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X-RAY STRUCTURAL STUDIES  
OF  
SELECTED GROUP VIII METAL COMPLEXES

*A THESIS*  
*PRESENTED TO THE*  
*UNIVERSITY OF AUCKLAND*  
*FOR THE DEGREE OF*  
DOCTOR OF PHILOSOPHY

*BY*  
Karen Marsden

*TO MY MOTHER AND FATHER*

## ABSTRACT

This thesis describes the single crystal x-ray analyses of six novel organometallic osmium complexes and three complexes of the tridentate ligand 1,6-bis(diphenylphosphino)-*trans*-hex-3-ene with the transition metals iridium, rhodium and ruthenium.

The complexes of carbon monosulphide and carbon monotelluride with osmium,  $\text{OsCl}_2(\text{CO})(\text{CS})(\text{PPh}_3)_2$  and  $\text{OsCl}_2(\text{CO})(\text{CTe})(\text{PPh}_3)_2$ , exhibit linear thio- and telluro-coordination similar to that of the carbonyl. The -CS and -CTe ligands exert strong *trans*-bond weakening influences.

In the *dihapto*-thioacyl complex of osmium,  $\text{Os}(\eta^1\text{-O}_2\text{CCF}_3)[\text{C}(\text{S})\text{-}(p\text{-tolyl})](\text{CO})(\text{PPh}_3)_2$ , the bidentate thioacyl is coordinated to the osmium through the carbon and sulphur atoms. This bonding involves a considerable degree of  $\pi$ -interaction between the C, S and Os atoms, concomitant with a lengthening of the C-S bond.

The dichlorocarbene complex,  $\text{OsCl}_2(\text{CO})(\text{CCl}_2)(\text{PPh}_3)_2$  is disordered in the crystalline state. Consequently, while the presence of the dichlorocarbene is verified, no unambiguous conclusions can be drawn from the associated geometry.

In the carbyne complex of osmium,  $\text{Os}(\text{C-}p\text{-tolyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ , the osmium is in a trigonal bipyramidal environment with an approximately linear arrangement of the Os-C-R group. The Os-C<sub>carbyne</sub> bond is short (corresponding to a bond order of *ca.* 3), confirming the formation of the C-*p*-tolyl group as a carbyne.

The formaldehyde ligand in the osmium complex,  $\text{Os}(\eta^2\text{-CH}_2\text{O})(\text{CO})_2\text{-}(\text{PPh}_3)_2$ , is bonded to the osmium centre *via* both the carbon and oxygen atoms. The C-O bond of the formaldehyde lengthens considerably upon coordination, resulting in a bond order apparently less than 1. Also present in the crystal structure are molecules of water which are hydrogen bonded into pairs (O...O separation 2.56 Å). The  $(\text{H}_2\text{O})_2$  units do not hydrogen bond to any other atoms, but rather occupy hydrophobic interstices in the structure.

The three complexes of 1,6-bis(diphenylphosphino)-*trans*-hex-3-ene, (BDPH),  $\text{Ir}^{\text{III}}\text{Cl}_3(\text{BDPH})$ ,  $\text{Rh}^{\text{III}}\text{Cl}_3(\text{BDPH})$ , and  $\text{Ru}^{\text{II}}\text{Cl}_2(\text{CO})(\text{BDPH})$  are isomorphous. The ruthenium complex is, however, disordered in the crystalline state. In each of the three structures the olefin of the BDPH moiety is only weakly bound to the metal, leaving the C=C double bond virtually unchanged from that of the free ligand. The olefin exerts a stronger *trans*-bond weakening influence than do the chlorine ligands in these complexes.

## PREFACE

The content of this thesis is divided into two parts. The first contains the structural studies of six organometallic complexes of osmium, while the second comprises the structural studies of three complexes of the tridentate ligand 1,6-bis(diphenylphosphino)-*trans*-hex-3-ene with iridium, rhodium and ruthenium.

