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THE SYNTHESIS AND
REACTIVITY OF NEW RUTHENIUM
AND OSMIUM SILYL COMPLEXES

A thesis presented to
The University of Auckland
for the degree of
Doctor of Philosophy in Chemistry

David Mark Salter

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"A wise man will hear and will increase learning"

Proverbs 1:5

ABSTRACT

ABSTRACT

The chemistry of transition metal silyl complexes still remains relatively undeveloped despite the recent advances that have been made in this area. This thesis describes the synthesis and reactivity of new ruthenium and osmium silyl complexes.

A general survey on the bonding, preparation and reactivity of transition metal silyl complexes is given in chapter one as an introduction to the chemistry discussed in the following chapters. Several reviews relating to transition metal-silicon chemistry have been published,¹⁻⁵ and therefore only the major features and more recent developments are highlighted in this overview. Emphasis has been placed on those aspects not previously reviewed.

Coordinatively unsaturated transition metal silyl complexes are uncommon and the chemistry of these complexes has been virtually unexplored. The synthesis of the novel coordinatively unsaturated ruthenium and osmium silyl complexes, $M(\text{SiR}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ ($M = \text{Ru, Os}$; $R = \text{Cl, alkyl group, alkoxy group}$), is described in chapter two. The reaction of $M(\text{Ph})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ ($M = \text{Ru, Os}$) with a silane, in some instances, provided a facile, high yield route to complexes of the type $M(\text{SiR}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ ($M = \text{Ru}$; $\text{SiR}_3 = \text{SiMe}_3, \text{SiEt}_3, \text{SiCl}_3, \text{SiMe}_2\text{Cl}$; $M = \text{Os}$; $\text{SiR}_3 = \text{SiCl}_3, \text{SiMe}_2\text{Cl}$). The chlorosilyl complexes were also prepared by treatment of $M\text{HCl}(\text{CO})(\text{PPh}_3)_3$ ($M = \text{Ru, Os}$) with HSiCl_3 and HSiMe_2Cl . X-ray crystal structures were obtained of $\text{Ru}(\text{SiEt}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ and $\text{Os}(\text{SiCl}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$.

Complexes containing chlorosilyl ligands proved synthetically useful, undergoing a variety of nucleophilic substitution reactions at silicon with retention of the transition metal-silicon bond. New complexes synthesized by this method included $\text{Ru}[\text{Si}(\text{OEt})_3]\text{Cl}(\text{CO})(\text{PPh}_3)_2$ and $\text{Os}(\text{SiMe}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$. X-ray crystal structures of these two compounds were also obtained. These exchange reactions illustrate a route to new transition metal silyl compounds that has rarely been utilised.

Also described in chapter two is the unprecedented formation of the novel compound $\text{Os}(\overbrace{\text{SiMe}_2\text{C}_6\text{H}_4\text{PPh}_2}^{\text{C}_6\text{H}_4\text{PPh}_2})(\text{C}_6\text{H}_4\text{PPh}_2)(\text{CO})(\text{PPh}_3)$, resulting from phenylation at silicon. The structure of this complex was determined by X-ray crystallography.

In chapter three, addition of the Lewis bases CO and CN(*p*-tolyl) to coordinatively unsaturated silyl complexes, $\text{M}(\text{SiR}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ ($\text{M} = \text{Ru}, \text{Os}$), is described. The coordinatively saturated osmium silyl complexes $\text{Os}(\text{SiR}_3)\text{Cl}(\text{CO})\text{L}(\text{PPh}_3)_2$ ($\text{SiR}_3 = \text{SiCl}_3, \text{SiMe}_2\text{Cl}, \text{SiMe}_2\text{OEt}, \text{SiMe}_3$; $\text{L} = \text{CO}, \text{CNR}$) were generated in this way. Similarly, addition of 4,4'-dimethyl-2,2'-bipyridine to $\text{Ru}(\text{SiEt}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ afforded $\text{Ru}(\text{SiEt}_3)\text{Cl}(\text{dimethylbipy})(\text{CO})(\text{PPh}_3)$. The six-coordinate complex $\text{Ru}(\text{SiEt}_3)(\eta^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ was synthesized by displacement of the labile chloride ligand from $\text{Ru}(\text{SiEt}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ by the dimethyldithiocarbamate anion. Characterization of $\text{Ru}(\text{SiEt}_3)(\eta^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$ included an X-ray crystallographic analysis. The exchange of silyl groups at the metal was also observed in several reactions. For example, heating $\text{Ru}(\text{SiMe}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ in the presence of excess HSiEt_3 yielded $\text{Ru}(\text{SiEt}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$. These reactions illustrate aspects of the chemistry that can occur at the metal centre of coordinatively unsaturated transition metal silyl complexes.

