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Oxidative addition of Group 14 hydrides to osmium(0), osmium(II) and ruthenium(0) complexes. Crystal structures of $Os(SiEt_3)H(CO)_2(PPh_3)_2$ and $Os(Ge[p\text{-tolyl}]_3)H(CO)_2(PPh_3)_2$ *

George R. Clark, Kevin R. Flower, Clifton E.F. Rickard, Warren R. Roper,
David M. Salter and L. James Wright

Department of Chemistry, University of Auckland, Private Bag 92019, Auckland (New Zealand)

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Abstract

Treatment of $M(CO)_2(PPh_3)_3$ with HER_2R' (M = Os; E = Si; R = R' = Me, Et, Ph; R = Ph, R' = H; E = Ge, Sn; R = R' = *p*-tolyl; M = Ru; E = Ge, Sn; R = R' = *p*-tolyl) affords the corresponding oxidative addition products $M(ER_2R')H(CO)_2(PPh_3)_2$ (**1–8**). The crystal structures of two complexes, $Os(SiEt_3)H(CO)_2(PPh_3)_2$ (**2**) and $Os(Ge[p\text{-tolyl}])_3H(CO)_2(PPh_3)_2$ (**6**) have been determined. Reaction between $HSnMe_3$ and any one of the following compounds, $OsHCl(CO)(PPh_3)_3$, $Os(Ph)X(CO)(PPh_3)_2$ (X = I, Cl), $Os(SiMe_2Cl)Cl(CO)(PPh_3)_2$, yields the osmium(IV) complex $Os(SnMe_3)_2H_2(CO)(PPh_3)_2$ (**9**). Determinations of T_1 suggest that the hydride ligands in **9** are coordinated in the classical manner rather than as η^2-dihydrogen.

1. Introduction

A large number of complexes containing heavier Group 14 element–transition metal bonds is known [1–3]. General methods for the preparation of these complexes include: (i) elimination of small molecules such as hydrogen, amines or alcohols in various condensation processes, (ii) insertion of a low valent Group 14 compound into either a transition metal–metal bond or a transition metal–halide bond, and (iii) oxidative addition of an E–X bond (where X can be carbon, halide or hydride) to a low oxidation state transition metal precursor [4–10].

We are currently interested in the synthesis and reactivity of osmium and ruthenium complexes containing heavier Group 14 elements [11–14]. In this paper we report the oxidative additions of heavier Group 14 element hydrides to low oxidation state osmium and ruthenium precursors, together with the single crystal X-ray structure determinations of $Os(SiEt_3)H(CO)_2(PPh_3)_2$ and $Os(Ge[p\text{-tolyl}]_3)H(CO)_2(PPh_3)_2$.

2. Results and discussion

2.1. *Reaction of Group 14 hydrides with ruthenium(0) and osmium(0) complexes*

Reaction of the compounds $M(CO)_2(PPh_3)_3$ with HER_2R' (M = Os; E = Si, R = R' = Me, Et, Ph; R = Ph, R' = H; E = Ge, Sn; R = R' = *p*-tolyl; M = Ru; E = Ge, Sn; R = R' = *p*-tolyl) affords the oxidative addition products $M(ER_2R')H(CO)_2(PPh_3)_2$ (**1–8**) in good yield. With the exception of compound **4** all of the spectral data are consistent with these compounds having structures similar to those determined by X-ray crystallography for **2** and **6**, *i.e.* Fig. 1, **4A**. Although the major isomer (*ca.* 60%) of compound **4** has this structure, the spectral data also show the presence of a second isomer, **4B** (*ca.* 40%). The data indicate that this isomer has the structure shown in Fig. 1, **4B**.

The IR spectra (Table 1) of compounds **1–8** all show a medium intensity band in the region 2003–2041 cm^{-1} which is assigned as ν(Os–H). In addition, the

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Correspondence to: Professor W.R. Roper.

* This paper is dedicated to Professor M.F. Lappert F.R.S. on the occasion of his 65th birthday.

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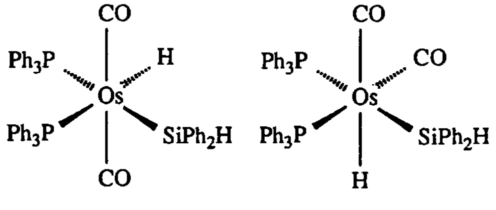


4A **4B**

Fig. 1. Geometries of the two isomers of compound 4.

spectra all show a strong, single ν(C≡O) band in the region 1920–1950 cm^{-1}, which is consistent with the complexes containing two mutually *trans* carbonyl ligands. Other bands which have been assigned to the ancillary ligands are listed in Table 1.

In the ^1H NMR spectra of the compounds **1–8** (see Table 2) the transition metal hydride resonance appears as a high field doublet of doublets. This is consistent with the two triphenylphosphine ligands being mutually *cis*. The $^2J(P_{trans}–H)$ values range between 27 and 58 Hz. These values are low compared with the $^2J(P_{trans}–H)$ values typically observed for related compounds [15]. In contrast, the $^2J(P_{cis}–H)$ values range between 17 and 23 Hz and these are typical for this coupling pathway. The low values of the $^2J(P_{trans}–H)$ coupling can be understood upon inspection of the crystal structures of **2** and **6**. We assume that the hydride ligand (which was not located by X-ray crystallography) is coordinated in the equatorial plane, between P(2) and the Group 14 element in both structures. Both structures show large distortions from ideal octahedral geometry, with the three bulky groups redistributing themselves in the equatorial plane such as to minimize interligand repulsions. A consequence of this is that the hydride ligand is not placed directly *trans* to a phosphine ligand, thus lowering the value of the $^2J(P_{trans}–H)$ coupling constant.

TABLE 1. IR data [a] for the complexes $M(ER_2R')H(CO)_2(PPh_3)_2$ and $Os(SnMe_3)_2H_2(CO)(PPh_3)_2$

Complex	ν(M–H)	ν(C≡O)	Other bands
1	2012	1929	835 [b]
	2003		828
2	2030	1925	999 [b]
	2013		
3	2021	1936	
4A	2017	1950	
4B		1984, 1912	
5	2037	1946	797 [c]
6	2028	1940	802 [c]
7	2038	1950	798 [c]
8	2041	1938	802 [c]
9	2026	1946	875 [d]
	1907		

[a] In cm^{-1}. Spectra recorded as Nujol mulls between KBr plates. [b] Bands associated with silyl groups. [c] Band associated with *p*-tolyl group. [d] Os–H.

The silicon hydride resonance for compound **4** appears as a doublet, rather than the expected doublet of doublets. Apparently the coupling constant to one phosphorus atom is very small and not observed. The three bond coupling constant value, $^3J(P–H)$, is probably dependent upon the rotational orientation of the silyl group and one of the coupling pathways may be unfavourable for the preferred silyl group orientation. All other resonances are as expected.

The ^{13}C NMR spectra of **2**, **3**, **4** and **6** (Table 3) all show the carbonyl resonance as an apparent triplet rather than the expected doublet of doublets arising from coupling to two inequivalent triphenylphosphine ligands. This must be because the values $^2J(P_1–C)$ and $^2J(P_2–C)$ are very similar. In the spectra for all the compounds the triphenylphosphine carbon resonances appear as doublets confirming the *cis* orientation of the phosphine ligands. The phosphorus resonances in the ^{31}P NMR spectra (Table 4) all appear as two

TABLE 2. ^1H NMR data [a] for the complexes $M(ER_2R')H(CO)_2(PPh_3)_2$ and $Os(SnMe_3)_2H_2(CO)(PPh_3)_2$

