}(\text{BARF}_{24})$ ..	124
Figure 2.21 – VT $^{31}\text{P}\{^1\text{H}\}$ NMR of the $\text{R}_x^{\text{n}}$ mixture $\text{cis-}[\text{RuCl}_2(\text{dmpe})_2] + \text{Tl}(\text{BF}_4)$ .....	127
Figure 3.1 – $^1\text{H}\{^{31}\text{P}\}$ NMR of $\text{trans-}[\text{RuCl}_2(\text{depe})_2](\text{OTf})$ .....	139
Figure 3.2 – VT $^{31}\text{P}\{^1\text{H}\}$ NMR of the $\text{R}_x^{\text{n}}$ mixture $\text{trans-}[\text{RuCl}_2(\text{depe})_2] + \text{Tl}(\text{OTf})$ .....	141
Figure 3.3 – $^{31}\text{P}$ - $^{31}\text{P}$ EXSY spectrum of $[\text{Ru}_2\text{Cl}_2(\text{depe})_4](\text{OTf})_2$ at 300 K .....	142
Figure 3.4 – Experimental and simulated ion envelopes of $[\text{Ru}_2\text{Cl}_2(\text{depe})_4]^+$ .....	143
Figure 3.5 – Representation of thallium-stabilised $\text{cis-}\{[\text{Ru}(\text{depe})_2]_2(\mu\text{-Cl})_2\}(\text{OTf})_2$ ..	146
Figure 3.6 – VT $^{31}\text{P}\{^1\text{H}\}$ NMR of the $\text{R}_x^{\text{n}}$ mixture $\text{trans-}[\text{RuCl}_2(\text{depe})_2] + \text{TMS}(\text{OTf})$ ..	149
Figure 3.7 – VT $^{31}\text{P}\{^1\text{H}\}$ NMR of the $\text{R}_x^{\text{n}}$ mixture $\text{trans-}[\text{RuCl}_2(\text{depe})_2] + \text{Ag}(\text{OTf})$ ...	150
Figure 3.8 – Representation of silver-stabilised $\text{cis-}\{[\text{Ru}(\text{depe})_2]_2(\mu\text{-Cl})_2\}(\text{OTf})_2$ ...	151
Figure 3.9 – VT $^{31}\text{P}\{^1\text{H}\}$ NMR of the $\text{R}_x^{\text{n}}$ mixture $\text{trans-}[\text{RuCl}_2(\text{depe})_2] + \text{Tl}(\text{BARF}_{24})$ ..	154
Figure 3.10 – ORTEP diagram of $\text{trans-}[\text{RuCl}(\text{N}_2)(\text{depe})_2](\text{BARF}_{24})$ .....	155
Figure 3.11 – VT $^{31}\text{P}\{^1\text{H}\}$ NMR of the $\text{R}_x^{\text{n}}$ mixture $\text{trans-}[\text{RuCl}_2(\text{depe})_2] + \text{Tl}(\text{BF}_4)$ ...	157
Figure 3.12 – MALDI-MS of the product from the $\text{R}_x^{\text{n}}$ of $\text{trans-}[\text{RuCl}_2(\text{depe})_2]$ with $\text{Tl}(\text{BF}_4)$ in methanol .....	158
Figure 3.13 – VT $^{31}\text{P}\{^1\text{H}\}$ NMR of the $\text{R}_x^{\text{n}}$ mixture $\text{cis-}[\text{RuCl}_2(\text{depe})_2] + \text{Tl}(\text{BARF}_{24})$ ..	161
Figure 3.14 – VT $^{31}\text{P}\{^1\text{H}\}$ NMR of the $\text{R}_x^{\text{n}}$ mixture $\text{cis-}[\text{RuCl}_2(\text{depe})_2] + \text{Tl}(\text{BF}_4)$ .....	162

