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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

January 1993
"A wise man will hear and will increase learning"

Proverbs 1:5
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, 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, $M(SiR_3)Cl(CO)(PPh_3)_2$ ($M = Ru, Os; R = Cl, alkyl group, alkoxy group$), is described in chapter two. The reaction of $M(Ph)Cl(CO)(PPh_3)_2$ ($M = Ru, Os$) with a silane, in some instances, provided a facile, high yield route to complexes of the type $M(SiR_3)Cl(CO)(PPh_3)_2$ ($M = Ru; SiR_3 = SiMe_3, SiEt_3, SiCl_3, SiMe_2Cl; M = Os; SiR_3 = SiCl_3, SiMe_2Cl$). The chlorosilyl complexes were also prepared by treatment of $MHCl(CO)(PPh_3)_3$ ($M = Ru, Os$) with $HSiCl_3$ and $HSiMe_2Cl$. X-ray crystal structures were obtained of $Ru(SiEt_3)Cl(CO)(PPh_3)_2$ and $Os(SiCl_3)Cl(CO)(PPh_3)_2$.

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 $Ru[Si(OEt)_3]Cl(CO)(PPh_3)_2$ and $Os(SiMe_3)Cl(CO)(PPh_3)_2$. 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 $\text{Os(SiMe}_2\text{C}_6\text{H}_4\text{PPh}_2)(\text{C}_6\text{H}_4\text{PPh}_2)(\text{CO})(\text{PPh}_3)$, 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, $\text{M(SiR}_3\text{Cl(CO)(PPh}_3\text{)}_2$ ($\text{M} = \text{Ru, Os}$), is described. The coordinatively saturated osmium silyl complexes $\text{Os(SiR}_3\text{Cl(CO)L(PPh}_3\text{)}_2$ ($\text{SiR}_3 = \text{SiCl}_3$, $\text{SiMe}_2\text{Cl}$, $\text{SiMe}_2\text{OEt}$, $\text{SiMe}_3$; $\text{L} = \text{CO}, \text{CNR}$) were generated in this way. Similarly, addition of 4,4'-dimethyl-2,2'-bipyridine to $\text{Ru(SiEt}_3\text{Cl(CO)(PPh}_3\text{)}_2$ afforded $\text{Ru(SiEt}_3\text{Cl(dimethylbipy)(CO)(PPh}_3\text{)}_2$. The six-coordinate complex $\text{Ru(SiEt}_3\text{(η}^2\text{-S}_2\text{CNMe}_2\text{)(CO)(PPh}_3\text{)}_2$ was synthesized by displacement of the labile chloride ligand from $\text{Ru(SiEt}_3\text{Cl(CO)(PPh}_3\text{)}_2$ by the dimethylthiocarbamate anion. Characterization of $\text{Ru(SiEt}_3\text{(η}^2\text{-S}_2\text{CNMe}_2\text{)(CO)(PPh}_3\text{)}_2$ included an X-ray crystallographic analysis. The exchange of silyl groups at the metal was also observed in several reactions. For example, heating $\text{Ru(SiMe}_3\text{Cl(CO)(PPh}_3\text{)}_2$ in the presence of excess HSiEt$_3$ yielded $\text{Ru(SiEt}_3\text{Cl(CO)(PPh}_3\text{)}_2$. 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 $\text{Os(CO)}_2(\text{PPh}_3)_3$, which yielded $\text{Os(SiR}_3\text{H(CO)}_2(\text{PPh}_3)_2$ ($\text{SiR}_3 = \text{SiMe}_3$, $\text{SiEt}_3$, $\text{SiPh}_3$, $\text{SiPh}_2\text{H}$). The synthesis of these complexes is also discussed in chapter three. An X-ray crystal structure determination of $\text{Os(SiEt}_3\text{H(CO)}_2(\text{PPh}_3)_2$ confirmed the presence of mutually trans carbonyl ligands.