Another route to coordinatively saturated osmium silyl complexes was via oxidative addition of a silane to $\text{Os}(\text{CO})_2(\text{PPh}_3)_3$, which yielded $\text{Os}(\text{SiR}_3)\text{H}(\text{CO})_2(\text{PPh}_3)_2$ ($\text{SiR}_3 = \text{SiMe}_3, \text{SiEt}_3, \text{SiPh}_3, \text{SiPh}_2\text{H}$). The synthesis of these complexes is also discussed in chapter three. An X-ray crystal structure determination of $\text{Os}(\text{SiEt}_3)\text{H}(\text{CO})_2(\text{PPh}_3)_2$ confirmed the presence of mutually *trans* carbonyl ligands.

The first thiocarbonyl-containing transition metal silyl complexes, $\text{M}(\text{SiMe}_2\text{Cl})\text{Cl}(\text{CS})(\text{PPh}_3)_2$ ($\text{M} = \text{Ru}, \text{Os}$), were prepared by treating $\text{M}(\text{Ph})\text{Cl}(\text{CS})(\text{PPh}_3)_2$ or $\text{MHCl}(\text{CS})(\text{PPh}_3)_3$ with HSiMe_2Cl . The Si-Cl bond in these compounds reacted readily with nucleophiles, yielding $\text{M}(\text{SiMe}_2\text{OR})\text{Cl}(\text{CS})(\text{PPh}_3)_2$ ($\text{OR} = \text{OEt}, \text{OMe}, \text{OH}$). In contrast to the addition of CO to $\text{Os}(\text{SiR}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$, addition of CO to $\text{Ru}(\text{SiMe}_2\text{R})\text{Cl}(\text{CS})(\text{PPh}_3)_2$ ($\text{R} = \text{Cl}, \text{OEt}, \text{OMe}, \text{OH}$) and to $\text{Os}(\text{SiMe}_2\text{OEt})\text{Cl}(\text{CS})(\text{PPh}_3)_2$ afforded *dihapto*-thioacyl complexes, $\text{M}[\eta^2\text{-C}(\text{S})\text{SiMe}_2\text{R}]\text{Cl}(\text{CO})(\text{PPh}_3)_2$, via a migratory insertion reaction involving the silyl group and the thiocarbonyl ligand. This reaction represents the first formal insertion of CS into a

transition metal-silicon bond. The structure of $\text{Ru}[\eta^2\text{-C(S)SiMe}_2\text{OEt}]\text{Cl}(\text{CO})(\text{PPh}_3)_2$ was obtained by X-ray crystallography and confirmed that bonding of the thioacyl ligand occurred in a *dihapto* fashion. These reactions are described in chapter four.

When $\text{Os}(\text{Ph})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ was reacted with HSiMe_3 , the formally osmium(IV) silyl complex $\text{Os}(\text{SiMe}_3)\text{H}_3(\text{CO})(\text{PPh}_3)_2$ was produced. Few compounds of this type are known. The synthesis, characterization and reactivity of $\text{Os}(\text{SiMe}_3)\text{H}_3(\text{CO})(\text{PPh}_3)_2$ are discussed in chapter five. The crystal structure of $\text{Os}(\text{SiMe}_3)\text{H}_3(\text{CO})(\text{PPh}_3)_2$ is also depicted. In solution, $\text{Os}(\text{SiMe}_3)\text{H}_3(\text{CO})(\text{PPh}_3)_2$ appeared to be in equilibrium with the highly reactive, coordinatively unsaturated species $\text{OsH}_2(\text{CO})(\text{PPh}_3)_2$. The reaction of $\text{Os}(\text{SiMe}_3)\text{H}_3(\text{CO})(\text{PPh}_3)_2$ with HSiR_3 ($\text{R} = \text{Et}, \text{Ph}$), $\text{HSn}(p\text{-tolyl})_3$ and HC_2Ph was carried out, using $\text{Os}(\text{SiMe}_3)\text{H}_3(\text{CO})(\text{PPh}_3)_2$ as an *in situ* source of $\text{OsH}_2(\text{CO})(\text{PPh}_3)_2$. These reactions afforded $\text{Os}(\text{SiR}_3)\text{H}_3(\text{CO})(\text{PPh}_3)_2$ ($\text{R} = \text{Et}, \text{Ph}$), $\text{Os}[\text{Sn}(p\text{-tolyl})_3]_2\text{H}_2(\text{CO})(\text{PPh}_3)_2$ and $\text{OsH}(\text{C}_2\text{Ph})(\text{CO})(\text{PPh}_3)_3$ respectively, most likely via a series of oxidative addition-reductive elimination reactions involving $\text{OsH}_2(\text{CO})(\text{PPh}_3)_2$.

