Compounds with ruthenium–silicon and osmium–silicon bonds

George R. Clark, Clifton E.F. Rickard, Warren R. Roper, David M. Salter,
and L. James Wright.
Department of Chemistry, University of Auckland, Auckland, New Zealand.

Abstract – As a first step in examining the effectiveness of metal-ligand
fragments such as $M(CO)_2(PPh_3)_2$ and $MCl_2(CO)(PPh_3)_2$ (M = Ru or Os) in
stabilising unsaturated silicon ligands (silylenes or silanediyls, SiR_2),
synthetic routes have been developed to various likely precursors. These
are ruthenium-silicon and osmium-silicon bonded compounds which have either
suitably functionalised silyl groups or are coordinatively unsaturated.
Reaction between $MPhCl(CO)(PPh_3)_2$ and silanes, R_3SiH, results in
elimination of C_6H_6 and formation of $M(SiR_3)Cl(CO)(PPh_3)_2$. In this way
$Ru(SiEt_3)Cl(CO)(PPh_3)_2$, $Ru(SiCl_3)Cl(CO)(PPh_3)_2$, and $Os(SiCl_3)Cl(CO)(PPh_3)_2$
have been prepared. The $SiCl_3$-ligand can be substituted at Si without
rupture of the metal-Si bond and compounds derived include
$Ru[Si(OEt)_3]Cl(CO)(PPh_3)_2$ and $Os(SiMe_3)Cl(CO)(PPh_3)_2$. The five coordinate
compounds are all coloured yellow to orange and X-ray crystal structure
determinations of $Ru(SiEt_3)Cl(CO)(PPh_3)_2$, $Ru[Si(OEt)_3]Cl(CO)(PPh_3)_2$ and
$Os(SiMe_3)Cl(CO)(PPh_3)_2$ reveal an approximately square pyramidal geometry
with the Si-ligand apical and the triphenylphosphine ligands arranged
mutually trans. Reaction between $Hg(SiMe_3)_2$ and $OsHCl(CO)(PPh_3)_3$ produces
a mixture of products, one of which is $Os(SiMe_3)Cl(CO)(PPh_3)_2$. Another is
$Os(SiMe_2C_6H_4PPh_2)(C_6H_4PPh_2)(CO)(PPh_3)$. The formation of this compound may
involve an electrophilic silylene complex as an intermediate.

INTRODUCTION

Despite much recent activity, which has seen the synthesis of well-defined complexes in
which divalent derivatives of germanium, tin, and lead function as ligands (ref. 1), the
corresponding silicon compounds remain elusive. However, several "base-stabilised" silylene
complexes are known including $[Cp(PMe_3)_2RuSiPh_2.CH_3CN]BPh_4$ (ref. 2),
$(CO)_4Fe[Si(Ot-Bu)_2].HMPT$ (ref. 3) (HMPT = hexamethylphosphorictriamide) and the "internally-
stabilised" example $Cp^*(CO)Fe(SiMe_2(OMe)SiMe(OMe))$ (ref. 4). The present lack of "base-
free" examples indicates that silylene ligands will be very electrophilic, a conclusion
supported by ab initio calculations (ref. 5), and suggests interesting reactivity for
silylene complexes similar perhaps to that exhibited by Fischer-type carbene complexes.

Triphenylphosphine-substituted metal-ligand fragments of ruthenium and osmium have proved
useful in identifying stable complexes of the ligands CH_2 (ref. 6), CF_2 (ref. 7), and CCl_2
(ref. 8). The reasons for the effectiveness of these fragments include: good π-donor
properties, steric protection of metal-ligand multiple bonds by the bulky triphenylphosphine
ligands, and the kinetic inertness of five coordinate d^8 and six coordinate d^6 complexes.
This study was initiated to examine the possibility of stabilising silylenes at ruthenium
and osmium centres and to explore the reactions of any transient silylene complexes which
might be produced. Following the successful strategies for the generation of dihalocarbene
complexes (ref. 9) our approach has been as follows:

$$L_nM\text{-}SiR_2X \longrightarrow [L_nM{=}SiR_2]^+ + X^- \qquad (1)$$
$$\text{18e}$$

