

GROUP IV DERIVATIVES OF $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}$. STRUCTURES OF $\text{HOs}_3(\mu\text{-H})_2(\text{CO})_{10}(\text{SiHPh}_2)$ AND $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}(\text{SnMe}_3)_2$

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Summary

The structures of $\text{HOs}_3(\mu\text{-H})_2(\text{CO})_{10}(\text{SiHPh}_2)$ (**1**) and $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}(\text{SnMe}_3)_2$ (**2**) have been determined by X-ray methods. Crystals of **1** are triclinic, space group $P\bar{1}$ with a 9.221(1), b 11.927(1), c 13.580(1) Å, α 110.94(1), β 101.28(1), γ 97.39(1)°, V 1335.3(4) Å³ and $Z = 2$. The structure was solved by heavy-atom methods and the structure refined to R 2.2% and R_w 2.3%. It consists of an Os_3 triangle, two edges of which are bridged by hydrogen ligands (Os–Os lengths of 3.0369(4) and 3.0847(5) Å vs. 2.9383(6) Å for the unbridged Os–Os bond). The terminal hydride and SiHPh_2 groups ligate different osmium atoms on the same edge of the Os_3 cluster (the Os–Si bond length is 2.455(2) Å); both are in the equatorial plane. This is first case where a terminal hydride ligand has been structurally characterized in an equatorial site for an Os_3 cluster. Crystals of **2** are monoclinic space group $P2_1/n$ with a 9.456(2), b 22.575(4), c 13.124(4) Å, β 95.40(2)°, V 2789(2) Å³ and $Z = 4$. The structure was also solved by standard heavy-atom techniques and the structure refined to R 5.3% and R_w 6.5% with only the Os and Sn atoms permitted to have anisotropic thermal parameters. The structure of **2** is similar to **1** except that the SnMe_3 ligands are bound on opposite edges of the Os_3 triangle. The Os–Os vectors are 2.896(3) (unbridged), 3.021(3), 3.070(2) Å (Os($\mu\text{-H}$)Os); the Os–Sn lengths are 2.726(5) and 2.696(4) Å.

Introduction

We have been concerned for some time with mononuclear derivatives of ruthenium and osmium carbonyl with Group IV ligands [1]. Some of these derivatives exhibit interesting properties such as stereochemical nonrigidity [2] and stereospecific exchange with ¹³CO [3]. More recently we have extended these investigations to cluster complexes of osmium. For example, $\text{Os}_3(\mu\text{-H})_3(\text{CO})_9(\text{SiMeCl}_2)_3$ [4], $\text{Os}_3(\text{CO})_{12}(\text{SiCl}_3)_2$ [5] and $\text{Os}_3(\mu\text{-H})_3(\text{CO})_9(\text{SiPh}_3)$ [6] have been synthesized and structurally characterized. The compounds have novel structures; the last cluster

also has unusual fluxional properties. Furthermore, these molecules possess terminal silyl ligands whereas, to our knowledge, there are no osmium clusters that contain structurally characterized, terminal alkyl ligands. (There have, however, been two recent reports of the synthesis of alkyl-substituted osmium clusters [7].)

Recent interest in osmium cluster derivatives with germanium and tin ligands [8,9] has prompted us to report here the structures of $\text{HOs}_3(\mu\text{-H})_2(\text{CO})_{10}(\text{SiHPh}_2)$ and $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}(\text{SnMe}_3)_2$. These represent new structural types for Group IV derivatives of osmium. The compounds were isolated as part of our study of the reaction of group IV hydrides with $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}$ [6]. The details of the variable temperature NMR studies of these and related compounds will be reported at a later date.

Experimental

Unless otherwise stated, manipulations of starting materials and products were carried out under a nitrogen atmosphere with use of standard Schlenk techniques. Solvents were dried and distilled under nitrogen before use. A minor modification of the literature method [10] was used to prepare $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}$; Me_3SnH was prepared by reduction of Me_3SnCl with LiAlH_4 ; Ph_2SiH_2 was commercially available.

Infrared spectra were recorded on a Perkin-Elmer 983 instrument, NMR spectra on a Bruker SY100 spectrometer, and mass spectra on a Kratos MS-50 instrument (regional facility, University of British Columbia). Microanalyses were performed by Mr. M.K. Yang of the Microanalytical Laboratory of Simon Fraser University.