Transition metal hydroxysilyl complexes are extremely rare. Only three systems have been reported containing a hydroxysilyl group bonded to a transition metal.^{6,7,8} Chapter six deals with the formation of compounds of this type. Hydroxysilyl-containing complexes of ruthenium and osmium were obtained via the hydrolysis of $\text{M}(\text{SiMe}_2\text{Cl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ and $\text{M}(\text{SiCl}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$. The complexes $\text{M}[\text{Si}(\text{OH})_3]\text{Cl}(\text{CO})(\text{PPh}_3)_2$ are the first trihydroxysilyl-containing transition metal complexes and therefore represent a new class of transition metal silyl compounds. Characterization of $\text{Os}[\text{Si}(\text{OH})_3]\text{Cl}(\text{CO})(\text{PPh}_3)_2$ included an X-ray crystal structure which showed that, remarkably, no inter- or intra-molecular hydrogen bonding of the type $\text{O}(\text{H})\cdots\text{O}$ or $\text{O}(\text{H})\cdots\text{Cl}$ was associated with the $\text{Si}(\text{OH})_3$ group. In contrast, intermolecular hydrogen bonding was found by X-ray crystallography for the dicarbonyl derivative, $\text{Os}[\text{Si}(\text{OH})_3]\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$. Subsequent reactions involving $\text{Os}[\text{Si}(\text{OH})_3]\text{Cl}(\text{CO})(\text{PPh}_3)_2$ led to the synthesis of the diosmium tetrahydroxydisiloxane complex, $[\text{OsCl}(\text{CO})(\text{PPh}_3)_2\text{Si}(\text{OH})_2]_2\text{O}$. For example, $[\text{OsCl}(\text{CO})(\text{PPh}_3)_2\text{Si}(\text{OH})_2]_2\text{O}$ was isolated after $\text{Os}(\text{SiCl}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ was added to a dichloromethane solution of $\text{Os}[\text{Si}(\text{OH})_3]\text{Cl}(\text{CO})(\text{PPh}_3)_2$. Formation of this tetrahydroxydisiloxane compound is significant

and models the first condensation reaction generating a Si-O-Si linkage in the hydrolysis of organochlorosilanes to polysiloxanes. The Si-O-Si linkage was clearly visible in the X-ray crystal structure of $[\text{OsCl}(\text{CO})(\text{PPh}_3)_2\text{Si}(\text{OH})_2]_2\text{O}$.

Chapter seven provides a short conclusion, highlighting the important features of the work discussed in this thesis and identifies areas for future investigation.

TABLE OF CONTENTS

Abstract	iii
List of Tables	xii
List of Important Figures	xv
List of Important Schemes	xvii
List of Abbreviations	xix
<u>Introduction</u>	1
Chapter One	
<u>The Chemistry of Transition Metal Silyl Complexes</u>	3
I. Transition Metal-Silicon Bonds	3
II. Preparative Routes to Transition Metal Silyl Complexes	10
A. Reaction between a Transition Metal Anion and a Halosilane	11
B. Reaction of a Silyl Anion with a Transition Metal Halide	12
C. Oxidative Addition Reactions	14
D. Miscellaneous Methods	22
E. Transition Metal Silylene and Related Complexes	23
III. Reactivity of Transition Metal Silyl Complexes	30
A. Substitution of Ligands at Silicon	30
(i) Hydrogen Replacement	31
(ii) Halo Group Replacement	33
(iii) Amine Group Replacement	38
(iv) Alkoxy Group Replacement	39
(v) Alkyl Group Replacement	40
(vi) Sulfide Group Replacement	41