Complex	^1H NMR data
1	−9.61 (dd, 1H, Os–*H*, *J*(HP) = 39.33; *J*(HP) = 23.43); 0.37 (s, 9H, $SiCH_3$); 7.26–7.79 (m, 30H, Ph–*H*).
2	−9.17 (dd, 1H, Os–*H*, *J*(HP) = 38.10; *J*(HP) = 22.10); 1.26–1.31 (m, 15H, $SiCH_2CH_3$); 6.8–7.45 (m, 30H, Ph–*H*).
3	−8.91 (dd, 1H, Os–*H*, *J*(HP) = 38.46; *J*(HP) = 22.37); 5.29 (s, 3H, CH_2Cl_2); 6.95–7.50 (m, 45H, Ph–*H*).
4A	−9.12 (dd, Os–H, *J*(HP) = 37.8; *J*(HP) = 20.19); 5.05 (d, Si*H*, *J*(HP) = 7.1; 6.95–7.85 (m, Ph–*H*).
4B	−6.89 (t, Os–*H*, *J*(HP) = 21.09); 4.88 (dd, Si*H*, *J*(HP) = 17.57, *J*(HP) = 4.93); 6.95–7.85 (m, Ph–*H*).
5	−8.24 (dd, 1H, Ru–*H*, *J*(HP) = 58.33, *J*(HP) = 20.75); 5.29 (s, 2H, CH_2Cl_2); 2.28 (s, 9H, CH_3); 6.89–7.55 (m, 42H, Ph–*H*).
6	−9.35 (dd, 1H, Os–*H*, *J*(HP) = 40.12; *J*(HP) = 20.93); 2.82 (s, 9H, CH_3); 5.29 (s, 2H, CH_2Cl_2); 6.76–7.21 (m, 42H, Ph–*H*).
7	−8.65 (dd, 1H, Ru–*H*, *J*(HP) = 27.4, *J*(HP) = 19.5) 2.29 (s, 9H, CH_3); 5.29 (s, 1H, CH_2Cl_2); 6.85–7.36 (m, 42H, Ph–*H*).
8	−9.94 (dd, 1H, Os–*H*, *J*(HP) = 37.8; *J*(HP) = 21.3); 2.29 (s, 9H, CH_3); 5.29 (s, 1H, CH_2Cl_2); 6.60–7.30 (m, 42H, Ph–*H*).
9 [b]	−8.13 (m, 2H, Os–*H*); 0.186 (s, 18H, $SnCH_3$, *J*(Sn–H) = 42.88); 7.14–7.26 (m, 30H, Ph–*H*).

[a] Spectra recorded in $CDCl_3$ at 25°C. Chemical shifts (δ) are given in ppm and are referenced to Me_4Si (δ = 0.00). Coupling constants (*J*) are in Hz. Splitting patterns and line shapes are indicated thus: s = singlet, dd = doublet of doublets, m = multiplet, t = triplet, b = broad. [b] Chemical shifts referenced to $CHCl_3$ impurity in $CDCl_3$ (δ = 7.26).

TABLE 3. ^{13}C NMR data [a] for the complexes $Os(ER_2R')H(CO)_2(PPh_3)_2$

Complex	^{13}C NMR data
2	193.60 (t, C≡O, *J*(PC) = 8.0); 137.96 (d, Ph–C, *J*(PC) 42.86); 137.32 (d, Ph–C, *J*(PC) = 40.86; 133.45 (d, Ph–C, *J*(PC) = 11.37); 133.25 (d, Ph–C, *J*(PC) = 11.47; 129.02 (s, Ph–C) 127.81 (d, Ph–C, *J*(PC) = 9.86); 127.66 (d, Ph–C, *J*(PC) = 9.67); 11.34 (s, $Si\mathit{C}H_2$) [b]; 9.49 (s, $Si\text{–}CH_2\mathit{C}H_3$) [b].
3	192.15 (t, C≡O, *J*(PC) = 8.5); ($SiPh_3$) = 145.16 (s, Ph–C); 136.55 (s, Ph–C); 126.82 (*s*, Ph–C); 126.56 (s, Ph–C); (PPh_3) = 136.99 (d, Ph–C, *J*(PC) = 45.17); 136.09 (d, Ph–C, *J*(PC) = 42.66); 133.49 (d, Ph–C, *J*(PC) = 11.37); 133.32 (d, Ph–C, *J*(PC) = 11.37); 129.47 (s, Ph–C); 129.36 (s, Ph–C); 127.91 (d, Ph–C, *J*(PC) = 9.96); 127.69 (d, Ph–C, *J*(PC) = 9.75).
4A	189.95 (t, C≡O, *J*(PC) = 8.70); 144.82–126.28 (m, Ph–C).
4B	186.89 (dd, C≡O, $J(P_{cis}\text{–}C)$ = 9.74, 3.79); 184.29 (dd, C≡O, $J(P_{trans}\text{–}C)$ = 74.7 ($J(P_{cis}\text{–}C)$ = 6.54); 144.82–126.28 (m, Ph–C).
6	190.65 (t, C≡O, *J*(PC) = 8.63); (Ge[*p*-tolyl]$_3$) = 143.35 (s, Ph–C); 135.34 (s, Ph–C); 127.60 (Ph–C); (PPh_3) = 136.64 (d, Ph–C), *J*(PC) 45.38); 136.21 (d, Ph–C, *J*(PC) = 41.15); 133.44 (d, Ph–C, *J*(PC) = 10.56); 133.13 (d, Ph–C, *J*(PC) = 10.67); 129.24 (s, Ph–C); 128.93 (s, Ph–C; 127.6–127.02 (m, Ph–C).
9	136.64 (ds, Ph–C, *J*(PC) = 44.59); 133.99 (d, Ph–C, *J*(PC) = 10.72); 129.70 (s, Ph–C); 127.84 (d, Ph–C, *J*(PC) = 9.56); 3.66 (s, $Sn\text{–}CH_3$).

[a] Spectra recorded in $CDCl_3$ at 25°C. Chemical shifts (δ) are given in ppm and are referenced to $CDCl_3$ (δ = 77.00). Coupling constants (*J*) are in Hz. Splitting patterns are indicated thus: t = triplet, s = singlet, d = doublet, m = multiplet. [b] Assignments made using DEPT 135 pulse sequence.

doublets. This pattern is also consistent with the presence of inequivalent, *cis* phosphine ligands.

The minor isomer of the compound $Os(SiPh_2H)H(CO)_2(PPh_3)_2$ (**4**) has been assigned the geometry **4B** shown in Fig. 1 on the basis of spectral data. The IR spectrum shows two equally intense carbonyl bands at 1984 and 1912 cm^{-1} indicating the presence of mutually *cis* carbonyl ligands. In the ^{31}P spectrum, the phosphorus resonances appear as two doublets indicating inequivalent *cis* triphenylphosphine ligands. In the ^1H NMR spectrum the hydride appears as an apparent triplet at high-field (^2J(P–H) 21.09 Hz). This is consistent with the hydride ligand being *cis* to both triphenylphosphine ligands, where the two *J*(P–H) values are very similar. The silicon hydride resonance appears as a doublet of doublets with $^3J(P_{trans}\text{–}H)$ 17.57 and $^3J(P_{cis}\text{–}H)$ 4.93 Hz. The ^{13}C NMR spectrum shows the presence of two different carbonyl ligands, each appearing as the expected doublet of doublets. For the CO which is *trans* to one phosphine ligand and *cis* to the other, the ^2J(P–C) coupling constants are 74.7 and 6.54 Hz. The carbonyl ligand *cis* to both phosphines has ^2J(P–C) coupling constant values of 9.74 and 3.79 Hz respectively.

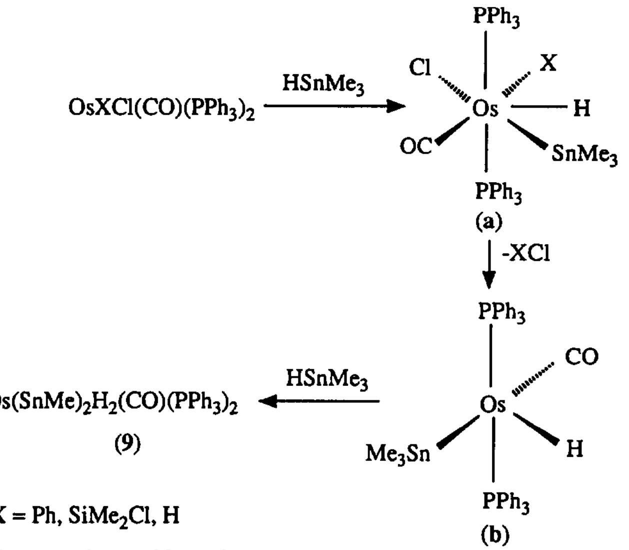
TABLE 4. ^{31}P NMR data [a] for the complexes $Os(ER_2R')H(CO)_2(PPh_3)_2$

Complex	^{31}P NMR data
1	5.50 (d, *J*(PP) = 10.02)
	4.31 (d, *J*(PP) = 10.02)
2	4.21 (d, *J*(PP) = 6.90)
	3.77 (d, *J*(PP) = 6.90)
3	2.81 (d, *J*(PP) = 6.83)
	1.36 (d, *J*(PP) = 7.41)
4A	5.50 (d, *J*(PP) = 8.39)
	3.58 (d, *J*(PP) = 8.39)
4B	9.31 (d, *J*(PP) = 24.36)
	3.89 (d, *J*(PP) = 24.36)
9	7.96 (bs)
	1.43 (bs)

[a] Spectra recorded in $CDCl_3$ at 25°C. Chemical shifts (δ) are given in ppm and are referenced to 85% H_3PO_4 (δ = 0). Coupling constants (*J*) are in Hz. Splitting patterns are indicated thus: d = doublet, bs = broad singlet.