The crystal structure analyses were determined with an Enraf-Nonius CAD4-F diffractometer using graphite-crystal monochromated Mo-K_α radiation [$\lambda(\alpha_1) = 0.70930 \text{ \AA}$; $\lambda(\alpha_2) = 0.71359 \text{ \AA}$]. Backgrounds to reflections were obtained by extending the scan by 25% on each side of the reflection.

Preparation of $\text{HOs}_3(\mu\text{-H})_2(\text{CO})_{10}(\text{SiHPh}_2)$

To $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}$ (0.10 g, 0.12 mmol) in hexane (15 ml), a hexane solution of Ph_2SiH_2 (0.022 g, 0.12 mmol) was added. The resultant solution was then stirred for 4 h. An infrared spectrum of the yellow solution at this stage indicated virtually quantitative formation of $\text{HOs}_3(\mu\text{-H})_2(\text{CO})_{10}(\text{SiHPh}_2)$. The volatile products of the reaction mixture were removed on the vacuum line and the remaining yellow solid was recrystallized twice from hexane to give the desired product, $\text{HOs}_3(\mu\text{-H})_2(\text{CO})_{10}(\text{SiHPh}_2)$, as yellow crystals (m.p. 101–102°C, sealed capillary). Found: C, 26.07; H, 1.42; $\text{C}_{22}\text{H}_{14}\text{O}_{10}\text{Os}_3\text{Si}$ calcd.: C, 25.48; H, 1.36%; MS: 980 ($P-2\text{CO}$)⁺; $\nu(\text{CO})$: 2130w, 2102m, 2072vw, 2058m, 2045vs, 2025s, 1994w, 1990w cm^{-1} (hexane solution); ^1H NMR: δ 8–7 (m, Ph), 6.62 (s, Si–H), –9.4 (d, $J(\text{H}-\text{H})$ 12.7 Hz, H(3T)), –17.35 (d, $J(\text{H}-\text{H})$ 12.7 Hz, H(23)), –17.5 (s, H(13)) ppm (C_6D_6 solution).

Preparation of $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}(\text{SnMe}_3)_2$

To a stirred solution of $\text{Os}_2(\mu\text{-H})_2(\text{CO})_{10}$ (0.10 g, 0.12 mmol) in hexane (20 ml) was added an excess of Me_3SnH (ca. 20 mmol) whereupon the color of the solution immediately changed from purple to yellow. The solution was stirred for 4 d at room temperature at which time an infrared spectrum of the reaction mixture indicated that the initially formed $\text{HOs}_3(\mu\text{-H})_2(\text{CO})_{10}(\text{SnMe}_3)$ had completely

reacted. The solvent and excess ligand were then removed on the vacuum line and the remaining solid recrystallized from hexane to give $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}(\text{SnMe}_3)_2$ (0.13 g, 94%) m.p. 86–87°C (sealed capillary). Found: C, 16.52; H, 1.77; $\text{C}_{16}\text{H}_{20}\text{O}_{10}\text{Os}_3\text{Sn}_2$ calcd.: C, 16.28; H, 1.71; MS: 1165 ($P - \text{Me}$)⁺; $\nu(\text{CO})$: 2117.5m, 2100.5vww, 2084m, 2072w, 2044sh, 2038vs, 2027w, 2019s, 2011m, 2007.5m, 1979m, 1967m cm^{-1} (hexane solution). ¹H NMR: isomer *A* (see Fig. 2): δ 0.87(s, Me), 0.59(s, Me), –16.6(d, $J(\text{H-H})$ 1.8 Hz, OsHOs), –17.6(d, $J(\text{H-H})$ 1.7 Hz, OsHOs); isomer *B*: 0.73 (s, Me), –16.9 (d, $J(\text{H-H})$ 1.0 Hz, OsHOs), –18.4 (d, $J(\text{H-H})$ 1.2 Hz, OsHOs) ppm ($\text{C}_6\text{D}_5\text{CD}_3$ solution; the ratio of *A/B* was 1/~1.2).

Crystal structure analysis of $\text{HOs}_3(\mu\text{-H})_2(\text{CO})_{10}(\text{SiHPh}_2)$

A crystal of $\text{HOs}_3(\mu\text{-H})_2(\text{CO})_{10}(\text{SiHPh}_2)$ in the form of a needle was selected and sealed in a thin-walled glass capillary. The orientation matrix and unit cell dimensions were obtained by least-squares from the setting angles of 25 well-centered reflections, $25^\circ < 2\theta < 31^\circ$, widely distributed in reciprocal space. Crystal data are given in Table 1.