B.	Ligand Substitution at the Metal Centre	42
C.	Cleavage of the Transition Metal-Silicon Bond	45
	(i) Cleavage of M-Si Bonds by Nucleophiles	45
	(ii) Cleavage of M-Si Bonds by Electrophiles	46
	(iii) Cleavage of M-Si Bonds by Other Reagents	46
	(iv) Migratory Insertion Reactions	46
	(a) Carbon Monoxide	47
	(b) Isocyanides	48
	(c) Aldehydes and ketones	48
	(d) Alkenes, alkynes and nitriles	49
	(e) Carbon Dioxide	50
	(v) Reductive Elimination	51

Chapter Two

Synthesis of New Coordinatively Unsaturated Ruthenium

	<u>and Osmium Silyl Complexes</u>	52
I.	Preparation of $M(\text{SiR}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ ($M = \text{Ru, Os}$; $R = \text{Cl, alkyl group}$)	52
	(i) Reactions using a Mercury Reagent	53
	(ii) Oxidative Addition-Reductive Elimination Reactions	61
A.	Synthesis of the Ruthenium Silyl Complexes, $\text{Ru}(\text{SiR}_2\text{R}')\text{Cl}(\text{CO})(\text{PPh}_3)_2$	
	($R = R' = \text{Me, Et, Cl}$; $R = \text{Me, R}' = \text{Cl}$)	62
	(a) Reactions of $\text{Ru}(\text{Ph})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ with HSiR_3	62
	(b) Reactions of $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ with HSiCl_3 and HSiMe_2Cl	74
B.	Synthesis of the Osmium Silyl Complexes, $\text{Os}(\text{SiR}_2\text{R}')\text{Cl}(\text{CO})(\text{PPh}_3)_2$	
	($R = R' = \text{Cl}$; $R = \text{Me, R}' = \text{Cl}$)	78
	(a) Reactions of $\text{Os}(\text{Ph})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ with HSiR_3	78
	(b) Reactions of $\text{OsHCl}(\text{CO})(\text{PPh}_3)_3$ with HSiCl_3 and HSiMe_2Cl	88

II.	Reactivity of Coordinatively Unsaturated Ruthenium and Osmium Silyl Complexes, $M(\text{SiR}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ ($M = \text{Ru, Os}$; $R = \text{Cl, alkyl group}$)	89
A.	Substitution Reactions at Silicon	89
	(a) Alkyl Nucleophiles	91
	(b) Hydroxy Nucleophiles	95
	(c) Alkoxy Nucleophiles	96
	(d) Other Nucleophiles	106
	General Experimental	121
	Experimental	123

Chapter Three

Synthesis of New Coordinatively Saturated Ruthenium

	<u>and Osmium Silyl Complexes</u>	131
I.	Reactions at the Metal Centre of the Five-Coordinate Complexes, $M(\text{SiR}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ ($M = \text{Ru, Os}$)	132
A.	Addition of Lewis Bases to $M(\text{SiR}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$	132
	(a) Addition of CO and CNR	132
	(i) Synthesis of $\text{Os}(\text{SiR}_3)\text{Cl}(\text{CO})\text{L}(\text{PPh}_3)_2$ ($L = \text{CO, CNR}$)	132
	(ii) Reactivity of $\text{Os}(\text{SiR}_3)\text{Cl}(\text{CO})\text{L}(\text{PPh}_3)_2$ ($\text{SiR}_3 = \text{SiCl}_3, \text{SiMe}_2\text{Cl}$; $L = \text{CO, CNR}$)	140
	(b) Addition of an Anionic Bidentate Ligand	142
	(c) Addition of a Neutral Bidentate Ligand	148
B.	Silyl Ligand Exchange Reactions	150
II.	Synthesis of Osmium Silyl Complexes via Oxidative Addition of Silanes to $\text{Os}(\text{CO})_2(\text{PPh}_3)_3$	151
	Experimental	168