$$L_nM\text{-}SiR_2X \longrightarrow L_nXM{=}SiR_2 \qquad (2)$$
$$\text{16e}$$

In equation (1) a saturated complex with a suitably functionalised silyl ligand is trans-
formed into a silylene complex by removal of X^-. A recent related example involves a
germanium derivative (ref. 10) and an equilibrium between germyl and germylene where L_nM is
the good π-donor, $[Cp^*Re(NO)(PPh_3)]^+$, and X is triflate. In equation (2), involving a coord-
inatively unsaturated metal centre, a migration of X from Si to M takes place. A good

example of this type of process for the production of a carbene complex is the following
(ref. 11):

$$Ir(COCF_2Cl)(CO)_2(PPh_3)_2 \xrightarrow[-2CO]{\Delta} Ir(CF_2Cl)(CO)(PPh_3)_2 \longrightarrow Ir(=CF_2)Cl(CO)(PPh_3)_2$$
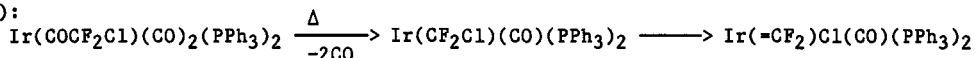
To pursue these approaches attention was directed towards the synthesis of coordinatively
unsaturated ruthenium and osmium silyl complexes.

REACTION BETWEEN MPhCl(CO)(PPh₃)₂ AND SILANES

Silyl groups have been introduced into ruthenium and osmium complexes via the oxidative-
addition of silanes either to $M(CO)_5$ (ref. 12) or to $Cp^*(PMe_3)_2Ru(CH_2SiMe_3)$ (ref. 2). The
availability of five coordinate complexes of formula, $MRCl(CO)(PPh_3)_2$ (ref. 13) suggested
that reaction with silanes might proceed via oxidative addition followed by reductive
elimination effecting an overall exchange of R-groups for silyl-groups. The electrophilic
cleavage of R-groups from other osmium(II) complexes has been demonstrated to proceed by this
this mechanism (ref. 14). This reaction, as illustrated in equation (3), gives good yields
at least for some silanes. The reaction is complete in times varying from minutes at room
temperature for $HSiCl_3$ to hours at 80 °C for Et_3SiH.

$$MPhCl(CO)(PPh_3)_2 + R_3SiH \longrightarrow M(SiR_3)Cl(CO)(PPh_3)_2 + C_6H_6 \qquad (3)$$
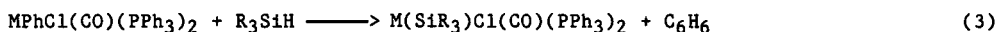
A selection of new compounds prepared by this method together with characterizing data is
presented in Table I. The reaction was unsuccessful for Ph_3SiH and with $Me_3SiSiMe_2H$ gave
$OsHPh(CO)(PPh_3)_3$ as product. All of the five coordinate silyl complexes are coloured yellow
to orange. $Os(SiCl_3)Cl(CO)(PPh_3)_2$ when treated with MeLi underwent substitution at silicon
yielding, finally, $Os(SiMe_3)Cl(CO)(PPh_3)_2$. The retention of the Os-Si bond during this
reaction augers well for the further elaboration of the silyl ligand. In a similar manner
$Ru(SiCl_3)Cl(CO)(PPh_3)_2$ was converted to $Ru[Si(OEt)_3]Cl(CO)(PPh_3)_2$ on treatment with EtOH.
To ascertain the geometry of these five coordinate complexes, and the metal-silicon bond
distance dependence on the substituents at silicon, single crystal X-ray crystal structure
determinations of $Ru(SiEt_3)Cl(CO)(PPh_3)_2$ and $Ru[Si(OEt)_3]Cl(CO)(PPh_3)_2$ were undertaken.
The structures are depicted in Figs 1 and 2, respectively, and in addition Fig. 3 depicts
$Os(SiMe_3)Cl(CO)(PPh_3)_2$. In each case the geometry is approximately square pyramidal with
the triphenylphosphine ligands mutually <u>trans</u> and the silyl ligand apical. Replacement of
Et-groups on Si by OEt-groups shortens the Ru-Si distance by almost 0.1 Å. Remarkably,
the presence of OEt-groups also shortens the Ru-P distances and the Ru-Cl distance.
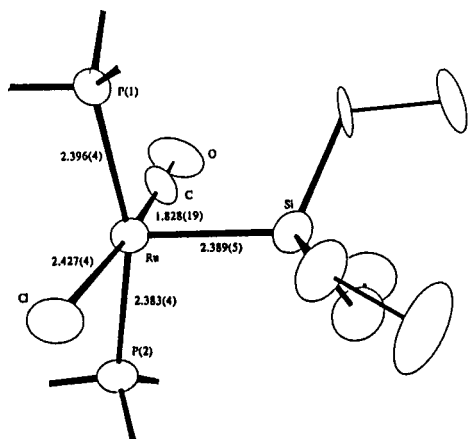