The first thiocarbonyl-containing transition metal silyl complexes, $\text{M(SiMe}_2\text{Cl(Cl(CS)(PPh}_3\text{)}_2$ ($\text{M} = \text{Ru, Os}$), were prepared by treating $\text{M(Ph)(CS)(PPh}_3\text{)}_2$ or $\text{MCl(CS)(PPh}_3\text{)}_3$ with HSiMe$_2$Cl. The Si-Cl bond in these compounds reacted readily with nucleophiles, yielding $\text{M(SiMe}_2\text{OR)(Cl(CS)(PPh}_3\text{)}_2$ ($\text{OR} = \text{OEt, OMe, OH}$). In contrast to the addition of CO to $\text{Os(SiR}_3\text{Cl(CO)(PPh}_3\text{)}_2$, addition of CO to $\text{Ru(SiMe}_2\text{R)(Cl(CS)(PPh}_3\text{)}_2$ ($\text{R} = \text{Cl, OEt, OMe, OH}$) and to $\text{Os(SiMe}_2\text{OEt)(Cl(CS)(PPh}_3\text{)}_2$ afforded dihapto-thioacyl complexes, $\text{M[η}^2\text{-C(S)SiMe}_2\text{R]}\text{Cl(CO)(PPh}_3\text{)}_2$, 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 Ru[η²-C(SiMe₂OEt)]Cl(CO)(PPh₃)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 Os(Ph)Cl(CO)(PPh₃)₂ was reacted with HSiMe₃, the formally osmium(IV) silyl complex Os(SiMe₃)H₃(CO)(PPh₃)₂ was produced. Few compounds of this type are known. The synthesis, characterization and reactivity of Os(SiMe₃)H₃(CO)(PPh₃)₂ are discussed in chapter five. The crystal structure of Os(SiMe₃)H₃(CO)(PPh₃)₂ is also depicted. In solution, Os(SiMe₃)H₃(CO)(PPh₃)₂ appeared to be in equilibrium with the highly reactive, coordinatively unsaturated species OsH₂(CO)(PPh₃)₂. The reaction of Os(SiMe₃)H₃(CO)(PPh₃)₂ with HSiR₃ (R = Et, Ph), HSn(p-tolyl)₃ and HC₂Ph was carried out, using Os(SiMe₃)H₃(CO)(PPh₃)₂ as an in situ source of OsH₂(CO)(PPh₃)₂. These reactions afforded Os(SiR₃)H₃(CO)(PPh₃)₂ (R = Et, Ph), Os[Sn(p-tolyl)₃]₂H₂(CO)(PPh₃)₂ and OsH(C₂Ph)(CO)(PPh₃)₃ respectively, most likely via a series of oxidative addition-reductive elimination reactions involving OsH₂(CO)(PPh₃)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 M(SiMe₂Cl)Cl(CO)(PPh₃)₂ and M(SiCl₃)Cl(CO)(PPh₃)₂. The complexes M[Si(OH)₃]Cl(CO)(PPh₃)₂ are the first trihydroxysilyl-containing transition metal complexes and therefore represent a new class of transition metal silyl compounds. Characterization of Os[Si(OH)₃]Cl(CO)(PPh₃)₂ included an X-ray crystal structure which showed that, remarkably, no inter- or intra-molecular hydrogen bonding of the type O(H)···O or O(H)···Cl was associated with the Si(OH)₃ group. In contrast, intermolecular hydrogen bonding was found by X-ray crystallography for the dicarbonyl derivative, Os[Si(OH)₃]Cl(CO)₂(PPh₃)₂. Subsequent reactions involving Os[Si(OH)₃]Cl(CO)(PPh₃)₂ led to the synthesis of the diosmium tetrahydroxydisiloxane complex, [OsCl(CO)(PPh₃)₂Si(OH)₂]₂O. For example, [OsCl(CO)(PPh₃)₂Si(OH)₂]₂O was isolated after Os(SiCl₃)Cl(CO)(PPh₃)₂ was added to a dichloromethane solution of Os[Si(OH)₃]Cl(CO)(PPh₃)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 [OsCl(CO)(PPh₃)₂Si(OH)₂]₂O.

Chapter seven provides a short conclusion, highlighting the important features of the work discussed in this thesis and identifies areas for future investigation.
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<th>Full Form</th>
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</thead>
<tbody>
<tr>
<td>acac</td>
<td>acetylacetonate</td>
</tr>
<tr>
<td>anal.</td>
<td>analysis</td>
</tr>
<tr>
<td>bipy</td>
<td>2,2'-bipyridine</td>
</tr>
<tr>
<td>iBu</td>
<td>i-butyl</td>
</tr>
<tr>
<td>nBu</td>
<td>n-butyl</td>
</tr>
<tr>
<td>tBu</td>
<td>t-butyl</td>
</tr>
<tr>
<td>Bz</td>
<td>benzyl</td>
</tr>
<tr>
<td>COD</td>
<td>cycloocta-1,5-diene</td>
</tr>
<tr>
<td>Cp</td>
<td>η⁵-cyclopentadienyl</td>
</tr>
<tr>
<td>Cp*</td>
<td>η⁵-pentamethylcyclopentadienyl</td>
</tr>
<tr>
<td>Cy</td>
<td>cyclohexyl</td>
</tr>
<tr>
<td>DBU</td>
<td>1,8-diazabicyclo[5.4.0]undec-7-ene</td>
</tr>
<tr>
<td>dcpe</td>
<td>1,2-bis(dicyclohexylphosphino)ethane</td>
</tr>
<tr>
<td>dimethylbipy</td>
<td>4,4'-dimethyl-2,2'-bipyridine</td>
</tr>
<tr>
<td>diphos</td>
<td>1,2-bis(diphenylphosphino)ethane (or another chelating diphosphine)</td>
</tr>
<tr>
<td>DME</td>
<td>1,2-dimethoxyethane</td>
</tr>
<tr>
<td>dppe</td>
<td>1,2-bis(diphenylphosphino)ethane</td>
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<tr>
<td>dppm</td>
<td>bis(diphenylphosphino)methane</td>
</tr>
<tr>
<td>dtbpm</td>
<td>bis(di-tert-butylphosphino)methane</td>
</tr>
<tr>
<td>Et</td>
<td>ethyl</td>
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<tr>
<td>Hampy</td>
<td>2-amino-6-methylpyridine</td>
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<tr>
<td>HMPA</td>
<td>hexamethylphosphoric triamide, OP(NMe₃)₃</td>
</tr>
<tr>
<td>Hz</td>
<td>hertz</td>
</tr>
<tr>
<td>m. p.</td>
<td>melting point</td>
</tr>
</tbody>
</table>
Me  methyl
MeCp  η⁵-methylcyclopentadienyl
Mes  mesityl
OTf  triflate
Ph  phenyl
phen  1,10-phenanthroline
iPr  i-propyl
nPr  n-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.