Chapter Four

Synthesis and Reactivity of

Transition Metal Silyl Complexes Containing Thiocarbonyl Ligands 174

- I. Synthesis of New Transition Metal Silyl Complexes Containing Thiocarbonyl Ligands, $M(\text{SiR}_3)\text{Cl}(\text{CS})(\text{PPh}_3)_2$
($M = \text{Ru, Os}$; $\text{SiR}_3 = \text{SiMe}_2\text{Cl, SiCl}_3, \text{SiMe}_2\text{OR, SiMe}_2\text{OH}$) 175
- II. Reactivity of $M(\text{SiR}_3)\text{Cl}(\text{CS})(\text{PPh}_3)_2$ ($M = \text{Ru, Os}$; $\text{SiR}_3 = \text{SiMe}_2\text{Cl, SiCl}_3$) 179
 - (a) Substitution at Silicon 179
 - (b) Migratory Insertion of Silyl and Thiocarbonyl Ligands in Ruthenium and Osmium Complexes 181
- Experimental 201

Chapter Five

Synthesis and Reactivity of New Osmium(IV) Silyl Complexes 205

- I. Synthesis of $\text{Os}(\text{SiMe}_3)\text{H}_3(\text{CO})(\text{PPh}_3)_2$ 205
- II. Reactivity of $\text{Os}(\text{SiMe}_3)\text{H}_3(\text{CO})(\text{PPh}_3)_2$ 224
 - (a) Reactions with Lewis Bases 224
 - (b) Reactions involving HSiR_3 225
 - (c) Reactions involving HSnR_3 227
 - (d) Reactions with H-C Bonds 233
- Experimental 239

Chapter Six

Synthesis and Reactivity of Ruthenium and Osmium Hydroxysilyl Complexes 241

- I. Hydrolysis Reactions of Ruthenium and Osmium Chlorodimethyl and Trichlorosilyl Complexes 242
 - (a) Preparation of $M[\text{SiMe}_2(\text{OH})]\text{Cl}(\text{CO})(\text{PPh}_3)_2$ ($M = \text{Ru, Os}$) 242
 - (b) Preparation of $M[\text{Si}(\text{OH})_3]\text{Cl}(\text{CO})(\text{PPh}_3)_2$ ($M = \text{Ru, Os}$) 243

II.	Reactivity of $\text{Os}[\text{SiMe}_2(\text{OH})]\text{Cl}(\text{CO})(\text{PPh}_3)_2$ and $\text{Os}[\text{Si}(\text{OH})_3]\text{Cl}(\text{CO})(\text{PPh}_3)_2$	252
(a)	Reactivity at the Metal Centre	252
(b)	Substitution Reactions at Silicon	262
III.	Formation of $[\text{OsCl}(\text{CO})(\text{PPh}_3)_2\text{Si}(\text{OH})_2]_2\text{O}$	265
(a)	Preparation of $[\text{OsCl}(\text{CO})(\text{PPh}_3)_2\text{Si}(\text{OH})_2]_2\text{O}$	266
(b)	Reactivity of $[\text{OsCl}(\text{CO})(\text{PPh}_3)_2\text{Si}(\text{OH})_2]_2\text{O}$	277
	Experimental	285