Attempts were made to prepare the analogous ruthenium silyl complexes via oxidative addition of silanes to $Ru(CO)_2(PPh_3)_3$. These reactions did not yield silyl-containing products, but instead $RuH_2(CO)_2(PPh_3)_2$ was obtained.

Preliminary investigations of the reactivity of **1–8** towards electrophilic reagents such as HCl and I_2 were carried out in an attempt to substitute the metal hydride for a halide and/or introduce functionality at the Group 14 element via alkyl group cleavage. However, these reactions did not occur and the outcome was loss of the Group 14 moiety. Thus further elaboration of **1–8** by these routes could not be achieved.



X = Ph, SiMe$_2$Cl, H

Compounds a and b not isolated

Scheme 1. Postulated mechanism for the formation of Os(SnMe$_3$)$_2$-H$_2$(CO)(PPh$_3$)$_2$ (9).

2.2. Reactions of HSnMe$_3$ with osmium(II) complexes

Reaction of either Os(Ph)X(CO)(PPh$_3$)$_2$ or Os(SiMe$_2$Cl)Cl(CO)(PPh$_3$)$_2$ with two equivalents of HSnMe$_3$ gives Os(SnMe$_3$)$_2$H$_2$(CO)(PPh$_3$)$_2$ (**9**) in good yield, with no unchanged osmium precursor remaining. Reaction with less than two equivalents of HSnMe$_3$ also gives **9**, but in reduced yield. Three equivalents of HSnMe$_3$ are required to produce **9** in good yield from OsHCl(CO)(PPh$_3$)$_3$, possibly because one equivalent of HCl is reductively eliminated during the reaction and this reacts rapidly with HSnMe$_3$ to give ClSnMe$_3$ and H$_2$(g).

The proposed reaction pathway for these reactions is shown in Scheme 1. Initially the HSnMe$_3$ oxidatively adds to the osmium(II) complexes to give intermediate (a), which then reductively eliminates XCl to afford intermediate (b). Intermediate (b) then reacts with the second equivalent of HSnMe$_3$ to yield **9**. The stoichiometry of the reaction between HSnMe$_3$ and either Os(Ph)X(CO)(PPh$_3$)$_2$ or Os(SiMe$_2$Cl)Cl(CO)(PPh$_3$)$_2$, together with the fact that the product **9** has two stannyl ligands and is formed in good yield, suggests that at no time is a stannyl group reductively eliminated in these reactions. Since Product **9** is formed even with less than two equivalents of HSnMe$_3$, it can be concluded that intermediate (b) reacts faster with HSnMe$_3$ than do any of the starting complexes.

The IR spectrum of **9** (Table 1) shows two medium intensity bands at 2026 and 1907 cm^{-1} which are assigned as ν(Os–H); there is also a strong ν(C≡O) at 1946 cm^{-1}. The ^{1}H NMR spectrum (Table 2) shows resonances for the phenyl, methyl and hydride groups with relative integrals of 30:18:2 respectively. The high-field hydride resonance appears as a broad triplet and T$_1$ measurements made at 248 and 298 K gave relaxation times of 305 and 706 ms, respectively, indicating that the two hydrogens are best considered as classical hydride ligands rather than as η^2-dihydrogen bonded [16].

The ^{31}P NMR spectrum of **9** at room temperature shows two broad phosphorus resonances, indicating that the phosphine ligands are not mutually *trans*. No coupling could be resolved. The ^{13}C NMR spectrum shows the triphenylphosphine carbon resonances as doublets, again indicating that the phosphine ligands are not arranged *trans*.

Compound **9** is remarkably stable. Preliminary investigations aimed at inducing reductive elimination of dihydrogen from **9** proved unsuccessful, as did attempts to introduce functionality selectively at the tin centre through reactions with electrophilic reagents such as HCl and I$_2$.

2.3. Structures of Os(SiEt$_3$)H(CO)$_2$(PPh$_3$)$_2$ and Os(Ge[p-tolyl]$_3$)H(CO)$_2$(PPh$_3$)$_2$

Single crystal X-ray structure determinations were carried out for Os(SiEt$_3$)H(CO)$_2$(PPh$_3$)$_2$ (**2**) and Os(Ge[p-tolyl]$_3$)H(CO)$_2$(PPh$_3$)$_2$ (**6**). The hydrogen atoms were not located in either structure. The molecular geometries of these compounds are depicted in Figs. 2 and 3 respectively. Important bond angles and bond lengths are listed in Tables 5–8.

Both structures are best described as highly distorted octahedra. The two carbonyl ligands are essen-

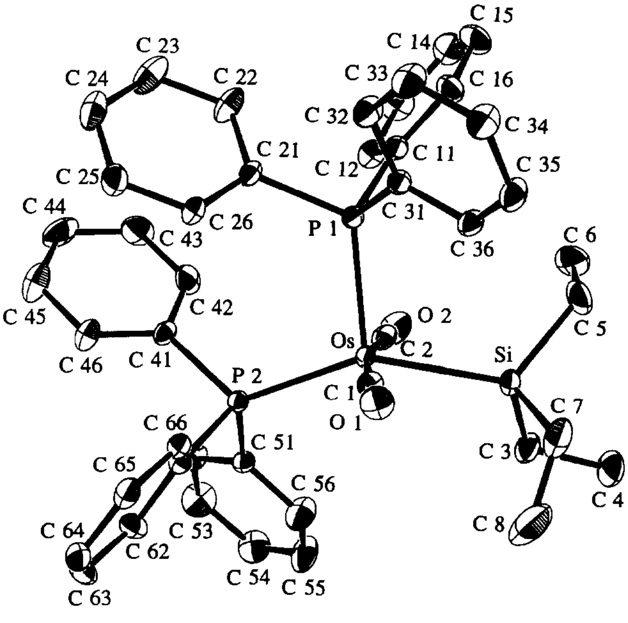


Fig. 2. Molecular structure of Os(SiEt$_3$)H(CO)$_2$(PPh$_3$)$_2$ (**2**).

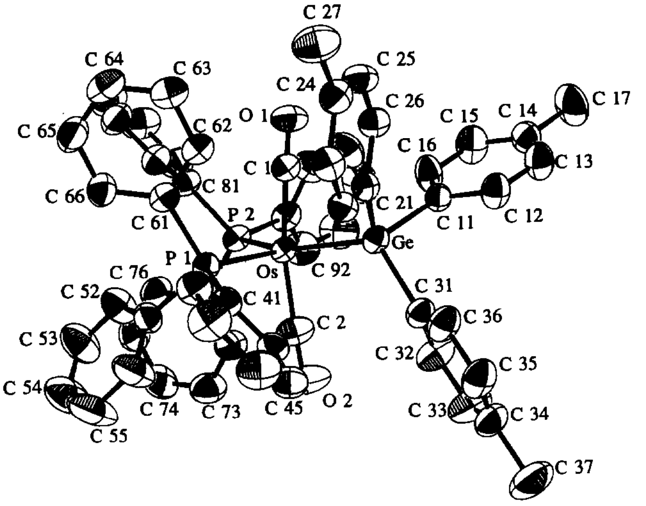


Fig. 3. Molecular structure of $Os(Ge[p\text{-}tolyl]_3)H(CO)_2(PPh_3)_2$ (**6**).