Fig. 1. Structure of Ru(SiEt₃)Cl(CO)(PPh₃)₂
(Phenyl rings omitted)
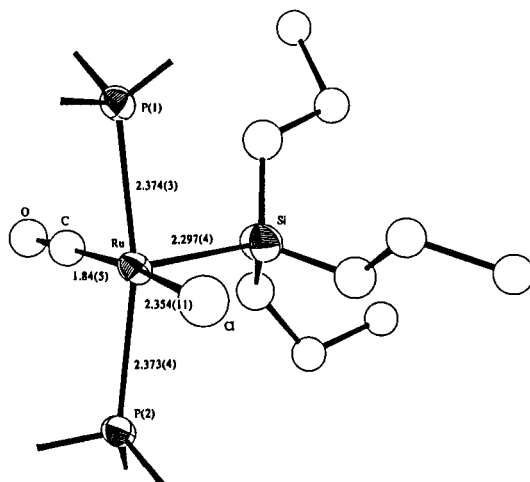
Fig. 2. Structure of Ru[Si(OEt)₃]Cl(CO)(PPh₃)₂
(Phenyl rings omitted)

REACTION BETWEEN MHCl(CO)(PPh₃)₃ AND Hg(SiMe₃)₂

Mercury silyl compounds have been used previously to introduce silyl ligands (ref. 15). The
"expected" product from reaction between $OsHCl(CO)(PPh_3)_2$ and $Hg(SiMe_3)_2$ is
$Os(SiMe_3)Cl(CO)(PPh_3)_2$. However, this is produced in very low yield. An unusual product,

in good yield, is $\overline{Os(SiMe_2C_6H_4PPh_2)}(C_6H_4PPh_2)(CO)(PPh_3)$. This product, the structure of

TABLE 1. Spectroscopic data for new compounds

Compound a	IR b (cm⁻¹)		NMR δ (ppm)		
	ν(CO) c	Other bands f	¹H	³¹P	²⁹Si
Ru(SiMe₃)Cl(CO)(PPh₃)₂	1898,1918 (1911) d	835	0.19(s) 9H -CH₃ 7.61-7.32(m) 30H -C₆H₅	32.76(s)	-21.90(t) ²J(Si,P)=7.4
Ru(SiEt₃)Cl(CO)(PPh₃)₂	1902	998	0.71(t) 9H -CH₃ ³J(H,H)=7.5 0.83(q) 6H -CH₂- ³J(H,H)=7.5 7.62-7.31(m) 30H -C₆H₅	32.81(s)	–
Ru[Si(OEt)₃]Cl(CO)(PPh₃)₂	1922	1072,940	0.91(t) 9H -CH₃ ³J(H,H)=7.0 3.50(q) 6H -CH₂- ³J(H,H)=7.0 7.68-7.30(m) 30H -C₆H₅	33.89(s)	-16.90(t) ²J(Si,P)=17.4
Ru(SiCl₃)Cl(CO)(PPh₃)₂	1955	e	–	–	18.17(t) ²J(Si,P)=20.8
Os(SiMe₃)Cl(CO)(PPh₃)₂	1885,1905 (1890) d	830	0.14(s) 9H -CH₃ 7.60-7.34(m) 30H -C₆H₅	21.85(s)	–
Os(SiCl₃)Cl(CO)(PPh₃)₂	1994	e	–	–	-66.72(t) ²J(Si,P)=11.4
Os(SiMe₂C₆H₄PPh₂)(C₆H₄PPh₂)(CO)(PPh₃)₂	1908	837,800	-1.14(s) 3H -CH₃ 0.11(s) 3H -CH₃ 7.70-5.60(m) 43H -C₆H₅, -C₆H₄	-63.72(dd) ²J(P,P'trans)=223.0 ²J(P,P"cis)=19.7 -7.96(dd) -P(C₆H₅)₃ ²J(P",Pcis)=19.7 ²J(P",P'cis)16.0 27.45(d,d) ²J(P'Ptrans)=223.0 ²J(P',P"cis)=16.0	–