Chapter Seven

<u>Conclusion</u>	289
-------------------	-----

<u>References</u>	292
-------------------	-----

<u>Acknowledgements</u>	305
-------------------------	-----

LIST OF TABLES

Chapter Two

Table 2.1	Important Bond Lengths (Å) for $\text{Os}(\text{SiMe}_2\text{C}_6\text{H}_4\text{PPh}_2)(\text{C}_6\text{H}_4\text{PPh}_2)(\text{CO})(\text{PPh}_3)$	56
Table 2.2	Important Bond Angles (°) for $\text{Os}(\text{SiMe}_2\text{C}_6\text{H}_4\text{PPh}_2)(\text{C}_6\text{H}_4\text{PPh}_2)(\text{CO})(\text{PPh}_3)$	56
Table 2.3	Ruthenium-Silicon Bond Distances	69
Table 2.4	Important Bond Lengths (Å) for $\text{Ru}(\text{SiEt}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$	71
Table 2.5	Important Bond Angles (°) for $\text{Ru}(\text{SiEt}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$	71
Table 2.6	Important Bond Lengths (Å) for $\text{Os}(\text{SiCl}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$	83
Table 2.7	Important Bond Angles (°) for $\text{Os}(\text{SiCl}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$	83
Table 2.8	Osmium-Silicon Bond Distances	86
Table 2.9	Important Bond Lengths (Å) for $\text{Os}(\text{SiMe}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$	94
Table 2.10	Important Bond Angles (°) for $\text{Os}(\text{SiMe}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$	94
Table 2.11	Important Bond Lengths (Å) for $\text{Ru}[\text{Si}(\text{OEt})_3]\text{Cl}(\text{CO})(\text{PPh}_3)_2$	100
Table 2.12	Important Bond Angles (°) for $\text{Ru}[\text{Si}(\text{OEt})_3]\text{Cl}(\text{CO})(\text{PPh}_3)_2$	100
Table 2.14	IR Spectral Data for Compounds reported in Chapter Two	112
Table 2.15	^1H NMR Spectral Data for Compounds reported in Chapter Two	114
Table 2.16	^{29}Si NMR Spectral Data for Selected Compounds reported in Chapter Two	116
Table 2.17	^{13}C NMR Spectral Data for Compounds reported in Chapter Two	117
Table 2.18	^{31}P NMR Spectral Data for Compounds reported in Chapter Two	119

Chapter Three

Table 3.1	Important Bond Lengths (Å) for Ru(SiEt ₃)(η ² -S ₂ CNMe ₂)(CO)(PPh ₃) ₂	147
Table 3.2	Important Bond Angles (°) for Ru(SiEt ₃)(η ² -S ₂ CNMe ₂)(CO)(PPh ₃) ₂	147
Table 3.3	Important Bond Lengths (Å) for Os(SiEt ₃)H(CO) ₂ (PPh ₃) ₂	155
Table 3.4	Important Bond Angles (°) for Os(SiEt ₃)H(CO) ₂ (PPh ₃) ₂	155
Table 3.5	IR Spectral Data for Compounds reported in Chapter Three	160
Table 3.6	¹ H NMR Spectral Data for Compounds reported in Chapter Three	162
Table 3.7	¹³ C NMR Spectral Data for Compounds reported in Chapter Three	164
Table 3.8	³¹ P NMR Spectral Data for Compounds reported in Chapter Three	167

Chapter Four

Table 4.1	Important Bond Lengths (Å) for Ru[η ² -C(S)SiMe ₂ OEt]Cl(CO)(PPh ₃) ₂	192
Table 4.2	Important Bond Angles (°) for Ru[η ² -C(S)SiMe ₂ OEt]Cl(CO)(PPh ₃) ₂	192
Table 4.3	IR Spectral Data for Compounds reported in Chapter Four	196
Table 4.4	¹ H NMR Spectral Data for Compounds reported in Chapter Four	197
Table 4.5	¹³ C NMR Spectral Data for Compounds reported in Chapter Four	198
Table 4.6	³¹ P NMR Spectral Data for Compounds reported in Chapter Four	200

Chapter Five

Table 5.1	Important Bond Lengths (Å) for Os(SiMe ₃)H ₃ (CO)(PPh ₃) ₂	210
Table 5.2	Important Bond Angles (°) for Os(SiMe ₃)H ₃ (CO)(PPh ₃) ₂	210
Table 5.3	T ₁ values observed for Os(SiR ₃)H ₃ (CO)(PPh ₃) ₃ (R = Me, Et, Ph)	213
Table 5.4	T ₁ values observed for Os[Sn(<i>p</i> -tolyl) ₃] ₂ H ₂ (CO)(PPh ₃) ₂	228
Table 5.5	IR Spectral Data for Compounds reported in Chapter Five	236
Table 5.6	¹ H NMR Spectral Data for Compounds reported in Chapter Five	237
Table 5.7	³¹ P NMR Spectral Data for Compounds reported in Chapter Five	237
Table 5.8	¹³ C NMR Spectral Data for Compounds reported in Chapter Five	238