## CONTENTS

	Page
ABSTRACT	
PREFACE	
LIST OF FIGURES	
LIST OF TABLES	
CHAPTER 1 <u>INTRODUCTION - PART I</u>	1
ORGANOMETALLIC OSMIUM COMPLEXES	
CHAPTER 2 <u>DATA COLLECTION AND DATA PROCESSING</u>	48
CHAPTER 3 <u>OSMIUM COMPLEXES CONTAINING THIOCARBONYL AND TELLUROCARBONYL LIGANDS:</u>	63
$\text{OsCl}_2(\text{CO})(\text{CS})(\text{PPh}_3)_2 \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$ AND $\text{OsCl}_2(\text{CO})(\text{CTe})(\text{PPh}_3)_2$	
CHAPTER 4 <u>THE CRYSTAL AND MOLECULAR STRUCTURE OF</u> $\text{Os}(\eta^1\text{-O}_2\text{CCF}_3)(\eta^2\text{-C(S)(p-tolyl)})(\text{CO})(\text{PPh}_3)_2$	125
CHAPTER 5 <u>THE CRYSTAL AND MOLECULAR STRUCTURE OF</u> $\text{OsCl}_2(\text{CO})(\text{CCl}_2)(\text{PPh}_3)_2$	158
CHAPTER 6 <u>THE CRYSTAL AND MOLECULAR STRUCTURE OF</u> $\text{Os}(\text{C-p-tolyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$	193
CHAPTER 7 <u>THE CRYSTAL AND MOLECULAR STRUCTURE OF</u> $\text{Os}(\eta^2\text{-CH}_2\text{O})(\text{CO})_2(\text{PPh}_3)_2 \cdot \text{H}_2\text{O}$	225
CHAPTER 8 <u>INTRODUCTION - PART II</u>	268
MULTIDENTATE PHOSPHINE-OLEFIN LIGANDS	
CHAPTER 9 <u>RHODIUM, IRIDIUM AND RUTHENIUM COMPLEXES CONTAINING THE TRIDENTATE LIGAND</u> <u>1,6-BIS(DIPHENYLPHOSPHINO)-TRANS-HEX-3-ENE:</u>	276
$\text{IrCl}_3(\text{BDPH}),$ $\text{RhCl}_3(\text{BDPH})$ and $\text{RuCl}_2(\text{CO})(\text{BDPH})$	

	Page
APPENDIX I <u>TRIPHENYLPHOSPHINE LIGANDS</u>	352
APPENDIX II <u>STRUCTURE FACTOR TABLES:</u>	
$\text{OsCl}_2(\text{CO})(\text{CS})(\text{PPh}_3)_2 \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$	360
$\text{OsCl}_2(\text{CO})(\text{CTe})(\text{PPh}_3)_2$	374
$\text{Os}(\eta^1\text{-O}_2\text{CCF}_3)(\eta^2\text{-C(S)-(p-tolyl)})_2(\text{CO})(\text{PPh}_3)_2$	385
$\text{OsCl}_2(\text{CO})(\text{CCl}_2)(\text{PPh}_3)_2$	396
$\text{Os}(\text{C-p-tolyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$	402
$\text{Os}(\eta^2\text{-CH}_2\text{O})(\text{CO})_2(\text{PPh}_3)_2 \cdot \text{H}_2\text{O}$	410
$\text{IrCl}_3(\text{BDPH})$	423
$\text{RhCl}_3(\text{BDPH})$	434
$\text{RuCl}_2(\text{CO})(\text{BDPH})$	441
REFERENCES	449
PUBLICATIONS RESULTING FROM THE RESEARCH IN THIS THESIS	470
ACKNOWLEDGEMENTS	471