tially *trans* with the angle C–Os–C for **2**, 167.2(2)° and for **6**, 169.3(2)°. If the CO ligands are taken as occupying the axial positions in the octahedron, then the two phosphines, the Group 14 ligand and the hydride occupy the equatorial plane in both compounds. Although the hydride was not located in either structural determination, it is reasonable to assume that it is coordinated in the equatorial plane between P(2) and the Group 14 element, and this is supported by the spectroscopic evidence. The angles between the two phosphines and between each of the phosphines and the Group 14 ligand are all greater than 90°. Thus for **2**, P(1)–Os–Si = 105.0(1)°, P(2)–Os–Si = 147.3(1)° and P(1)–Os–P(s) = 107.0(1)° and for **6** P(1)–Os–Ge = 99.90(2)°, P(2)–Os–Ge = 152.59(2)° and P(2)–Os–P(1) = 106.17(3)°. Both structures, like other reported Group 14 alkyl and aryl containing complexes, show deviation from tetrahedral geometry about the Group 14 elements. The Os–E–C bond angles open to around 114° and the C–E–C bond angles close to *ca.* 103°. All other bond angles appear normal. The Os–Si bond length in **2** is 2.493(2) Å and this is the longest Os–Si distance yet reported [17–19]. The Os–Ge bond length is 2.5600(3) Å. This is the first Os–Ge distance to be reported, and it is close to the value of 2.55 Å predicted from the sum of the covalent radii of Os and Ge

TABLE 5. Interatomic distances (Å) for $Os(SiEt_3)H(CO)_2(PPh_3)_2$ (**2**)

P(1)–Os	2.397(1)	C(24)–C(23)	1.360(12)
P(2)–Os	2.381(1)	C(25)–C(24)	1.371(12)
Si–Os	2.493(2)	C(26)–C(25)	1.370(9)
C(1)–Os	1.921(5)	C(32)–C(31)	1.374(8)
C(2)–Os	1.910(6)	C(36)–C(31)	1.385(8)
C(11)–P(1)	1.842(5)	C(33)–C(32)	1.397(9)
C(21)–P(1)	1.850(5)	C(34)–C(33)	1.364(10)
C(31)–P(1)	1.853(5)	C(35)–C(34)	1.360(9)
C(41)–P(2)	1.831(6)	C(36)–C(35)	1.390(8)
C(51)–P(2)	1.840(6)	C(42)–C(41)	1.386(9)
C(61)–P(2)	1.838(5)	C(46)–C(41)	1.374(9)
C(3)–Si	1.894(7)	C(43)–C(42)	1.381(10)
C(5)–Si	1.878(8)	C(44)–C(43)	1.409(13)
C(7)–Si	1.893(9)	C(45)–C(44)	1.360(13)
C(1)–O(1)	1.134(6)	C(46)–C(45)	1.386(10)
C(2)–O(2)	1.137(7)	C(52)–C(51)	1.395(8)
C(4)–C(3)	1.535(9)	C(56)–C(51)	1.385(9)
C(8)–C(7)	1.492(13)	C(54)–C(53)	1.366(12)
C(12)–C(11)	1.391(8)	C(55)–C(54)	1.368(12)
C(16)–C(11)	1.382(9)	C(56)–C(55)	1.379(10)
C(13)–C(12)	1.394(8)	C(62)–C(61)	1.400(8)
C(14)–C(13)	1.370(11)	C(66)–C(61)	1.388(7)
C(15)–C(14)	1.372(12)	C(63)–C(62)	1.383(8)
C(16)–C(15)	1.391(9)	C(64)–C(63)	1.369(9)
C(22)–C(21)	1.370(9)	C(65)–C(64)	1.368(9)
C(23)–C(22)	1.407(10)		

TABLE 6. Interatomic distances for $Os(Ge[p\text{-}tolyl]_3)H(CO)_2(PPh_3)_2$ (**6**)

Ge–Os	2.5600(3)	C(36)–C(35)	1.395(8)
P(1)–Os	2.3955(8)	C(42)–C(41)	1.378(7)
P(2)–Os	2.3856(9)	C(46)–C(41)	1.382(7)
C(1)–Os	1.916(5)	C(43)–C(42)	1.382(6)
C(2)–Os	1.903(6)	C(44)–C(43)	1.395(10)
C(11)–Ge	1.981(4)	C(45)–C(44)	1.364(8)
C(21)–Ge	1.985(4)	C(46)–C(45)	1.398(6)
C(31)–Ge	1.974(5)	C(52)–C(51)	1.393(6)
C(41)–P(1)	1.835(4)	C(56)–C(51)	1.382(9)
C(51)–P(1)	1.838(5)	C(53)–C(52)	1.364(8)
C(61)–P(1)	1.841(5)	C(54)–C(53)	1.383(11)
C(71)–P(2)	1.840(5)	C(55)–C(54)	1.351(9)
C(81)–P(2)	1.850(5)	C(56)–C(55)	1.383(10)
C(91)–P(2)	1.836(5)	C(62)–C(61)	1.373(6)
C(3)–C(11)	1.79(2)	C(66)–C(61)	1.385(7)
C(3)–C(12)	1.64(2)	C(63)–C(62)	1.386(8)
C(1)–O(1)	1.140(6)	C(64)–C(63)	1.372(8)
C(2)–O(2)	1.165(8)	C(65)–C(64)	1.360(8)
C(12)–C(11)	1.391(5)	C(66)–C(65)	1.382(10)
C(16)–C(11)	1.380(6)	C(72)–C(71)	1.404(8)
C(13)–C(12)	1.381(7)	C(76)–C(71)	1.367(6)
C(14)–C(13)	1.379(7)	C(73)–C(72)	1.408(8)
C(15)–C(14)	1.370(7)	C(74)–C(73)	1.376(9)
C(17)–C(14)	1.507(8)	C(75)–C(74)	1.387(11)
C(16)–C(15)	1.399(7)	C(76)–C(75)	1.365(9)
C(22)–C(21)	1.394(6)	C(82)–C(81)	1.376(6)
C(26)–C(21)	1.398(7)	C(86)–C(81)	1.374(7)
C(23)–C(22)	1.361(6)	C(83)–C(82)	1.373(9)
C(24)–C(23)	1.392(7)	C(84)–C(83)	1.374(9)
C(25)–C(24)	1.382(7)	C(85)–C(84)	1.380(8)
C(27)–C(24)	1.520(8)	C(86)–C(85)	1.377(8)
C(26)–C(25)	1.368(7)	C(92)–C(91)	1.391(9)
C(32)–C(31)	1.376(8)	C(96)–C(91)	1.393(8)
C(36)–C(31)	1.397(5)	C(93)–C(92)	1.395(10)
C(33)–C(32)	1.394(9)	C(94)–C(93)	1.375(12)
C(34)–C(33)	1.378(7)	C(95)–C(94)	1.349(12)
C(35)–C(34)	1.368(10)	C(96)–C(95)	1.370(9)
C(37)–C(34)	1.537(10)		

[20]. All other bond lengths in the two compounds appear to fall in the expected ranges.

3. Experimental details

All reactions were carried out by use of standard Schlenk techniques under nitrogen. Final recrystallisations were carried out in the open. Benzene, toluene and hexane were each dried over and distilled from sodium benzophenoneketyl; dichloromethane was dried over and distilled from calcium hydride; and methanol was dried over and distilled from magnesium methoxide formed from magnesium turnings. Each solvent was subjected to three freeze-evacuate-thaw cycles before use. The compounds $M(CO)_2(PPh_3)_3$ (M = Os, Ru) [2], $OsHCl(CO)(PPh_3)_3$ [22], $Os(Ph)Cl(CO)(PPh_3)_2$ [23], $Os(SiMe_2Cl)Cl(CO)(PPh_3)_2$ [24], $HSiMe_3$ [25], HGe(*p*-tolyl)$_3$ [26], HSn(*p*-tolyl)$_3$ [27] and $HSnMe_3$ [28], were prepared by published methods. All other compounds were obtained commercially and used without further purification.