Figure 4.1 – Proposed equilibrium mixture of <i>cis</i> -[ $\{\text{Ru}(\text{depe})_2\}_2(\mu\text{-Cl})_2](\text{OTf})_2$ , <i>cis</i> -[ $\text{RuCl}(\text{depe})_2](\text{OTf})$ and <i>cis</i> -[ $\text{RuCl}(\text{OTf})(\text{depe})_2]$ .....	166
Figure 4.2 – Representations of thallium-stabilised <i>cis</i> -[ $\{\text{Ru}(\text{depe})_2\}_2(\mu\text{-Cl})_2](\text{OTf})_2$ .....	168
Figure 4.3 – Comparison of experimental (MALDI-MS) and simulated ion envelopes of <i>cis</i> -[ $\text{RuCl}(\text{CO})(\text{depe})_2]^+$ .....	170
Figure 4.4 – Comparison of experimental (MALDI-MS) and simulated ion envelopes of <i>cis</i> -[ $\text{Ru}(\text{NC})(\text{depe})_2]^+$ .....	173
Figure 4.5 – Comparison of experimental (MALDI-MS) and simulated ion envelopes of <i>cis</i> -[ $\text{RuCl}(\text{CN}^t\text{Bu})(\text{depe})_2]^+$ .....	176
Figure 4.6 – ORTEP diagram of <i>trans</i> -[ $\text{RuCl}(^t\text{BuCN})(\text{depe})_2](\text{BPh}_4)$ .....	178
Figure 4.7 – Stack plot of 1D $^1\text{H}$ NMR $T_1$ inversion-recovery experiments .....	184
Figure 4.8 – Fitted $T_1$ relaxation curve of <i>trans</i> -[ $\text{RuCl}(\eta^2\text{-H}_2)(\text{depe})_2](\text{OTf})$ .....	185
Figure 4.9 – Comparison of experimental (MALDI-MS) and simulated ion envelopes of <i>trans</i> -[ $\text{RuCl}(\text{CO})(\text{depe})_2]^+$ .....	187
Figure 4.10 – Phosphine labelling for simulated $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of unsymmetrical <i>cis</i> complexes prepared in this work .....	192
Figure 4.11 – Simulated and experimental $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of <i>cis</i> - [ $\text{RuCl}(\text{CO})(\text{depe})_2]^+$ .....	192
Figure 5.1 – Types of poly-phosphine ligands .....	202
Figure 5.2 – $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the product formed from the $\text{LiN}(^i\text{Pr})_2$ catalysed coupling of dimethylphosphine and triallylphosphine .....	209
Figure 5.3 – Assigned $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of <i>sec</i> - $\text{P}^3\text{P}^{\prime}_3$ in $d_8$ -thf .....	211
Figure 5.4 – $\text{LiN}(^i\text{Pr})_2$ catalysed sequential double-bond migration in triallylphosphine .....	213

## List of Tables

---

Table 1.1 – Physico-chemical characteristics of the N <sub>2</sub> molecule.....	1
Table 1.2 – N <sub>2</sub> spectral properties of literature ruthenium-dinitrogen complexes in comparison to dinitrogen, diphenyldiazene and hydrazine.....	68
Table 2.1 – Selected bond lengths and angles in <i>trans</i> -[RuCl <sub>2</sub> (dmpe) <sub>2</sub> ].....	85
Table 2.2 – Selected bond lengths and angles in <i>trans</i> -[RuCl <sub>2</sub> (dmpe) <sub>2</sub> ](OTf).....	90
Table 2.3 – Selected bond lengths and angles in <i>trans</i> -[RuCl(CO)(dmpe) <sub>2</sub> ](Cl).....	119
Table 4.1 – Infrared ν <sub>CO</sub> absorptions for selected complexes of the type [Ru(L)(CO)(P-P) <sub>2</sub> ] <sup>x+</sup> (L = Cl, H; P-P = bidentate phosphine; x = 0, 1)	169
Table 4.2 – Infrared ν <sub>NC</sub> absorptions for selected complexes of the type [Ru(L)(CO)(P) <sub>2</sub> ] <sup>+</sup> (L = anionic ligand; P = alkyl- or arylphosphine)....	174
Table 4.3 – Selected preliminary bond lengths and angles in <i>trans</i> - [RuCl( <sup>t</sup> BuCN)(depe) <sub>2</sub> ](BPh <sub>4</sub> ) .....	178
Table 4.4 – A comparison of dihydrogen <sup>1</sup> H T <sub>1</sub> and <sup>1</sup> J <sub>(HD)</sub> values in ruthenium dihydrogen complexes .....	183
Table 4.5 – A comparison of selected ν <sub>NN</sub> values in ruthenium azido/dinitrogen complexes of the type <i>cis</i> -[Ru(X)(Y)(LL) <sub>2</sub> ] <sup>x+</sup> (X, Y = N <sub>3</sub> <sup>-</sup> , N <sub>2</sub> ; LL = en, 2 x PMe <sub>3</sub> , depe; x = 0, 1, 2) .....	190
Table 4.6 – Simulated <sup>31</sup> P{ <sup>1</sup> H} chemical shifts and coupling constants for a series of <i>cis</i> -[RuCl(X)(P-P) <sub>2</sub> ] complexes (P-P = dmpe, depe) .....	194