LIST OF FIGURES

		Page
<hr/>		
COMPOUND:	$\text{OsCl}_2(\text{CO})(\text{CS})(\text{PPh}_3)_2 \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$	
Figure 3.1.1	Inner Coordination Geometry	88
3.1.2	Inner Coordination Sphere with 50% Probability Boundaries	89
3.1.3	A General View of the Molecule with Phenyl Ring Labelling	90
3.1.4	A Stereoscopic View of the Molecular Packing	91
COMPOUND:	$\text{OsCl}_2(\text{CO})(\text{CTe})(\text{PPh}_3)_2$	
Figure 3.2.1	Inner Coordination Geometry	92
3.2.2	Inner Coordination Sphere with 50% Probability Boundaries	93
3.2.3	A General View of the Molecule with Phenyl Ring Labelling	94
3.2.4	A Stereoscopic View of the Molecular Packing	95
COMPOUND:	$\text{Os}(\eta^1\text{-O}_2\text{CCF}_3)[\eta^2\text{-C(S)-(p-tolyl)}](\text{CO})(\text{PPh}_3)_2$	
Figure 4.1	Inner Coordination Geometry	138
4.2	Inner Coordination Sphere with 50% Probability Boundaries	139
4.3	A General View of the Molecule with Phenyl Ring Labelling	140
4.4	A Stereoscopic View of the Molecular Packing	141
COMPOUND:	$\text{OsCl}_2(\text{CO})(\text{CCl}_2)(\text{PPh}_3)_2$	
Figure 5.1	Inner Coordination Geometry	173
5.2	Inner Coordination Sphere with 50% Probability Boundaries	174
5.3	A General View of the Molecule with Phenyl Ring Labelling	175
5.4	A Stereoscopic View of the Molecular Packing	176

	Page
<u>COMPOUND:</u> <u>Os(C-<i>p</i>-tolyl)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub></u>	
Figure 6.1      Inner Coordination Geometry	205
6.2      Inner Coordination Sphere with 50% Probability Boundaries	206
6.3      A General View of the Molecule with Phenyl Ring Labelling	207
6.4      A Stereoscopic View of the Molecular Packing	208
 <u>COMPOUND:</u> <u>Os(η<sup>2</sup>-CH<sub>2</sub>O)(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub></u>	
Figure 7.1      Inner Coordination Geometry	245
7.2      Inner Coordination Sphere with 50% Probability Boundaries	246
7.3      A General View of the Molecule with Phenyl Ring Labelling	247
7.4      A Stereoscopic View of the Molecular Packing	248
7.5      A Stereoscopic View of the Environment of the Water Dimer in Os(η <sup>2</sup> CH <sub>2</sub> O)(CO) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	249
7.6      A Stereoscopic View of the Environment of the Water Dimer in RuI <sub>2</sub> [CHN(CH <sub>3</sub> )( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> )](CO)- (CN - <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> )(PPh <sub>3</sub> ) <sub>3</sub>	250
 <u>COMPOUND:</u> <u>IrCl<sub>3</sub>(BDPH)</u>	
Figure 9.1.1      Inner Coordination Geometry	301
9.1.2      Inner Coordination Sphere with 50% Probability Boundaries	302
9.1.3      A General View of the Molecule with Phenyl Ring Labelling	303
9.1.4      Relative Orientation of the C=C	304
9.1.5      A Stereoscopic View of the Molecular Packing	305
 <u>COMPOUND:</u> <u>RhCl<sub>3</sub>(BDPH)</u>	
Figure 9.2.1      Inner Coordination Geometry	306

	Page	
Figure 9.2.2	Inner Coordination Sphere with 50% Probability Boundaries	307
9.2.3	A General View of the Molecule with Phenyl Ring Labelling	308
9.2.4	Relative Orientation of the C=C	309
9.2.5	A Stereoscopic View of the Molecular Packing	310
<u>COMPOUND:</u>	<u><math>\text{RuCl}_2(\text{CO})(\text{BDPH})</math></u>	
Figure 9.3.1	Inner Coordination Geometry	311
9.3.2	Inner Coordination Sphere with 50% Probability Boundaries	312
9.3.3	A General View of the Molecule with Phenyl Ring Labelling	313
9.3.4	Relative Orientation of the C=C	314
9.3.5	A Stereoscopic View of the Molecular Packing	315