An intensity data set was obtained as indicated in Table 1. A total of 4682 unique reflections (h , $-10 \rightarrow 10$; k , $-14 \rightarrow 14$; l , $0 \rightarrow 16$) were measured, of which 3772 with $I > 2.3\sigma(I)$ were regarded as observed and were used in structure solution and refinement. Two standard reflections were monitored at intervals of 2 h of X-ray exposure time and showed a general decrease in intensity of ca. 6% over the period of data collection: data were scaled according to a smoothed curve derived from these measurements. An empirical adsorption correction [11] (range 1.00–0.54) was also applied to the data.

The structure was solved by heavy-atom methods and all non-hydrogen atoms were located from electron density difference maps interspersed with successive least-squares refinement (isotropic temperature factors). Hydrogen atom coordinates for the phenyl groups were determined geometrically and their temperature factors were set equal to those of the carbon atoms to which they were bonded. The hydrogen atom parameters were not refined but were recalculated from time to time. Non-hydrogen atoms were refined with anisotropic temperature factors in further cycles and an extinction parameter [12] was indicated and then introduced. At this stage an electron density difference map based on reflections with $\sin\theta/\lambda < 0.4 \text{ \AA}^{-1}$ was searched for the remaining hydrogen atoms. The largest peak corresponded to the hydrogen of the silane and the next three to the hydrides. The latter peaks would, however, give unreasonably asymmetric Os–H bond lengths, so the locations of the hydrides were calculated geometrically * [13]; the parameters for these H atoms, also, were not refined. Least-squares refinement was continued until all shift/error ratios < 0.01 . Final $R = 0.022$, $R_w = 0.023$. All major features in a final difference map were close to Os atoms and of magnitude $< 1.1(1) \text{ e\AA}^{-3}$.

Refinement was by the least-squares method minimizing the function $\sum w(|F_0| - |F_c|)^2$ using the block-diagonal approximation for early calculations but full-matrix for the final cycles. Initially, $w = 1$ but in later stages $w = [(\sigma(F_0))]^2$

* The hydrides were assumed to lie in the Os_3 plane, H(13) and H(23) bridging with symmetric Os–H distances of 1.83 Å and H(3T) at 1.66 Å from Os(3) with angle Os(2)–Os(3)–H(3T) 180°. Distances were from ref. 13.

TABLE 1

CRYSTALLOGRAPHIC DATA FOR $\text{HOs}_3(\mu\text{-H})_2(\text{CO})_{10}(\text{SiHPh}_2)$ (1) AND $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}(\text{SnMe}_3)_2$ (2)

	1	2
Formula	$\text{C}_{22}\text{H}_{14}\text{O}_{10}\text{Os}_3\text{Si}$	$\text{C}_{16}\text{H}_{20}\text{O}_{10}\text{Os}_3\text{Sn}_2$
Formula wt.	1037.03	1180.31
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n^a$
Z	2	4
$\rho_{\text{calcd.}}$	2.579 g cm^{-3}	2.810 g cm^{-3}
μ	143.47 cm^{-1}	158.3 cm^{-1}
a	$9.221(1) \text{ \AA}$	$9.456(2) \text{ \AA}$
b	$11.927(1) \text{ \AA}$	$22.575(4) \text{ \AA}$
c	$13.580(1) \text{ \AA}$	$13.124(4) \text{ \AA}$
α	$110.94(1)^\circ$	—
β	$101.28(1)^\circ$	$95.40(2)^\circ$
γ	$97.39(1)^\circ$	—
V	$1335.3(4) \text{ \AA}^3$	$2789(2) \text{ \AA}^3$
ω scan width	$(0.6 + 0.35 \tan \theta)^\circ$ for $0^\circ < 2\theta < 30^\circ$ $(0.5 + 0.35 \tan \theta)^\circ$ for $30^\circ < 2\theta < 50^\circ$	$(0.80 + 0.35 \tan \theta)^\circ$
ω scan speeds	$1.64\text{--}0.5^\circ \text{ min}^{-1}$ for $0^\circ < 2\theta < 30^\circ$ $4.11\text{--}0.55^\circ \text{ min}^{-1}$ for $30^\circ < 2\theta < 50^\circ$	$5.48\text{--}0.78^\circ \text{ min}^{-1}$
2 θ range	$0\text{--}50^\circ$	$0\text{--}40^\circ$
Size of crystal	$0.35 \times 0.10 \times 0.13 \text{ mm}$	$0.33 \times 0.04 \times 0.28 \text{ mm}$
Total no. reflections	4682	2593
Observed reflections ^b	3772	1386
No. variables	326	150
Final R	0.022	0.053
Final R_w	0.023	0.065
GOF ^c	1.39	1.57