## List of Abbreviations

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16-TMC	1,5,9,13-tetramethyl-1,5,9,13-tetraazacyclohexadecane
2D	two dimensional (NMR)
3D	three dimensional (NMR)
acac	acetylacetonato
AMU	atomic mass units
APCI	atmospheric pressure chemical ionisation
app.	apparent (NMR)
Ar	aromatic ring
ATP	adenosine triphosphate
ATR	attenuated total reflection IR spectroscopy
b	broad (IR, NMR)
BARF <sub>24</sub>	<i>tetrakis(3,5-bis(trifluoromethyl)phenyl)borate</i>
COSY	correlation spectroscopy (NMR)
cyttp	PhP(CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> PCy <sub>2</sub> ) <sub>2</sub>
δ	chemical shift (NMR)
<i>d</i>	deutero
d	doublet (NMR)
dd; dt	doublet of doublets; doublet of triplets, etc. (NMR)
dce	1,2-dichloroethane
dcm	dichloromethane
dcy pb	1,4- <i>bis</i> (dicyclohexylphosphino)butane
depe	1,2- <i>bis</i> (diethylphosphino)ethane

dippae	1,2- <i>bis</i> ((diisopropylphosphino)amino)ethane
dippe	1,2- <i>bis</i> (diisopropylphosphino)ethane
dmf	N,N-dimethylformamide
dmpe	1,2- <i>bis</i> (dimethylphosphino)ethane
DPB	diporphyrinatobiphenylene <sup>4-</sup>
dppa	Ph <sub>2</sub> PCCPh <sub>2</sub>
dppa	Ph <sub>2</sub> PCCPh <sub>2</sub>
dppb	1,4- <i>bis</i> (diphenylphosphino)butane
dppe	1,2- <i>bis</i> (diphenylphosphino)ethane
dppen	(Ph <sub>2</sub> P) <sub>2</sub> CCH <sub>2</sub>
dppen	CH <sub>2</sub> =C(PPh <sub>2</sub> ) <sub>2</sub>
edta	ethylenediaminetetraacetic acid
en	H <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>
EPR	electron paramagnetic resonance
ESI	electrospray ionisation
EXAFS	Extended X-ray Absorption Fine Structure
EXSY	exchange spectroscopy (NMR)
FID	recorded free induction decay signal (NMR)
FTIR	fourier transfer infrared
GB	gaussian broadening factor (NMR)
GM	Gaussian multiplication window function (NMR)
hex.	hexet (NMR)
HIPT	hexaisopropylterphenyl
HMQC	heteronuclear multiple-quantum coherence (NMR)