TABLE 7. Bond angles (deg.) for $Os(SiEt_3)H(CO)_2(Ph_3)_2$ (**2**)

P(2)–Os–P(1)	107.0(1)	C(22)–C(21)–P(1)	123.3(5)
Si–Os–P(1)	105.0(1)	C(26)–C(21)–P(1)	118.2(5)
Si–Os–P(2)	147.3(1)	C(26)–C(21)–C(22)	118.5(6)
C(1)–Os–P(1)	88.8(2)	C(23)–C(22)–C(21)	119.4(8)
C(1)–Os–P(2)	100.9(2)	C(24)–C(23)–C(22)	120.8(8)
C(1)–Os–Si	86.6(2)	C(25)–C(24)–C(23)	119.4(7)
C(2)–Os–P(1)	95.1(2)	C(26)–C(25)–C(24)	119.6(8)
C(2)–Os–P(2)	89.7(2)	C(25)–C(26)–C(21)	122.1(7)
C(2)–Os–Si	80.7(2)	C(32)–C(31)–P(1)	121.0(4)
C(2)–Os–C(1)	167.2(2)	C(36)–C(31)–P(1)	119.9(4)
C(11)–P(1)–Os	117.8(2)	C(36)–C(31)–C(32)	119.0(5)
C(21)–P(1)–Os	118.8(2)	C(33)–C(32)–C(31)	119.3(6)
C(21)–P(1)–C(11)	100.1(3)	C(34)–C(33)–C(32)	121.5(6)
C(31)–P(1)–Os	115.4(2)	C(35)–C(34)–C(33)	119.1(6)
C(31)–P(1)–C(11)	101.9(3)	C(36)–C(35)–C(34)	120.5(6)
C(31)–P(1)–C(21)	99.8(2)	C(35)–C(36)–C(31)	120.5(5)
C(41)–P(2)–Os	120.7(2)	C(42)–C(41)–P(2)	117.7(5)
C(51)–P(2)–Os	111.7(2)	C(46)–C(41)–P(2)	123.9(5)
C(51)–P(2)–C(41)	100.2(3)	C(46)–C(41)–C(42)	118.3(6)
C(61)–P(2)–Os	118.2(2)	C(43)–C(42)–C(41)	121.1(7)
C(61)–P(2)–C(41)	101.1(3)	C(44)–C(43)–C(42)	120.1(8)
C(61)–P(2)–C(51)	102.1(3)	C(45)–C(44)–C(43)	118.0(7)
C(3)–Si–Os	109.3(2)	C(46)–C(45)–C(44)	121.6(8)
C(5)–Si–Os	119.3(3)	C(45)–C(46)–C(41)	120.8(7)
C(5)–Si–C(3)	105.4(4)	C(52)–C(51)–P(2)	122.3(4)
C(7)–Si–Os	114.8(3)	C(56)–C(51)–P(2)	120.9(5)
C(7)–Si–C(3)	103.7(4)	C(56)–C(51)–C(52)	116.8(6)
C(7)–Si–C(5)	102.9(4)	C(53)–C(52)–C(51)	121.4(7)
O(1)–C(1)–Os	177.0(6)	C(54)–C(53)–C(52)	120.4(8)
O(2)–C(2)–Os	178.1(5)	C(55)–C(54)–C(53)	118.8(7)
C(4)–C(3)–Si	116.1(6)	C(56)–C(55)–C(54)	121.3(8)
C(6)–C(5)–Si	116.0(7)	C(55)–C(56)–C(51)	121.3(8)
C(8)–C(7)–Si	117.2(8)	C(62)–C(61)–P(2)	121.5(4)
C(12)–C(11)–P(1)	117.7(5)	C(66)–C(61)–P(2)	119.4(4)
C(16)–C(11)–P(1)	123.1(5)	C(66)–C(61)–C(62)	119.1(5)
C(16)–C(11)–C(12)	119.2(5)	C(63)–C(62)–C(61)	119.3(6)
C(13)–C(12)–C(11)	120.2(7)	C(64)–C(63)–C(62)	121.0(6)
C(14)–C(13)–C(12)	120.4(7)	C(65)–C(64)–C(63)	120.2(6)
C(15)–C(14)–C(13)	119.5(6)	C(66)–C(65)–C(64)	120.1(6)
C(16)–C(15)–C(14)	121.1(8)	C(65)–C(66)–C(61)	120.3(6)
C(15)–C(16)–C(11)	119.7(7)		

TABLE 8. Bond angles for Os(Ge[*p*-tolyl]$_3$)H(CO)$_2$(PPh$_3$)$_2$ (**6**)

P(1)–Os–Ge	99.90(2)	C(34)–C(33)–C(32)	120.1(6)
P(2)–Os–Ge	152.59(2)	C(35)–C(34)–C(33)	118.9(6)
P(2)–Os–Ge	80.2(1)	C(37)–C(34)–C(35)	120.8(5)
C(1)–Os–P(1)	95.9(1)	C(36)–C(35)–C(34)	120.6(4)
C(1)–Os–P(2)	88.8(1)	C(35)–C(36)–C(31)	121.5(5)
C(2)–Os–Ge	89.4(1)	C(42)–C(41)–P(1)	121.5(4)
C(2)–Os–P(1)	88.2(2)	C(46)–C(41)–P(1)	119.9(3)
C(2)–Os–P(2)	99.6(1)	C(46)–C(41)–C(42)	118.5(4)
C(2)–Os–C(1)	169.3(2)	C(43)–C(42)–C(41)	120.4(5)
C(11)–Ge–Os	110.6(1)	C(44)–C(43)–C(42)	120.8(5)
C(21)–Ge–Os	114.3(1)	C(45)–C(44)–C(43)	119.1(5)
C(21)–Ge–C(11)	102.0(2)	C(46)–C(45)–C(44)	119.8(5)
C(31)–Ge–Os	119.8(1)	C(45)–C(46)–C(41)	121.3(5)
C(31)–Ge–C(11)	101.4(2)	C(52)–C(51)–P(1)	119.9(4)
C(31)–Ge–C(21)	106.5(2)	C(56)–C(51)–P(1)	122.0(3)
C(41)–P(1)–Os	117.2(2)	C(56)–C(51)–C(52)	118.0(5)
C(51)–P(1)–Os	115.1(2)	C(53)–C(52)–C(51)	120.9(5)
C(51)–P(1)–C(41)	99.7(2)	C(54)–C(53)–C(52)	120.0(5)
C(61)–P(1)–Os	115.8(1)	C(55)–C(54)–C(53)	120.1(7)
C(61)–P(1)–C(41)	101.7(2)	C(56)–C(55)–C(54)	120.3(7)
C(61)–P(1)–C(51)	105.3(2)	C(55)–C(56)–C(51)	120.7(5)
C(71)–P(2)–Os	120.3(2)	C(62)–C(61)–P(1)	117.7(4)
C(81)–P(2)–Os	119.6(1)	C(66)–C(61)–P(1)	123.7(4)
C(81)–P(2)–C(71)	102.6(2)	C(66)–C(61)–C(62)	118.6(5)
C(91)–P(2)–Os	109.8(1)	C(63)–C(62)–C(61)	121.0(4)
C(91)–P(2)–C(71)	103.0(2)	C(64)–C(63)–C(62)	119.4(5)
C(91)–P(2)–C(81)	98.2(2)	C(65)–C(64)–C(63)	120.4(6)
O(1)–C(1)–Os	177.8(4)	C(66)–C(65)–C(64)	120.2(6)
O(2)–C(2)–Os	177.1(4)	C(65)–C(66)–C(61)	120.4(5)
C(12)–C(3)–C(11)	109.8(11)	C(72)–C(71)–P(2)	116.9(3)
C(12)–C(11)–Ge	118.4(3)	C(76)–C(71)–P(2)	124.4(4)
C(16)–C(11)–Ge	124.8(3)	C(76)–C(71)–C(72)	118.6(5)
C(16)–C(11)–C(12)	116.7(4)	C(73)–C(72)–C(71)	119.5(5)
C(13)–C(12)–C(11)	121.7(4)	C(74)–C(73)–C(72)	119.7(7)
C(14)–C(13)–C(12)	121.2(4)	C(75)–C(74)–C(73)	120.2(6)
C(15)–C(14)–C(13)	117.8(5)	C(76)–C(75)–C(74)	119.6(5)
C(17)–C(14)–C(13)	119.9(4)	C(75)–C(76)–C(71)	122.3(6)
C(17)–C(14)–C(15)	122.3(4)	C(82)–C(81)–P(2)	121.3(4)
C(16)–C(15)–C(14)	121.2(4)	C(86)–C(81)–P(2)	120.1(3)
C(15)–C(16)–C(11)	121.3(4)	C(86)–C(81)–C(82)	118.6(5)
C(22)–C(21)–Ge	123.9(3)	C(83)–C(82)–C(81)	120.9(5)
C(26)–C(21)–Ge	119.0(3)	C(84)–C(83)–C(82)	120.2(5)
C(26)–C(21)–C(22)	116.8(4)	C(85)–C(84)–C(83)	119.5(6)
C(23)–C(22)–C(21)	121.8(4)	C(86)–C(85)–C(84)	119.7(6)
C(24)–C(23)–C(22)	121.1(4)	C(85)–C(86)–C(81)	121.0(4)
C(25)–C(24)–C(23)	117.6(4)	C(92)–C(91)–P(2)	123.4(4)
C(27)–C(24)–C(23)	120.5(4)	C(96)–C(91)–P(2)	117.7(4)
C(27)–C(24)–C(25)	121.9(5)	C(96)–C(91)–C(92)	118.8(5)
C(26)–C(25)–C(24)	121.6(5)	C(93)–C(92)–C(91)	119.2(6)
C(25)–C(26)–C(21)	121.1(4)	C(94)–C(93)–C(92)	120.1(8)
C(32)–C(31)–Ge	120.3(3	C(95)–C(94)–C(93)	120.9(7)
C(36)–C(31)–Ge	123.1(4)	C(96)–C(95)–C(94)	120.1(7)
C(36)–C(31)–C(32)	116.4(5)	C(95)–C(96)–C(91)	120.9(6)
C(33)–C(32)–C(31)	122.4(4)		