Chapter Six

Table 6.1	Important Bond Lengths (Å) for Os[Si(OH) ₃]Cl(CO)(PPh ₃) ₂	248
Table 6.2	Important Bond Angles (°) for Os[Si(OH) ₃]Cl(CO)(PPh ₃) ₂	248
Table 6.3	Important Bond Lengths (Å) for Os[Si(OH) ₃]Cl(CO) ₂ (PPh ₃) ₂	257
Table 6.4	Important Bond Angles (°) for Os[Si(OH) ₃]Cl(CO) ₂ (PPh ₃) ₂	257
Table 6.5	Important Bond Lengths (Å) for [OsCl(CO)(PPh ₃) ₂ Si(OH) ₂] ₂ O	271
Table 6.6	Important Bond Angles (°) for [OsCl(CO)(PPh ₃) ₂ Si(OH) ₂] ₂ O	272
Table 6.7	IR Spectral Data for Compounds reported in Chapter Six	279
Table 6.8	¹ H NMR Spectral Data for Compounds reported in Chapter Six	280
Table 6.9	¹³ C NMR Spectral Data for Compounds reported in Chapter Six	281
Table 6.10	³¹ P NMR Spectral Data for Compounds reported in Chapter Six	283
Table 6.11	²⁹ Si NMR Spectral Data for Selected Compounds reported in Chapter Six	284

 LIST OF IMPORTANT FIGURES

Chapter Two

Figure 2.1	Inner Coordination Sphere of $\text{Os}(\overbrace{\text{SiMe}_2\text{C}_6\text{H}_4\text{PPh}_2}^{\text{---}})(\text{C}_6\text{H}_4\text{PPh}_2)(\text{CO})(\text{PPh}_3)$	55
Figure 2.2	Molecular Geometry of $\text{Ru}(\text{SiEt}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$	70
Figure 2.3	Inner Coordination Sphere of $\text{Os}(\text{SiCl}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$	82
Figure 2.4	Inner Coordination Sphere of $\text{Os}(\text{SiMe}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$	93
Figure 2.5	Inner Coordination Sphere of $\text{Ru}[\text{Si}(\text{OEt})_3]\text{Cl}(\text{CO})(\text{PPh}_3)_2$	99

Chapter Three

Figure 3.1	Inner Coordination Sphere of $\text{Ru}(\text{SiEt}_3)(\eta^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$	146
Figure 3.2	Inner Coordination Sphere of $\text{Os}(\text{SiEt}_3)\text{H}(\text{CO})_2(\text{PPh}_3)_2$	154

Chapter Four

Figure 4.1	Molecular Geometry of $\text{Ru}[\eta^2\text{-C}(\text{S})\text{SiMe}_2\text{OEt}]\text{Cl}(\text{CO})(\text{PPh}_3)_2$	191
------------	---	-----

Chapter Five

Figure 5.1	^1H NMR Hydride Resonances of $\text{Os}(\text{SiMe}_3)\text{H}_3(\text{CO})(\text{PPh}_3)_2$ at $-50\text{ }^\circ\text{C}$	207
Figure 5.2	Molecular Geometry of $\text{Os}(\text{SiMe}_3)\text{H}_3(\text{CO})(\text{PPh}_3)_2$	209
Figure 5.3	T_1 measurement of $\text{Os}(\text{SiMe}_3)\text{H}_3(\text{CO})(\text{PPh}_3)_2$ ($-50\text{ }^\circ\text{C}$)	214
Figure 5.5	^1H NMR Hydride Resonances of $\text{Os}[\text{Sn}(p\text{-tolyl})_3]_2\text{H}_2(\text{CO})(\text{PPh}_3)_2$ at $-50\text{ }^\circ\text{C}$	229

Chapter Six

Figure 6.1	Molecular Geometry of $\text{Os}[\text{Si}(\text{OH})_3]\text{Cl}(\text{CO})(\text{PPh}_3)_2$	247
Figure 6.2	Molecular Geometry of $\text{Os}[\text{Si}(\text{OH})_3]\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$	256
Figure 6.3	Orientation of Molecules of $\text{Os}[\text{Si}(\text{OH})_3]\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$	260
Figure 6.4	Intermolecular Hydrogen-Bonding in $\text{Os}[\text{Si}(\text{OH})_3]\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$	261
Figure 6.6	Inner Coordination Sphere of $[\text{OsCl}(\text{CO})(\text{PPh}_3)_2\text{Si}(\text{OH})_2]_2\text{O}$	270