HSQC	heteronuclear single-quantum coherence (NMR)
I	nuclear spin number (NMR)
*Im	1- <i>tert</i> -butyl-5-phenylimidazole
IR	infrared
<i>J</i>	coupling constant (NMR)
$\kappa$	denticity
LB	line broadening factor (NMR)
m	medium (IR), or multiplet (NMR)
<i>m/z</i>	mass to charge ratio
MALDI	matrix assisted laser desorption and ionisation
MS	mass spectroscopy
'N <sub>2</sub> Me <sub>2</sub> S <sub>2</sub> '	1,2-ethanediamine- <i>N,N'</i> -dimethyl- <i>N,N'</i> -bis(2-benzenethiolate) <sup>2-</sup>
NMR	nuclear magnetic resonance
NN'N	2,6- <i>bis</i> [(dimethylamino)methyl]pyridine
NNNN	2,5,9,12-tetramethyl-2,5,9,12-tetraazatridecane
OEP	2,3,7,8,12,13,17,18-octaethylporphyrin <sup>2-</sup>
ORTEP	Oak Ridge thermal ellipsoid plot program
OTf	CF <sub>3</sub> SO <sub>3</sub> <sup>-</sup>
p	pentet (NMR)
P <sup>2</sup> P <sub>3</sub>	<i>tris</i> (2-diphenylphosphinoethyl)phosphine
P <sup>2</sup> P <sup>3</sup> P' <sub>2</sub>	2-dimethylphosphinoethyl- <i>bis</i> -(3-dimethylphosphinopropyl)- phosphine
P <sup>3</sup> P <sup>2</sup> P' <sub>2</sub>	<i>bis</i> (3-dimethylphosphinoproyl)(2-dimethylphosphinoethyl)- phosphine

P <sub>c</sub>	central phosphorus atom in molecules containing axial symmetry (NMR)
P <sub>t</sub>	terminal phosphorus atom in molecules containing axial symmetry (NMR)
PCP- <sup>t</sup> Bu	2,6-(CH <sub>2</sub> P <sup>t</sup> Bu <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> <sup>-</sup>
pn	Ph <sub>2</sub> PCH <sub>2</sub> CH <sub>2</sub> NMe <sub>2</sub>
PNP- <sup>t</sup> Bu	2,6- <i>bis</i> -(di- <i>tert</i> -butylphosphinomethyl)pyridine
P-O	(1,3-dioxan-2-ylmethyl)diphenylphosphine
POP- <sup>i</sup> Pr	( <sup>i</sup> Pr <sub>2</sub> PCH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> O
POP- <sup>t</sup> Bu	( <sup>t</sup> Bu <sub>2</sub> PCH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> O
P-P	any <i>bis</i> -diphosphine
PP <sub>3</sub>	<i>tris</i> (2-diphenylphosphinoethyl)phosphine
ppm	parts per million
py <sup>bu</sup> S <sub>4</sub>	2,6- <i>bis</i> [(3,5-di- <i>tert</i> -butyl-2-sulfanylphenyl)thiomethyl]-pyridine <sup>2-</sup>
pz	pyrazol-1-yl
q	quartet (NMR)
R,R'-dippach	(R,R')-1,2- <i>bis</i> ((diisopropylphosphino)amino)cyclohexane
R,R'-Me-DuPHOS	1,2- <i>bis</i> ((2R,5R)-2,5-dimethylphospholano)benzene
R,R-CHIRAPHOS	(R,R)-2,3- <i>bis</i> (diphenylphosphine)butane
R <sub>f</sub>	retention factor
R <sub>x</sub> <sup>⊥</sup>	reaction
s	singlet (NMR)
sept.	septet (NMR)
sh	sharp

st	strong
t	triplet (NMR)
$T_1$	longitudinal relaxation time (NMR)
thf	tetrahydrofuran
TMP	5,10,15,20-tetramesitylporphyrin
TMS	trimethylsilyl
TOF	time-of-flight
Tp	$[\text{HB}(\text{pz}_3)]^-$ = hydrotris(pyrazol-1-yl)borate
trien	$\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$
triflate	trifluoromethylsulfonate
triphos**	2,2'-(phenylphosphinediyl) <i>bis</i> (2,1-phenylene) <i>bis</i> - (diphenylphosphine)
UV	ultraviolet
VT	variable temperature (NMR)
w	weak (IR)
$\eta$	hapticity
$\kappa^4\text{-PNP}_{\text{Si}}\text{-}^t\text{Bu}$	$\kappa^4\text{-HN}^+(\text{SiMe}_2\text{CH}_2\text{P}^t\text{Bu}_2)(\text{SiMe}_2\text{CH}_2\text{P}^t\text{Bu}(\text{CMe}_2\text{C}^-\text{H}_2))$
$\nu$	vibrational stretch (IR)