Analytical data were obtained by the Microanalytical Laboratory, University of Otago. IR spectra (4000–400 cm^{-1}) were recorded on a Digilab FTS-7 Spectrophotometer as nujol mulls between KBr plates. ^1H NMR spectra were recorded on either a Bruker AM 400 or a Bruker AC 200 in $CDCl_3$ and referenced to either tetramethylsilane (0.00 ppm) or residual $CHCl_3$ (7.26 ppm). ^{13}C and ^{31}P NMR spectra were recorded on a Bruker AM 400 instrument (^{13}C at 100.614 MHz and ^{31}P at 161.978 MHz) and referenced to $CDCl_3$ (77.00 ppm) or 85% H_3PO_4 (0.00 ppm) respectively. Melting points (uncorrected) were recorded on a Reichert hot-stage microscope.

3.1. $Os(SiMe_3)(H)(CO)_2(PPh_3)_2$ (1)

The complex $Os(CO)_2(PPh_3)_3$ (0.200 g, 0.19 mmol) was suspended in toluene (10 cm^3) in a Schlenk tube under nitrogen and an excess of $HSiMe_3$ was bubbled through the solution for *ca.* 10 s. The Schlenk tube was then sealed and irradiated with a 1000 W tungsten/halogen sun-lamp for 20 min to result in a colourless solution. The solvent volume was then reduced *in vacuo* to 1 cm^3 and hexane (50 cm^3) added to precipitate $Os(SiMe_3)H(CO)_2(PPh_3)_2$ (**1**). Recrystallisation from CH_2Cl_2/EtOH afforded pure colourless crystals of **1** (0.139 g, 85%), m.p. 178–179°C. Anal. Found: C, 57.51; H, 4.53. $C_{41}H_{40}O_2OsP_2Si$ calcd.: C, 58.28; H, 4.77%.

3.2. $Os(SiEt_3)H(CO)_2(PPh_3)_2$ (2) and analogues

The complex $Os(CO)_2(PPh_3)_3$ (0.200 g, 0.19 mmol) was suspended in toluene (10 cm^3) with continuous stirring under a stream of dry nitrogen and $HSiEt_3$ (0.033 g, 0.28 mmol) was added. After irradiation with a 1000 W tungsten/halogen sun-lamp for 20 min a colourless solution was formed. Reduction of the solvent volume *in vacuo* to 1 cm^3 followed by the addition of hexane (50 cm^3) precipitated the white complex $Os(SiEt_3)H(CO)_2(PPh_3)_2$ (**2**). Recrystallisation from CH_2Cl_2/MeOH afforded pure colourless crystals of **2** (0.143 g, 83%), m.p. 139–140°C. Anal. Found: C, 59.56, H, 5.40. $C_{44}H_{46}O_2OsP_2Si$ calcd.: C, 59.58, H, 5.23%. Crystals suitable for X-ray diffraction were grown by slow diffusion of methanol into a saturated CH_2Cl_2 solution of **2**.

Similarly, $Os(CO)_2(PPh_3)_3$ (0.200 g, 0.19 mmol) was treated with $HSiPh_3$ (0.073 g, 0.28 mmol) at room temperature to afford the analogous complex, $Os(SiPh_3)H(CO)_2(PPh_3)_2$ (**3**). Recrystallisation of the crude product from CH_2Cl_2/EtOH yielded pure colourless crystals of **3** (0.173 g, 77%), m.p. 175–176°C. Anal. (as 3/2 dichloromethane solvate, as confirmed by ^1H NMR) Found: C, 62.38; H, 4.72. $C_{56}H_{46}O_2OsP_2Si \cdot 3/2CH_2Cl_2$ calcd.: C, 62.57; H, 4.39%.

Similar treatment of $Os(CO)_2(PPh_3)_3$ (0.200 g, 0.19 mmol) with H_2SiPh_2 (0.052 g, 0.28 mmol) at room temperature gave the analogous complex, $Os(SiPh_2H)H(CO)_2(PPh_3)_2$ (**4**). Recrystallisation from CH_2Cl_2/EtOH yielded pure, colourless crystals of **4** (0.100 g, 54%), m.p. 192–194°C. Anal. Found: C, 62.97; H, 4.31. $C_{50}H_{42}O_2OsP_2Si$ calcd.: C, 62.88; H, 4.43%.

3.3. $Ru(Ge[p\text{-tolyl}]_3)H(CO)_2(PPh_3)_2$ (5) and analogue

The complex $Ru(CO)_2(PPh_3)_3$ (0.100 g, 0.11 mmol) was suspended in benzene (10 cm^3) with continuous stirring under a stream of dry nitrogen and HGe(*p*-tolyl)$_3$ (0.050 g, 0.14 mmol) was added. After 40 min stirring the solvent volume was reduced *in vacuo* to 1 cm^3 and hexane (50 cm^3) added slowly to precipitate colourless crystals of **5**, which on recrystallisation from CH_2Cl_2/EtOH afforded pure **5** (0.052 g, 44%), m.p. 184°C. Anal. (as dichloromethane solvate, as confirmed by ^1H NMR) Found: C, 63.87; H, 4.71. $C_{59}H_{52}GeO_2P_2Ru \cdot CH_2Cl_2$ calcd.: C, 64.71; H, 4.88%.

Similarly $Ru(CO)_2(PPh_3)_3$ (0.100 g, 0.11 mmol) was treated with HSn(*p*-tolyl)$_3$ (0.055 g, 0.14 mmol) at room temperature to afford the analogous complex Ru(Sn[*p*-tolyl)]$_3$)H(CO)$_2$(PPh$_3$)$_2$ (**7**). Recrystallisation of the crude product from CH_2Cl_2/EtOH, yielded colourless crystals of pure **7** (0.086 g, 73%), m.p. 195°C. Anal. (as 1/2 dichloromethane solvate, as confirmed by ^1H NMR) Found: C, 64.45; H, 4.92. $C_{59}H_{52}O_2P_2RuSn \cdot 1/2CH_2Cl_2$ calcd.: C, 63.96; H, 4.78%.

3.4. $Os(Ge[p\text{-tolyl}]_3)H(CO)_2(PPh_3)_2$ (6) and analogue

To a continuously stirred suspension of $Os(CO)_2(PPh_3)_3$ (0.150 g, 0.14 mmol) in benzene (15 cm^3) under a stream of dry nitrogen, was added HGe(*p*-tolyl)$_3$ (0.060 g, 0.17 mmol). After irradiation with a 1000 W tungsten/halogen sun-lamp for 20 min a colourless solution had been formed. The solvent volume was then reduced to 1 cm^3 *in vacuo* and hexane (50 cm^3) added to precipitate the white complex **6**. Recrystallisation from CH_2Cl_2/EtOH afforded colourless crystals of pure Os(Ge[*p*-tolyl]$_3$)H(CO)$_2$(PPh$_3$)$_2 \cdot$ CH$_2$Cl$_2$ (0.104 g, 66%), m.p. 203°C. Anal. (as dichloromethane solvate, as confirmed by ^1H NMR) Found: C, 60.38; H, 4.75. $C_{59}H_{52}GeO_2OsP_2 \cdot CH_2Cl_2$ calcd.: C, 59.91; H, 4.52%. Crystals suitable for X-ray diffraction were grown from CH_2Cl_2/EtOH using the vapour diffusion method.

Similarly $Os(CO)_2(PPh_3)_3$ (0.150 g, 0.14 mmol) was treated with HSn(*p*-tolyl)$_3$ (0.067 g, 0.17 mmol) at room temperature to afford the analogous complex Os(Sn[*p*-tolyl]$_3$)H(CO)$_2$(PPh$_3$)$_2$ (**8**). Recrystallisation of the crude product from CH_2Cl_2/EtOH yielded colourless crystals of pure Os(Sn[*p*-tolyl]$_3$)H(CO)$_2$(PPh$_3$)$_2 \cdot$ CH$_2$Cl$_2$ (0.105 g, 60%), m.p. 219°C. Anal. (as 1/2 dichloromethane solvate, as confirmed by ^1H NMR) Found: C, 59.48; H, 4.68. $C_{59}H_{52}O_2OsP_2Sn \cdot 1/2CH_2Cl_2$ calcd.: C, 59.24; H, 4.42%.