 LIST OF IMPORTANT SCHEMES

Chapter Two

Scheme 2.1	Possible pathways to $\text{Os}(\overbrace{\text{SiMe}_2\text{C}_6\text{H}_4\text{PPh}_2}^{\text{C}_6\text{H}_4\text{PPh}_2})(\text{CO})(\text{PPh}_3)$	58
Scheme 2.3	Reactions of $\text{Ru}(\text{Ph})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ with HSiR_3	64
Scheme 2.4	Proposed pathway for the reaction of $\text{MHCl}(\text{CO})(\text{PPh}_3)_3$ with chlorosilanes	75
Scheme 2.6	Reactions of $\text{Os}(\text{Ph})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ with HSiR_3	80
Scheme 2.7	Reactions of $\text{M}(\text{SiMe}_2\text{Cl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ ($\text{M} = \text{Ru}, \text{Os}$) with nucleophiles	90
Scheme 2.8	Reactions of $\text{M}(\text{SiCl}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ ($\text{M} = \text{Ru}, \text{Os}$) with nucleophiles	90

Chapter Three

Scheme 3.1	Addition of CO to $\text{Ru}(\text{R})\text{X}(\text{CO})(\text{PPh}_3)_2$	134
Scheme 3.2	Reactions of $\text{M}(\text{SiR}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ ($\text{M} = \text{Ru}, \text{Os}$) with CO and $\text{CN}(p\text{-tolyl})$	139

Chapter Four

Scheme 4.1	Formation of $\text{M}(\text{SiMe}_2\text{Cl})\text{Cl}(\text{CS})(\text{PPh}_3)_2$ ($\text{M} = \text{Ru}, \text{Os}$)	177
Scheme 4.2	Reactions of $\text{M}(\text{SiMe}_2\text{Cl})\text{Cl}(\text{CS})(\text{PPh}_3)_2$ ($\text{M} = \text{Ru}, \text{Os}$) with nucleophiles	181

Chapter Five

Scheme 5.1	Proposed pathway for the formation of $\text{Os}(\text{SiMe}_3)\text{H}_3(\text{CO})(\text{PPh}_3)_2$	220
------------	---	-----

Chapter Six

Scheme 6.1	Hydrolysis of $M(\text{SiMe}_2\text{Cl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ and $M(\text{SiCl}_3)\text{Cl}(\text{CO})(\text{PPh}_3)_2$	245
Scheme 6.2	Formation of $\text{Os}[\text{SiMe}_2(\text{OH})]\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$	252
Scheme 6.3	Formation of $\text{Os}[\text{Si}(\text{OH})_3]\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$	253
Scheme 6.4	Formation of $[\text{OsCl}(\text{CO})(\text{PPh}_3)_2\text{Si}(\text{OH})_2]_2\text{O}$	268
Scheme 6.5	Addition of Lewis Bases to $[\text{OsCl}(\text{CO})(\text{PPh}_3)_2\text{Si}(\text{OH})_2]_2\text{O}$	277

LIST OF ABBREVIATIONS

acac	acetylacetonate
anal.	analysis
bipy	2,2'-bipyridine
<i>i</i> Bu	<i>i</i> -butyl
<i>n</i> Bu	<i>n</i> -butyl
<i>t</i> Bu	<i>t</i> -butyl
Bz	benzyl
COD	cycloocta-1,5-diene
Cp	η^5 -cyclopentadienyl
Cp*	η^5 -pentamethylcyclopentadienyl
Cy	cyclohexyl
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
dcpe	1,2-bis(dicyclohexylphosphino)ethane
dimethylbipy	4,4'-dimethyl-2,2'-bipyridine
diphos	1,2-bis(diphenylphosphino)ethane (or another chelating diphosphine)
DME	1,2-dimethoxyethane
dppe	1,2-bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
dtbpm	bis(di- <i>tert</i> -butylphosphino)methane
Et	ethyl
Hampy	2-amino-6-methylpyridine
HMPA	hexamethylphosphoric triamide, OP(NMe ₃) ₃
Hz	hertz
m. p.	melting point

Me	methyl
MeCp	η^5 -methylcyclopentadienyl
Mes	mesityl
OTf	triflate
Ph	phenyl
phen	1,10-phenanthroline
<i>i</i> Pr	<i>i</i> -propyl
<i>n</i> Pr	<i>n</i> -propyl
py	pyridine
s	second
THF	tetrahydrofuran

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