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**CHEMISTRY  
OF  
LOW-VALENT  
OSMIUM**

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

Kevin Rodger Grundy

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# ABSTRACT

This study concerns the synthesis, structure and reactivity of complexes of  $d^6$  and  $d^8$  osmium. The reactivity of certain ligands coordinated to low-valent osmium has also been investigated.

Various hydride complexes of osmium(II) were prepared as potential precursors of osmium(0).  $\text{OsH}_4(\text{PPh}_3)_3$  reacts with *p*-tolylisocyanide (TIC) and 4-ethyl-2,6,7-trioxo-1-phosphabicyclo[2.2.2]octane (ETPO) to yield  $\text{OsH}_2(\text{L})(\text{PPh}_3)_3$  from which were derived  $\text{OsH}_2(\text{L}^\dagger)(\text{L})(\text{PPh}_3)_2$  (L,  $\text{L}^\dagger = \text{CO}, \text{TIC}, \text{ETPO}$ ). Attempts to eliminate hydrogen from the dihydrides failed.  $\text{OsHCl}(\text{CO})(\text{PPh}_3)_3$  reacts with neutral ligands L (= TIC, ETPO,  $\text{P}(\text{OMe})_3$ ,  $\text{P}(\text{OPh})_3$ ,  $\text{PPh}_2\text{Me}$ ) to give  $\text{OsHCl}(\text{CO})(\text{L})(\text{PPh}_3)_2$  which, with silver perchlorate (L = TIC, ETPO only) afford  $\text{OsH}(\text{OClO}_3)(\text{CO})(\text{L})(\text{PPh}_3)_2$ . The labile perchlorate ligand can be replaced by ligands  $\text{L}^\dagger$  affording  $[\text{OsH}(\text{CO})(\text{L})(\text{L}^\dagger)(\text{PPh}_3)_2]\text{ClO}_4$  (L = TIC,  $\text{L}^\dagger = \text{CO}, \text{TIC}, \text{PPh}_3$ ; L = ETPO,  $\text{L}^\dagger = \text{CO}, \text{ETPO}$ ).  $\text{OsHCl}(\text{CO})(\text{PPh}_3)_3$  reacts with silver perchlorate in acetonitrile to yield  $[\text{OsH}(\text{CO})(\text{CH}_3\text{CN})_2(\text{PPh}_3)_2]\text{ClO}_4$ , which in turn reacts with neutral ligands to give  $[\text{OsH}(\text{CO})(\text{CH}_3\text{CN})(\text{L})(\text{PPh}_3)_2]\text{ClO}_4$  (L = CO, TIC, ETPO,  $\text{PPh}_3$ ). Cationic  $[\text{OsH}(\text{CO})_2(\text{PPh}_3)_3]^+$  and  $[\text{OsH}(\text{TIC})_2(\text{PPh}_3)_3]^+$  can be prepared from the action of  $\text{PPh}_3$  on  $[\text{OsH}(\text{CO})_2(\text{CH}_3\text{CN})(\text{PPh}_3)_2]^+$  and TIC on  $\text{OsH}(\text{O}_2\text{CCH}_3)(\text{PPh}_3)_3$  respectively.

With base,  $[\text{OsH}(\text{CO})(\text{CH}_3\text{CN})(\text{PPh}_3)_3]\text{ClO}_4$  affords  $\text{OsH}(\text{OH})(\text{CO})(\text{PPh}_3)_3$  from which a series of hydroxide complexes  $\text{OsH}(\text{OH})(\text{CO})(\text{L})(\text{PPh}_3)_2$  (L = CO, TIC, ETPO) can be obtained. The hydroxide group in  $\text{OsH}(\text{OH})(\text{CO})(\text{PPh}_3)_3$  is cleaved by acids HX to yield  $\text{OsHX}(\text{CO})(\text{PPh}_3)_3$  (X = F, Br, Cl, I,  $\text{CH}_3\text{CO}_2$ ,  $\text{CF}_3\text{CO}_2$ ,  $\text{SC}_7\text{H}_7$ ,  $\text{OClO}_3$ ). Those members of the series with X = CN,  $\text{N}_3$ , OCN, SCN were obtained from  $\text{OsH}(\text{OClO}_3)(\text{CO})(\text{PPh}_3)_3$  and the appropriate anion. From the values of  $\nu_{\text{CO}}$  for this series can be gained some understanding of the bonding properties of the anionic ligands.