3.5. $Os(SnMe_3)_2H_2(CO)(PPh_3)_2$ (9)

Method (i): To a stirred solution of $Os(Ph)Cl(CO)(PPh_3)_2$ (0.400 g, 0.467 mmol) in benzene (30 cm^3) under a stream of dry nitrogen was added $HSnMe_3$ (0.230 g, 1.41 mmol). After 20 min the solution became colourless and the solvent volume was reduced *in vacuo* to 2 cm^3. Addition of hexane (50 cm^3) precipitated **9**. Recrystallisation from CH_2Cl_2/EtOH afforded pure, colourless crystals of **9** (0.300 g, 60%), m.p. 196°C. Anal. Found: C, 48.96; H, 4.50. $C_{43}H_{50}OOsP_2Sn_2$ calcd.: C, 48.16; H, 4.69%.

Similar reactions between either $Os(Ph)I(CO)(PPh_3)_2$ or $Os(SiMe_2Cl)Cl(CO)(PPh_3)_2$ gave the same complex **9**.

Method (ii): To a continuously stirred suspension of $OsHCl(CO)(PPh_3)_3$ (0.200 g, 0.192 mmol) in benzene (15 cm^3) under a stream of dry nitrogen was added, $HSnMe_3$ (0.127 g, 0.768 mmol). The solution was then heated to reflux for 30 min. After cooling of the solution and reduction of the volume to 1 cm^3, hexane (50 cm^3) was added to precipitate $Os(SnMe_3)_2H_2(CO)(PPh_3)_2$ (**9**). Recrystallisation from CH_2Cl_2/EtOH afforded pure **9** (0.150 g, 73%).

3.6. X-ray diffraction studies of $Os(SiEt_3)H(CO)_2(PPh_3)_2$ (2) and $Os(Ge[p\text{-tolyl}])_3H(CO)_2(PPh_3)_2$ (6)

Crystal data. Details of crystal data and intensity collection parameters are given in Table 9. Unit cell parameters were obtained from least squares fits to the four circle coordinates of 25 reflections determined on a Nonius CAD-4 diffractometer. Intensity data collections used graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) and employed $2\theta/\omega$ scans with a peak to background count time of 2:1. The omega scan angles were $0.80 + 0.347 \tan \theta$. Reflections were counted for 60 s or until $\sigma(I)/I$ was 0.02. Three reflections were monitored throughout data collections as checks on crystal alignment and decomposition, no systematic effects being observed. The data sets were corrected for Lorentz, polarisation and absorption [29] effects using locally written programs and equivalent reflections averaged.

TABLE 9. Crystal data for $Os(SiEt_3)H(CO)_2(PPh_3)_2$ (2) and $Os(Ge[p\text{-tolyl}]_3)H(CO)_2(PPh_3)_2$ (6)

	$Os(SiEt_3)H(CO)_2(PPh_3)_2$ (2)	$Os(Ge[p\text{-tolyl}]_3)H(CO)_2(PPh_3)_2$ (6)
Formula	$C_{44}H_{46}O_2OsP_2Si$	$C_{59}H_{52}GeO_2OsP_2 \cdot CH_2Cl_2$
Molecular weight	886.59	1202.66
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a	11.309(1) Å	12.260(10) Å
b	16.343(1) Å	12.398(3) Å
c	22.441(4) Å	18.513(5) Å
α	90.0°	108.34(2)°
β	103.14(1)°	99.34(4)°
γ	90.0°	95.75(4)°
V	4039.1(9) Å^3	2608(2) Å^3
Z	4	2
d(calc)	1.457 g cm^{-3}	1.490 g cm^{-3}
d(obs)		1.469 g cm^{-3}
$F(000)$	1784	1204
μ	34.8 cm^{-1}	47.3 cm^{-1}
Radiation Mo Kα (Monochromatic) λ	0.71069 Å	0.71069 Å
Temperature	295 K	298 K
Diffractometer	Nonius CAD-4	Nonius CAD-4
Scan technique	$\omega/2\theta$	$\omega/2\theta$
2θ (min-max)	2–50°	2–60°
No. of unique reflections	8073	11911
No. of observed reflections	6122	10057
Crystal size	0.12 × 0.24 × 0.34 mm	0.17 × 0.26 × 0.37 mm
A (min-max)	1.00–0.62	1.00–0.68
Least squares weights	$1.0/[\sigma^2(F) + 0.006F^2]$	$1.62/[\sigma^2(F) + 0.0009F^2]$
Function minimised	$\Sigma w[\lvert F_o \rvert - \lvert F_c \rvert]^2$	$\Sigma w[\lvert F_o \rvert - \lvert F_c \rvert]^2$
R and R'	0.035, 0.038	0.036, 0.040

The structures were solved by Patterson and difference Fourier techniques and refined by full-matrix least squares [30]. Atomic scattering factors were for neutral atoms [31]. After initial isotropic refinement all atoms were allowed to assume anisotropic motion. Hydrogen atoms were included in calculated positions, assuming a C–H distance of 0.95 Å and allowed to ride on the atom to which they were bonded with a common thermal parameter. At convergence final shifts were less than 15% of standard deviations and final peaks in difference maps were less than 1 eÅ^{-3}, randomly distributed. Final refinement details are included in Table 9. Interatomic distances and atomic coordinates for **2** are given in Tables 5 and 10 respec-

TABLE 10. Atomic coordinates for Os(SiEt$_3$)H(CO)$_2$(PPh$_3$)$_2$ (**2**)

	x	*y*	*z*	U_{iso}
Os	0.69467(2)	0.25617(1)	0.42069(1)	0.03256(12)
P(1)	0.48330(12)	0.27320(8)	0.41880(6)	0.0346(6)
P(2)	0.80299(12)	0.27662(8)	0.52372(6)	0.0360(6)
Si	0.70013(16)	0.20725(11)	0.31615(7)	0.0479(9)
O(1)	0.6981(4)	0.4279(2)	0.3674(2)	0.067(3)
O(2)	0.7002(5)	0.0722(2)	0.4431(2)	0.081(3)
C(1)	0.6960(5)	0.3650(3)	0.3886(2)	0.045(3)
C(2)	0.6962(5)	0.1409(3)	0.4348(2)	0.050(3)
C(3)	0.8258(7)	0.1290(4)	0.3220(3)	0.070(4)
C(4)	0.8419(9)	0.0925(6)	0.2613(4)	0.103(7)
C(5)	0.5614(7)	0.1581(5)	0.2673(3)	0.086(5)
C(6)	0.5290(9)	0.0745(6)	0.2878(5)	0.131(9)
C(7)	0.7400(9)	0.2885(5)	0.2639(3)	0.091(6)
C(8)	0.8645(11)	0.3242(7)	0.2811(5)	0.152(11)
C(11)	0.3851(5)	0.1821(3)	0.4037(2)	0.045(3)
C(12)	0.4160(6)	0.1152(3)	0.4424(3)	0.056(3)
C(13)	0.3420(7)	0.0459(3)	0.4347(3)	0.073(4)
C(14)	0.2381(8)	0.0434(4)	0.3893(4)	0.078(5)
C(15)	0.2079(7)	0.1094(4)	0.3510(4)	0.077(5)
C(16)	0.2804(6)	0.1790(4)	0.3578(3)	0.058(3)
C(21)	0.4396(5)	0.3133(3)	0.4879(2)	0.042(2)
C(22)	0.3529(7)	0.2776(4)	0.5132(3)	0.073(4)
C(23)	0.3249(8)	0.3125(5)	0.5656(3)	0.093(6)
C(24)	0.3803(8)	0.3825(5)	0.5903(3)	0.077(5)
C(25)	0.4660(7)	0.4184(5)	0.5644(3)	0.075(5)
C(26)	0.4957(6)	0.3828(4)	0.5144(3)	0.062(4)
C(31)	0.4008(5)	0.3465(3)	0.3611(2)	0.039(2)
C(32)	0.3019(6)	0.3889(3)	0.3706(3)	0.058(3)
C(33)	0.2405(6)	0.4424(4)	0.3254(3)	0.070(4)
C(34)	0.2742(6)	0.4514(4)	0.2711(3)	0.063(4)
C(35)	0.3723(6)	0.4095(4)	0.2618(3)	0.064(4)
C(36)	0.4355(5)	0.3564(3)	0.3062(2)	0.048(3)
C(41)	0.7277(5)	0.2629(3)	0.5871(2)	0.045(2)
C(42)	0.6581(7)	0.1931(4)	0.5871(3)	0.066(4)
C(43)	0.6027(8)	0.1767(6)	0.6347(4)	0.086(5)
C(44)	0.6166(9)	0.2313(6)	0.6844(4)	0.097(6)
C(45)	0.6824(9)	0.3006(5)	0.6829(3)	0.090(6)
C(46)	0.7401(7)	0.3159(4)	0.6357(3)	0.068(4)
C(51)	0.9290(5)	0.2035(3)	0.5461(2)	0.044(3)
C(52)	0.9585(6)	0.1675(3)	0.6039(3)	0.062(4)
C(53)	1.0533(8)	0.1116(4)	0.6196(4)	0.084(6)
C(54)	1.1205(8)	0.0908(4)	0.5784(4)	0.081(5)
C(55)	1.0931(8)	0.1262(5)	0.5217(4)	0.094(6)
C(56)	0.9999(7)	0.1822(5)	0.5057(3)	0.083(5)
C(61)	0.8795(4)	0.3753(3)	0.5439(2)	0.040(2)
C(62)	0.9925(5)	0.3804(3)	0.5852(3)	0.050(3)
C(63)	1.0426(6)	0.4565(4)	0.6020(3)	0.059(4)
C(64)	0.9848(6)	0.5266(3)	0.5778(3)	0.057(3)
C(65)	0.8759(6)	0.5222(3)	0.5361(2)	0.056(3)
C(66)	0.8228(5)	0.4468(3)	0.5190(2)	0.044(3)