a Satisfactory elemental analyses were obtained for all new compounds

b Measured as nujol mulls between KBr plates

c All absorptions strong

d In CH₂Cl₂ solution

e ν(SiCl) obscured by PPh₃ absorption at 517 cm⁻¹

f Absorption bands associated with the silyl groups (all medium intensity)

g Chemical shift values (CDCl₃ solution) referenced to : ¹H, TMS (= 0.00 ppm) or CHCl₃ (= 7.26 ppm); ³¹P, 85 % H₃PO₄ external reference (= 0.00 ppm); ²⁹Si, TMS (= 0.00 ppm).
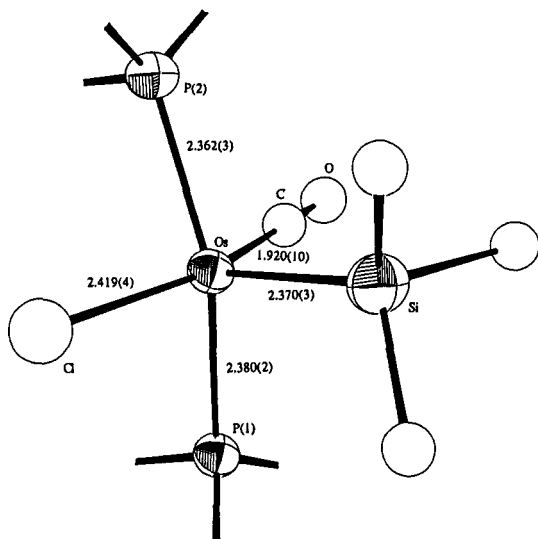
Fig. 3. Structure of $Os(SiMe_3)Cl(CO)(PPh_3)_2$
(Phenyl rings omitted)
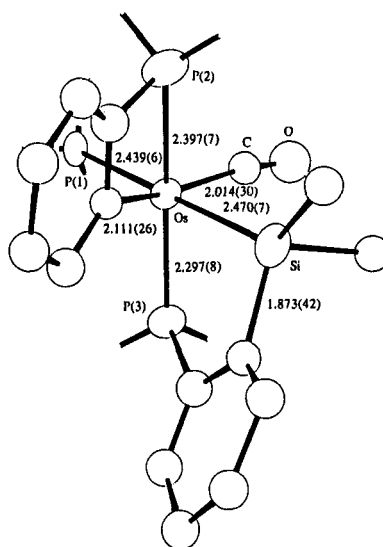
Fig. 4. $Os(SiMe_2C_6H_4PPh_2)(C_6H_4PPh_2)(CO)(PPh_3)$
(Some phenyl rings omitted)

which is depicted in Fig. 4 could arise from an intermediate silylene complex "$OsHCl(=SiMe_2)(CO)(PPh_3)_2$". A parallel reaction occurs for the chlorocarbene complex,

$[OsCl(=CHCl)(CO)_2(PPh_3)_2]^+$, which forms $Os(CHClC_6H_4PPh_2)Cl(CO)_2(PPh_3)_2$ (ref. 16). The postulated silylene complex could be formed in a reaction which again has parallels in transition metal carbene chemistry, the formation of $Ru(=CF_2)(CO)(PPh_3)_2$ from $Ru(CF_3)(CdCF_3)(CO)_2(PPh_3)_2$ by elimination of CF_3CdF (ref. 7).

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