^a Non-standard setting of $P2_1/c$. Equivalent positions: $x, y, z; 1/2 - x, 1/2 + y, 1/2 - z; x, y, z; 1/2 + x, 1/2 - y, 1/2 + z$. ^b Reflections with $I > 2.3\sigma(I)$. ^c $GOF = [\sum w(|F_o| - |F_c|)^2 / (\text{no. obsns} - \text{no. vars})]^{1/2}$

+ $0.0001(F_o)^2]^{-1}$. The final value for the extinction parameter was $0.24(1) \times 10^{-6}$. Neutral-atom scattering factors with anomalous dispersion corrections were used [14]. Computer programs were run on a VAX 11/750 computer [15]. Fractional atomic coordinates of the non-hydrogen atoms of $\text{HOs}_3(\mu\text{-H})_2(\text{CO})_{10}(\text{SiHPh}_2)$ are given in Table 2.

A rigid body analysis [16] of the Os_3Si fragment alone was ill-conditioned and failed. Approximate corrections can be obtained by considering the whole molecule as a rigid body and give Os(1)–Os(2) 2.943, Os(1)–Os(3) 3.045 and Os(2)–Os(3) 3.092 Å. A riding-motion model [17] with the Os having the larger mean-square displacement riding on the other Os gave similar results.

Riding-motion corrections were also calculated for the Os–Si bond (0.003 \AA), Os–C bonds (range $0.004\text{--}0.014 \text{ \AA}$, except Os(3)–C(32), 0.029 \AA) and C–O bonds (range $0.005\text{--}0.021 \text{ \AA}$). They are not listed in detail as they were only 1–2 esd's in magnitude.

TABLE 2

FRACTIONAL ATOMIC COORDINATES AND B_{eq} ^a FOR THE NONHYDROGEN ATOMS OF $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}(\text{SiHPh}_2)$ (1)

Atom	x	y	z	B_{eq}
Os(1)	0.18317(3)	0.50680(2)	0.32361(2)	2.907
Os(2)	0.25999(3)	0.77061(2)	0.46322(2)	3.492
Os(3)	0.25583(3)	0.68694(3)	0.21970(2)	3.921
Si	0.1236(2)	0.3027(2)	0.1745(2)	3.44
C(11)	0.3878(8)	0.4844(6)	0.3543(5)	3.8
O(11)	0.5060(6)	0.4637(5)	0.3713(4)	5.6
C(12)	0.1469(7)	0.4499(6)	0.4321(6)	3.6
O(12)	0.1255(6)	0.4153(5)	0.4963(4)	5.0
C(13)	-0.0316(8)	0.5016(6)	0.2754(5)	3.6
O(13)	-0.1580(6)	0.4900(5)	0.2425(5)	5.9
C(21)	0.4687(10)	0.7487(7)	0.4863(6)	5.0
O(21)	0.5909(7)	0.7403(6)	0.4989(5)	7.3
C(22)	0.2315(8)	0.7240(7)	0.5814(6)	4.5
O(22)	0.2153(6)	0.6981(5)	0.6517(4)	6.0
C(23)	0.0450(9)	0.7693(6)	0.4196(6)	4.2
O(23)	-0.0792(6)	0.7727(5)	0.3937(5)	5.7
C(24)	0.3178(9)	0.9449(7)	0.5463(7)	5.3
O(24)	0.3530(8)	1.0475(5)	0.5952(6)	8.6
C(31)	0.4665(9)	0.6714(7)	0.2397(7)	5.1
O(31)	0.5852(7)	0.6573(6)	0.2423(6)	7.7
C(32)	0.3050(12)	0.8286(8)	0.1907(8)	7.1
O(32)	0.3346(11)	0.9126(6)	0.1722(7)	12.1
C(33)	0.0440(11)	0.6770(8)	0.1681(7)	5.6
O(33)	-0.0833(8)	0.6672(7)	0.1314(5)	8.3
C(51)	0.2968(8)	0.2676(6)	0.1281(5)	4.2
C(52)	0.3696(9)	0.1788(7)	0.1478(6)	5.0
C(53)	0.5032(11)	0.1596(9)	0.1178(8)	6.9
C(54)	0.5666(10)	0.2281(10)	0.0694(8)	6.8
C(55)	0.4973(10)	0.3137(9)	0.0467(7)	6.3
C(56)	0.3631(9)	0.3331(7)	0.0752(6)	4.9
C(61)	0.0364(7)	0.1694(6)	0.2017(5)	3.8
C(62)	-0.0918(8)	0.0833(6)	0.1279(6)	4.4
C(63)	-0.1585(9)	-0.0144(7)	0.1457(7)	6.0
C(64)	-0.0991(11)	-0.0301(7)	0.2397(8)	6.0
C(65)	0.0258(11)	0.0511(8)	0.3140(7)	5.8
C(66)	0.0916(9)	0.1488(7)	0.2953(6)	5.0