TABLE 11. Atomic coordinates for $Os(Ge[p\text{-tolyl}]_3)H(CO)_2(PPh_3)_2$ (6)

Atom	x	y	z	U_{iso}
Os	0.08598(1)	0.00665(1)	0.23473(1)	0.03307(9)
Ge	0.14037(3)	0.20960(3)	0.33360(2)	0.0358(2)
P(1)	0.24006(9)	−0.08162(9)	0.27561(6)	0.0363(4)
P(2)	−0.04537(9)	−0.14449(9)	0.14012(6)	0.0382(5)
Cl(1)	0.4341(2)	0.3814(3)	0.05547(18)	0.171(2)
Cl(2)	0.5782(4)	0.3010(3)	0.1542(3)	0.254(5)
O(1)	−0.0460(3)	−0.0126(3)	0.3577(2)	0.059(2)
O(2)	0.2235(4)	0.0818(4)	0.1300(2)	0.097(3)
C(1)	0.0040(3)	−0.0074(3)	0.3119(2)	0.039(2)
C(2)	0.1707(4)	0.0504(4)	0.1684(2)	0.059(2)
C(3)	0.4510(17)	0.2776(13)	0.1035(11)	0.280(20)
C(11)	0.0077(3)	0.2899(3)	0.3436(2)	0.041(2)
C(12)	0.0231(3)	0.4043(3)	0.3908(3)	0.051(2)
C(13)	−0.0658(4)	0.4648(4)	0.4026(3)	0.057(2)
C(14)	−0.1743(4)	0.4132(4)	0.3694(3)	0.059(2)
C(15)	−0.1908(4)	0.3009(4)	0.3220(3)	0.065(3)
C(16)	−0.1009(3)	0.2397(4)	0.3090(3)	0.055(2)
C(17)	−0.2697(4)	0.4800(5)	0.3864(4)	0.087(4)
C(21)	0.1948(3)	0.2147(3)	0.4418(2)	0.0364(19)
C(22)	0.3057(3)	0.2119(3)	0.4725(2)	0.040(2)
C(23)	0.3371(3)	0.2034(3)	0.5443(2)	0.042(2)
C(24)	0.2589(3)	0.1955(3)	0.5898(2)	0.046(2)
C(25)	0.1490(3)	0.2002(3)	0.5605(2)	0.050(2)
C(26)	0.1172(3)	0.2101(3)	0.4887(2)	0.043(2)
C(27)	0.2945(4)	0.1815(5)	0.6685(2)	0.068(3)
C(31)	0.2447(3)	0.3226(3)	0.3142(2)	0.044(2)
C(32)	0.2259(4)	0.3428(4)	0.2445(3)	0.063(3)
C(33)	0.2939(5)	0.4259(5)	0.2297(3)	0.075(3)
C(34)	0.3850(4)	0.4898(4)	0.2851(3)	0.066(3)
C(35)	0.4041(4)	0.4740(4)	0.3557(3)	0.059(2)
C(36)	0.3340(3)	0.3927(3)	0.3709(3)	0.053(2)
C(37)	0.4607(5)	0.5808(5)	0.2686(4)	0.094(4)
C(41)	0.3828(3)	0.0123(3)	0.3247(20	0.040(2)
C(42)	0.4455(3)	−0.0100(4)	0.3816(2)	0.052(2)
C(43)	0.5474(4)	0.0587(4)	0.4150(3)	0.062(3)
C(44)	0.5796(4)	0.1502(5)	0.3908(3)	0.064(3)
C(45)	0.5086(3)	0.1720(4)	0.3339(3)	0.055(2)
C(46)	0.4047(3)	0.1037(3)	0.3015(2)	0.044(2)
C(51)	0.2877(3)	−0.1867(3)	0.1967(2)	0.047(2)
C(52)	0.2134(4)	−0.2812(4)	0.1459(3)	0.058(2)
C(53)	0.2453(5)	−0.3569(5)	0.0845(3)	0.075(4)
C(54)	0.3530(6)	−0.3408(6)	0.0724(4)	0.091(4)
C(55)	0.4269(6)	−0.2506(6)	0.1217(4)	0.101(5)
C(56)	0.3954(5)	−0.1735(5)	0.1842(3)	0.076(3)
C(61)	0.2190(3)	−0.1559(3)	0.3452(2)	0.042(2)
C(62)	0.1885(3)	−0.0943(3)	0.4128(2)	0.045(2)
C(63)	0.1645(3)	−0.1462(4)	0.4657(2)	0.053(2)
C(64)	0.1716(4)	−0.2608(4)	0.4503(3)	0.067(3)
C(65)	0.2031(4)	−0.3229(4)	0.3842(3)	0.069(3)
C(66)	0.2270(4)	−0.2711(4)	0.3314(3)	0.055(2)
C(71)	−0.0142(4)	−0.2166(3)	0.0441(2)	0.047(2)
C(72)	0.0351(4)	−0.1464(4)	0.0081(3)	0.062(3)
C(73)	0.0586(5)	−0.1963(5)	−0.0662(3)	0.077(3)
C(74)	0.0348(5)	−0.3134(5)	−0.1022(3)	0.076(3)
C(75)	−0.0140(6)	−0.3817(5)	−0.0661(3)	0.077(3)
C(76)	−0.0400(5)	−0.3319(4)	0.0048(3)	0.066(3)

TABLE 11 (*continued*)

Atom	x	y	z	U_{iso}
C(81)	−0.1031(3)	−0.2662(3)	0.1667(2)	0.045(2)
C(82)	−0.2063(4)	−0.3283(4)	0.1291(3)	0.057(2)
C(83)	−0.2479(5)	−0.4194(5)	0.1485(3)	0.070(3)
C(84)	−0.1871(5)	−0.4491(4)	0.2067(3)	0.071(3)
C(85)	−0.0847(5)	−0.3856(4)	0.2462(3)	0.067(3)
C(86)	−0.0444(4)	−0.2938(3)	0.2266(2)	0.051(2)
C(91)	−0.1767(3)	−0.0903(3)	0.1164(2)	0.048(2)
C(92)	−0.2150(5)	−0.0784(5)	0.0447(3)	0.074(3)
C(93)	−0.3119(5)	−0.0290(6)	0.0340(4)	0.095(5)
C(94)	−0.3711(5)	0.0025(6)	0.0925(5)	0.093(5)
C(95)	−0.3344(5)	−0.0093(5)	0.1620(4)	0.076(4)
C(96)	−0.2369(4)	−0.0531(5)	0.1750(3)	0.062(3)

tively and corresponding values for **6** are in Tables 6 and 11.

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