The neutral osmium(0) complexes  $\text{Os}(\text{CO})_2(\text{TIC})(\text{PPh}_3)_2$ ,  $\text{Os}(\text{CO})_2(\text{ETPO})(\text{PPh}_3)_2$ ,  $\text{Os}(\text{CO})_2(\text{PPh}_3)_3$  and  $\text{Os}(\text{CO})(\text{TIC})(\text{PPh}_3)_3$  were prepared by deprotonation of the corresponding cations  $[\text{OsH}(\text{CO})_2(\text{TIC})(\text{PPh}_3)_2]^+$ ,  $[\text{OsH}(\text{CO})_2(\text{ETPO})(\text{PPh}_3)_2]^+$ ,  $[\text{OsH}(\text{CO})_2(\text{PPh}_3)_3]^+$  and  $[\text{OsH}(\text{CO})(\text{TIC})(\text{PPh}_3)_3]^+$ . Oxidative addition reactions of these  $d^8$  complexes have been investigated. Those of  $\text{Os}(\text{CO})_2(\text{TIC})(\text{PPh}_3)_2$  and  $\text{Os}(\text{CO})_2(\text{ETPO})(\text{PPh}_3)_2$  closely parallel the reactions of  $\text{Os}(\text{CO})_3(\text{PPh}_3)_2$  with various oxidants. Protic acids regenerate the hydride cations as the trans isomers. Halogens and mercuric halides also produce cationic products. Dioxygen gives the chelated carbonate complexes  $\text{Os}(\text{CO}_3)(\text{CO})\text{L}(\text{PPh}_3)_2$  ( $\text{L} = \text{TIC}, \text{ETPO}$ ). Whereas non-coordinating acids with  $\text{Os}(\text{CO})_2(\text{PPh}_3)_3$  and  $\text{Os}(\text{CO})(\text{TIC})(\text{PPh}_3)_3$  regenerate the hydride cations, hydrohalic acids afford  $\text{OsHX}(\text{CO})(\text{PPh}_3)_3$ ,  $[\text{OsX}(\text{CO})(\text{TIC})(\text{PPh}_3)_3]^+$  ( $\text{X} = \text{Cl}, \text{Br}$ ) and  $\text{OsI}_2(\text{CO})(\text{TIC})(\text{PPh}_3)_2$ . Halogens yield  $\text{OsX}_2(\text{CO})_2(\text{PPh}_3)_2$  ( $\text{X} = \text{Cl}, \text{I}$ ),  $[\text{OsBr}(\text{CO})_2(\text{PPh}_3)_3]^+$ ,  $[\text{OsX}(\text{CO})(\text{TIC})(\text{PPh}_3)_3]^+$  ( $\text{X} = \text{Cl}, \text{Br}$ ) and  $\text{OsI}_2(\text{CO})(\text{TIC})(\text{PPh}_3)_2$ . Three isomeric forms of  $\text{OsI}_2(\text{CO})_2(\text{PPh}_3)_2$  were isolated. In a novel reaction, sulphonyl chlorides react with all four complexes affording  $[\text{OsCl}(\text{CO})(\text{L})(\text{L}')(\text{PPh}_3)_2]\text{RSO}_3$  ( $\text{L} = \text{CO}, \text{L}' = \text{TIC}, \text{PPh}_3, \text{ETPO}$ ;  $\text{L} = \text{TIC}, \text{L}' = \text{PPh}_3$ ;  $\text{R} = \text{Me}, p\text{-tolyl}$ ).

$\text{Os}(\text{CO})_2(\text{PPh}_3)_3$  and  $\text{Os}(\text{CO})(\text{TIC})(\text{PPh}_3)_3$  undergo substitution reactions and oxidatively add  $\text{H}_2$ ,  $\text{C}_2\text{H}_4$  and  $\text{CS}_2$ . These reactions appear to proceed via dissociation of a labile phosphine to form a transient 16 electron species:- a unique process in osmium(0) chemistry. Adducts with  $\text{PhC}_2\text{H}$  and  $\text{PhC}_2\text{Ph}$  were obtained only with  $\text{Os}(\text{CO})_2(\text{PPh}_3)_3$ , which also reacts with dioxygen to form the first dioxygen adduct of osmium,  $\text{Os}(\text{O}_2)(\text{CO})_2(\text{PPh}_3)_2$ . This complex reacts with  $\text{SO}_2$  and  $\text{N}_2\text{O}_4$  to give sulphate and dinitrate complexes of osmium(II).