LIST OF TABLES

		Page
<u>COMPOUND:</u>	<u>OsCl<sub>2</sub>(CO)(CS)(PPh<sub>3</sub>)<sub>2</sub> · ½CH<sub>2</sub>Cl<sub>2</sub></u>	
Table 3.1.1	Crystal Data	97
3.1.2	Parameters Associated with Data Collection	98
3.1.3	Weighting Scheme Analysis as a Function of F <sub>obs</sub>	99
3.1.4	Weighting Scheme Analysis as a Function of sin <sup>2</sup> θ/λ <sup>2</sup>	100
3.1.5	Positional and Isotropic Thermal Parameters with Standard Deviations	101
3.1.6	Anisotropic Thermal Parameters with Standard Deviations	103
3.1.7	Calculated Hydrogen Atom Positions	104
3.1.8	Interatomic Distances (Å) with Standard Deviations	105
3.1.9	Intermolecular Approaches < 3.5 Å with Standard Deviations	106
3.1.10	Interatomic Angles (°) with Standard Deviations	107
3.1.11	Least-Squares Planes	109
 <u>COMPOUND:</u>	 <u>OsCl<sub>2</sub>(CO)(CTe)(PPh<sub>3</sub>)<sub>2</sub></u>	
Table 3.2.1	Crystal Data	111
3.2.2	Parameters Associated with Data Collection	112
3.2.3	Weighting Scheme Analysis as a Function of F <sub>obs</sub>	113
3.2.4	Weighting Scheme Analysis as a Function of sin <sup>2</sup> θ/λ <sup>2</sup>	114
3.2.5	Positional and Isotropic Thermal Parameters with Standard Deviations	115

	Page	
Table 3.2.6	Anisotropic Thermal Parameters with Standard Deviations	117
3.2.7	Calculated Hydrogen Atom Positions	118
3.2.8	Interatomic Distances ( $\text{\AA}$ ) with Standard Deviations	119
3.2.9	Intermolecular Approaches $< 3.5 \text{\AA}$ with Standard Deviations	120
3.2.10	Interatomic Angles ( $^\circ$ ) with Standard Deviations	121
3.2.11	Least-Squares Planes	123
COMPOUND:	<u><math>\text{Os}(\eta^1\text{-O}_2\text{CCF}_3)(\eta^2\text{-C(S)-(p-tolyl)})(\text{CO})(\text{PPh}_3)_2</math></u>	
Table 4.1	Crystal Data	143
4.2	Parameters Associated with Data Collection	144
4.3	Weighting Scheme Analysis as a Function of $F_{\text{obs}}$	145
4.4	Weighting Scheme Analysis as a Function of $\sin^2\theta/\lambda^2$	146
4.5	Positional and Isotropic Thermal Parameters with Standard Deviations	147
4.6	Anisotropic Thermal Parameters with Standard Deviations	149
4.7	Calculated Hydrogen Atom Positions	150
4.8	Interatomic Distances ( $\text{\AA}$ ) with Standard Deviations	151
4.9	Intermolecular Approaches $< 3.5 \text{\AA}$ with Standard Deviations	152
4.10	Interatomic Angles ( $^\circ$ ) with Standard Deviations	153
4.11	Least-Squares Planes	155
COMPOUND:	<u><math>\text{OsCl}_2(\text{CO})(\text{CCL}_2)(\text{PPh}_3)_2</math></u>	
Table 5.1	Crystal Data	178
5.2	Parameters Associated with Data Collection	179
5.3	Weighting Scheme Analysis as a Function of $F_{\text{obs}}$	180

		Page
Table 5.4	Weighting Scheme Analysis as a Function of $\sin^2\theta/\lambda^2$	181
5.5	Positional and Isotropic Thermal Parameters with Standard Deviations	182
5.6	Anisotropic Thermal Parameters with Standard Deviations	184
5.7	Calculated Hydrogen Atom Positions	185
5.8	Interatomic Distances ( $\text{\AA}$ ) with Standard Deviations	186
5.9	Intermolecular Approaches $< 3.5 \text{\AA}$ with Standard Deviations	187
5.10	Interatomic Angles ( $^\circ$ ) with Standard Deviations	188
5.11	Least-Squares Planes	190

COMPOUND:  $\text{Os}(\text{C-}p\text{-tolyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$