To study the susceptibility towards nucleophilic attack of carbon monoxide and TIC coordinated to osmium(II) a series of complex cations

was chosen.  $\text{OsHCl}(\text{CO})(\text{TIC})(\text{PPh}_3)_2$  reacts with perchloric acid to give  $\text{OsCl}(\text{OClO}_3)(\text{CO})(\text{TIC})(\text{PPh}_3)_2$ , of which two isomeric forms were isolated. With neutral ligands, the perchlorate group can be displaced to give  $[\text{OsCl}(\text{CO})(\text{TIC})(\text{L})(\text{PPh}_3)_2]\text{ClO}_4$  ( $\text{L} = \text{CO}, \text{TIC}$ ).  $[\text{OsCl}(\text{CO})_2(\text{TIC})(\text{PPh}_3)_2]^+$  reacts with azide ions to give  $\text{OsCl}(\text{NCO})(\text{CO})(\text{TIC})(\text{PPh}_3)_2$ , and reversibly with primary amines yielding  $\text{OsCl}(\text{CONHR})(\text{CO})(\text{TIC})(\text{PPh}_3)_2$ . Basic alcohols afford  $\text{OsCl}(\text{CO}_2\text{R})(\text{CO})(\text{TIC})(\text{PPh}_3)_2$  ( $\text{R} = \text{Me}, \text{Et}$ ), and with 2-chloroethanol a heterocyclic carbene complex  $[\text{OsCl}(\text{CO})(\text{TIC})(\overline{\text{COC}_2\text{H}_4\text{O}})(\text{PPh}_3)_2]^+$  results.  $[\text{OsCl}(\text{CO})(\text{TIC})_2(\text{PPh}_3)_2]^+$  reacts only with methoxide ions to give  $[\text{Os}(\text{OMe})(\text{CO})(\text{TIC})_2(\text{PPh}_3)_2]^+$  which, with perchloric acid, affords  $[\text{Os}(\text{OClO}_3)(\text{CO})(\text{TIC})_2(\text{PPh}_3)_2]^+$ .  $[\text{OsCl}(\text{CO})_2(\text{TIC})(\text{PPh}_3)_2]^+$  reacts with hydrosulphide ions at the isocyanide ligand affording a  $\pi$ -isothiocyanate complex  $\text{Os}(\pi\text{-SCNp-tolyl})(\text{CO})_2(\text{PPh}_3)_2$ . This complex can be protonated and methylated at nitrogen to give bidentate thiocarboxamide complexes,  $[\text{Os}(\text{h}^2\text{-SCNRP-tolyl})(\text{CO})_2(\text{PPh}_3)_2]^+$  ( $\text{R} = \text{H}, \text{Me}$ ).

The ligand reactivity of certain  $\pi$ -complexes has been investigated.  $\text{Os}(\text{C}_2\text{H}_4)(\text{CO})_2(\text{PPh}_3)_2$  reacts with excess hydrochloric acid to produce the hydroxycarbene complex  $\text{OsCl}_2(\text{CO})(\text{C}[\text{OH}]\text{C}_2\text{H}_5)(\text{PPh}_3)_2$ , which reacts reversibly with base to give  $\text{OsCl}(\text{C}_2\text{H}_5)(\text{CO})_2(\text{PPh}_3)_2$ . With other acids, the ethyl complexes  $\text{Os}(\text{C}_2\text{H}_5)\text{X}(\text{CO})_2(\text{PPh}_3)_2$  ( $\text{X} = \text{I}, \text{CF}_3\text{CO}_2, \text{OClO}_3$ ) result.  $\text{Os}(\text{C}_2\text{H}_5)(\text{OClO}_3)(\text{CO})_2(\text{PPh}_3)_2$  reacts with neutral ligands and sodium diethyldithiocarbamate affording  $[\text{Os}(\text{C}_2\text{H}_5\text{CO})(\text{CO})(\text{L})_2(\text{PPh}_3)_2]\text{ClO}_4$  ( $\text{L} = \text{CO}, \text{TIC}$ ) and  $\text{Os}(\text{C}_2\text{H}_5\text{CO})(\text{S}_2\text{CNET}_2)(\text{CO})(\text{PPh}_3)_2$  respectively.

$\text{Os}(\pi\text{-CS}_2)(\text{CO})_2(\text{PPh}_3)_2$  reacts with methyl iodide to give  $\text{OsI}(\text{CS}_2\text{Me})(\text{CO})_2(\text{PPh}_3)_2 \cdot \text{MeI}$ . The methyldithioester ligand of this complex chelates in polar media affording  $[\text{Os}(\text{h}^2\text{-C}[\text{S}]\text{SMe})(\text{CO})_2(\text{PPh}_3)_2]^+$ . With acids  $\text{HX}$ ,  $\text{Os}(\pi\text{-CS}_2)(\text{CO})_2(\text{PPh}_3)_2$  yields the first osmium thiocarbonyl complexes,  $\text{OsX}_2(\text{CO})(\text{CS})(\text{PPh}_3)_2$  ( $\text{X} = \text{Cl}, \text{I}$ ).

Dibromoalkanes,  $\text{Br}(\text{CH}_2)_n\text{Br}$ , react with  $\text{Os}(\pi\text{-CS}_2)(\text{CO})_2(\text{PPh}_3)_2$  affording complexes of new heterocyclic carbenes,  $[\text{OsBr}(\text{CO})_2(\overline{\text{CS}[\text{CH}_2]_n\text{S}})(\text{PPh}_3)_2]^+$  ( $n = 1, 2, 3$ ), from which can be derived  $\text{OsBr}_2(\text{CO})(\overline{\text{CS}[\text{CH}_2]_n\text{S}})(\text{PPh}_3)_2$  ( $n = 2, 3$ ).  $\text{Os}(\pi\text{-CS}_2)(\text{CO})(\text{TIC})(\text{PPh}_3)_2$  behaves similarly in giving  $[\text{Os}(\text{h}^2\text{-C}[\text{S}]\text{SMe})(\text{CO})(\text{TIC})(\text{PPh}_3)_2]^+$ ,  $\text{OsCl}_2(\text{CS})(\text{TIC})(\text{PPh}_3)_2$  and  $[\text{OsBr}(\text{CO})(\text{TIC})(\overline{\text{CSC}_2\text{H}_4\text{S}})(\text{PPh}_3)_2]^+$ .

To investigate the reactivity of a complexed functional isocyanide, various complexes of tosylmethylisocyanide (TMIC) were synthesized. Whereas deprotonation of  $[\text{OsH}(\text{CO})_2(\text{TMIC})(\text{PPh}_3)_2]^+$  gives  $\text{Os}(\text{CO})_2(\text{TMIC})(\text{PPh}_3)_2$ , attempted deprotonation of  $[\text{OsH}(\text{CO})(\text{TMIC})(\text{PPh}_3)_3]^+$  results in the dealkylation of TMIC to yield  $\text{OsH}(\text{CN})(\text{CO})(\text{PPh}_3)_3$ .

$\text{OsHCl}(\text{CO})(\text{TMIC})(\text{PPh}_3)_2$  reacts with base and carbonyl compounds to give heterocyclic carbene complexes  $\text{OsHCl}(\text{CO})(\overline{\text{CNHXYO}})(\text{PPh}_3)_2$ ,  $\text{XY} = \text{CH}=\text{C}(\text{Ar})$ , ( $\text{Ar} = \text{Ph}$ , *p*-tolyl);  $\text{CH}(\text{OR}_1)\text{CR}_2\text{R}_3$ , ( $\text{R}_1 = \text{Me}$ ,  $\text{R}_2 = \text{R}_3 = \text{H}$ ;  $\text{R}_1 = \text{Me}$ ,  $\text{Et}$ ,  $\text{R}_2 = \text{H}$ ,  $\text{R}_3 = \text{Me}$ ;  $\text{R}_1 = \text{R}_2 = \text{R}_3 = \text{Me}$ ). Under similar conditions,  $[\text{OsCl}(\text{CO})_2(\text{TMIC})(\text{PPh}_3)_2]^+$  yields  $\text{OsCl}(\overline{\text{C}=\text{NCH}[\text{Tos}]\text{CH}[\text{R}]\text{O}})(\text{CO})_2(\text{PPh}_3)_2$  ( $\text{R} = \text{Me}$ ,  $\text{Ph}$ ), which can be protonated at nitrogen ( $\text{R} = \text{Me}$ ) to give a cationic carbene complex. Base and acetaldehyde with  $[\text{OsH}(\text{CO})_2(\text{TMIC})(\text{PPh}_3)_2]^+$  gives trans- $[\text{OsH}(\text{CO})_2(\overline{\text{CNHCH}[\text{OMe}]\text{CH}[\text{Me}]\text{O}})(\text{PPh}_3)_2]^+$ .