Table 6.1	Crystal Data	210
6.2	Parameters Associated with Data Collection	211
6.3	Weighting Scheme Analysis as a Function of $F_{\text{obs}}$	212
6.4	Weighting Scheme Analysis as a Function of $\sin^2\theta/\lambda^2$	213
6.5	Positional and Isotropic Thermal Parameters with Standard Deviations	214
6.6	Anisotropic Thermal Parameters with Standard Deviations	216
6.7	Calculated Hydrogen Atom Positions	217
6.8	Interatomic Distances ( $\text{\AA}$ ) with Standard Deviations	218
6.9	Intermolecular Approaches $< 3.5 \text{\AA}$ with Standard Deviations	219
6.10	Interatomic Angles ( $^\circ$ ) with Standard Deviations	220
6.11	Least-Squares Planes	222

		Page
<u>COMPOUND: Os(<math>\eta^2</math>-CH<sub>2</sub>O)(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O</u>		
Table 7.1	Crystal Data	252
7.2	Parameters Associated with Data Collection	253
7.3	Weighting Scheme Analysis as a Function of F <sub>obs</sub>	254
7.4	Weighting Scheme Analysis as a Function of $\sin^2\theta/\lambda^2$	255
7.5	Positional and Isotropic Thermal Parameters with Standard Deviations	256
7.6	Anisotropic Thermal Parameters with Standard Deviations	258
7.7	Calculated Hydrogen Atom Positions	259
7.8	Interatomic Distances ( $\text{\AA}$ ) with Standard Deviations	261
7.9	Intermolecular Approaches < 3.5 $\text{\AA}$ with Standard Deviations	262
7.10	Interatomic Angles ( $^\circ$ ) with Standard Deviations	263
7.11	Least-Squares Planes	265
 <u>COMPOUND: IrCl<sub>3</sub>(BDPH)</u>		
Table 9.1.1	Crystal Data	317
9.1.2	Parameters Associated with Data Collection	318
9.1.3	Weighting Scheme Analysis as a Function of F <sub>obs</sub>	319
9.1.4	Weighting Scheme Analysis as a Function of $\sin^2\theta/\lambda^2$	320
9.1.5	Positional and Isotropic Thermal Parameters with Standard Deviations	321
9.1.6	Anisotropic Thermal Parameters with Standard Deviations	322
9.1.7	Hydrogen Atom Positions	323
9.1.8	Interatomic Distances ( $\text{\AA}$ ) with Standard Deviations	324

	Page	
Table 9.1.9	Interatomic Angles (°) with Standard Deviations	325
9.1.10	Least-Squares Planes	326
<u>COMPOUND:</u>	<u>RhCl<sub>3</sub>(BDPH)</u>	
Table 9.2.1	Crystal Data	328
9.2.2	Parameters Associated with Data Collection	329
9.2.3	Weighting Scheme Analysis as a Function of F <sub>obs</sub>	330
9.2.4	Weighting Scheme Analysis as a Function of $\sin^2\theta/\lambda^2$	331
9.2.5	Positional and Isotropic Thermal Parameters with Standard Deviations	332
9.2.6	Anisotropic Thermal Parameters with Standard Deviations	333
9.2.7	Hydrogen Atom Positions	334
9.2.8	Interatomic Distances (Å) with Standard Deviations	335
9.2.9	Interatomic Angles (°) with Standard Deviations	336
9.2.10	Least-Squares Planes	337
<u>COMPOUND:</u>	<u>RuCl<sub>2</sub>(CO)(BDPH)</u>	
9.3.1	Crystal Data	339
9.3.2	Parameters Associated with Data Collection	340
9.3.3	Weighting Scheme Analysis as a Function of F <sub>obs</sub>	341
9.3.4	Weighting Scheme Analysis as a Function of $\sin^2\theta/\lambda^2$	342
9.3.5	Positional and Isotropic Thermal Parameters with Standard Deviations	343
9.3.6	Anisotropic Thermal Parameters with Standard Deviations	344
9.3.7	Hydrogen Atom Positions	345
9.3.8	Interatomic Distances (Å) with Standard Deviations	346



		Page
Table 9.3.9	Interatomic Angles ( $^{\circ}$ ) with Standard Deviations	348
9.3.10	Least-Squares Planes	350
Table A	Os-P Distances and P-Os-P Angles for Some Osmium Complexes	84
Table B	Os-Cl Distances for Some Osmium Complexes	85
Table C	Os-Carbonyl, and C-O Distances and Os-C-O Angles for Some Osmium Complexes	86