The action of silver perchlorate and carbon monoxide on  $\text{OsHCl}(\text{CO})(\overline{\text{CNHXYO}})(\text{PPh}_3)_2$  produces  $[\text{OsH}(\text{CO})_2(\overline{\text{CNHXYO}})(\text{PPh}_3)_2]^+$  ( $\text{XY} = \text{CH}(\text{OMe})\text{CH}(\text{Me})$ ,  $\text{CH}(\text{OMe})\text{C}(\text{Me})_2$ ,  $\text{CH}=\text{C}(\text{Ph})$ ) from which can be obtained  $\text{OsH}(\overline{\text{C}=\text{NXYO}})(\text{CO})_2(\text{PPh}_3)_2$  ( $\text{XY} = \text{CH}(\text{OMe})\text{CH}(\text{Me})$ ,  $\text{CH}(\text{OMe})\text{C}(\text{Me})_2$ ) by reversible deprotonation at the ligand. Methyl iodide and  $\text{OsH}(\overline{\text{C}=\text{NXYO}})(\text{CO})_2(\text{PPh}_3)_2$  react to give  $[\text{OsH}(\text{CO})_2(\overline{\text{CN}[\text{Me}]\text{XYO}})(\text{PPh}_3)_2]^+$  which do not deprotonate at the metal.  $\text{OsHCl}(\text{CO})(\overline{\text{CNHCH}[\text{OMe}]\text{C}[\text{Me}]_2\text{O}})(\text{PPh}_3)_2$  reacts with perchloric acid affording  $\text{OsCl}(\text{OClO}_3)(\text{CO})(\overline{\text{CNHCH}[\text{OMe}]\text{C}[\text{Me}]_2\text{O}})(\text{PPh}_3)_2$  which has been used to prepare  $[\text{OsCl}(\text{CO})_2(\overline{\text{CNHCH}[\text{OMe}]\text{C}[\text{Me}]_2\text{O}})(\text{PPh}_3)_2]^+$ ,  $\text{OsCl}(\overline{\text{C}=\text{NCH}[\text{OMe}]\text{C}[\text{Me}]_2\text{O}})(\text{CO})_2(\text{PPh}_3)_2$  and  $[\text{OsCl}(\text{CO})_2(\overline{\text{CN}[\text{Me}]\text{CH}[\text{OMe}]\text{C}[\text{Me}]_2\text{O}})(\text{PPh}_3)_2]^+$ .

Infrared and  $^1\text{H}$  n.m.r. spectroscopy, conductivity and elemental analysis have been used in formulation and structural assignment.

ABBREVIATIONS:

PPh <sub>3</sub>	:	triphenylphosphine	
TIC	:	p-tolylisocyanide	
ETPO	:	4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane	
TMIC	:	tosylmethylyisocyanide	
dppe	:	1,2-bis(diphenylphosphino)ethane	
dmpe	:	1,2-bis(dimethylphosphino)ethane	
depe	:	1,2-bis(diethylphosphino)ethane	
dppm	:	bis(diphenylphosphino)methane	
diars	:	o-phenylenebis(dimethylarsine)	
PCy <sub>3</sub>	:	tricyclohexylphosphine	
1,3-COD	:	1,3-cyclooctadiene	
1,5-COD	:	1,5-cyclooctadiene	
COT	:	cyclooctatetraene	NBD : norbornadiene
Me	:	methyl	<sup>n</sup> Bu : n-butyl
Et	:	ethyl	<sup>t</sup> Bu : t-butyl
R	:	unspecified organic group	
L	:	unspecified neutral ligand	
X	:	unspecified anionic ligand	
DMF	:	dimethylformamide	
THF	:	tetrahydrofuran	
DMSO	:	dimethylsulphoxide	
conc.	:	concentrated	



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