^a $B_{\text{eq}} = 8\pi^2(U_1 + U_2 + U_3)/3$ where the U_n (in \AA^2) are the principal axes of the thermal ellipsoid.

Crystal structure analysis of $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}(\text{SnMe}_3)_2$

Crystals of $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}(\text{SnMe}_3)_2$ were obtained as very thin colorless plates. Several of the thickest and best-formed crystal fragments were selected and sealed in thin-wall glass capillaries. X-ray photographs taken of them using Cu radiation revealed only one to be of sufficient quality to collect intensity data. This crystal was transferred to the diffractometer and the unit cell dimensions and orientation matrix were obtained by least-squares from the setting angles of 25 well-centered reflections $17^\circ < 2\theta < 22^\circ$ widely distributed in reciprocal space. Crystal data are given in Table 1.

The intensities of a unique data set ($\pm h, k, l$) were collected as outlined in Table 1. Two standards were measured after every 2 h of X-ray exposure time and showed

an overall decrease in intensity of 10% during data acquisition. Data were therefore scaled according to a five-point-smoothed curve derived from these standards. Absorption [18] and Lp corrections were also applied (T range 0.532–0.053).

The structure was solved by standard heavy-atom techniques. All non-hydrogen atoms were located and refined, Os and Sn with anisotropic temperature factors and O and C isotropically. Methyl H coordinates were calculated assuming C–H bonds of 0.95 Å staggered with respect to the Sn–C bonds. Examination of the Os–Os distances and the Os–Os–X angles indicated that Os(1)–Os(2) and Os(1)–Os(3) were bridged by hydrides. Coordinates for these atoms were calculated assuming them to lie in the Os_3 plane with symmetric Os–H bond lengths of 1.83 Å [13]. Hydrogen atoms were included in the structure factor calculations but their parameters were not refined in the least-squares.

All major features in a difference electron-density map ($2.5(3)$ – $1.4(3)$ $e\text{\AA}^{-3}$) after the refinement were close to the Os and Sn atoms, suggesting that there were systematic errors in the data arising from the irregular shape of the crystal and the extreme absorption. Inclusion of anisotropic temperature factors for the O and C atoms would therefore not be justified.

The structure was refined until all shift/error ratios < 0.1 . Refinement was by full-matrix least-squares minimizing the function $\sum w(|F_o| - |F_c|)^2$. The weights, w , were originally unity but in the final cycles $w = [(\sigma(F_o))^2 + 0.0009(F_o)^2]^{-1}$ where $\sigma(F_o)$ comes from the counting statistics. Examination of $w(|F_o| - |F_c|)^2$ as a function of $(\sin\theta)/\lambda$ and F_o showed no systematic trends. Computer programs [15] were run on a VAX 11/750 computer, using neutral-atom scattering factors with anomalous dispersion corrections for the non-hydrogen atoms [14]. Fractional atomic coordinates for the non-hydrogen atoms of $Os_3(\mu-H)_2(CO)_{10}(SnMe_3)_2$ are given in Table 3.

Description of the structures

$HOs_3(\mu-H)_2(CO)_{10}(SiHPh_2)$

Complexes of the type $HOs_3(\mu-H)_2(CO)_{10}(ER_3)$ are the initial products from the reaction of HER_3 ($E = Si, Ge, Sn; R = H$ or alkyl) with $Os_3(\mu-H)_2(CO)_{10}$. They are precursors to the clusters $Os_3(\mu-H)_3(CO)_9(ER_3)$ [6] and $Os_3(\mu-H)_2(CO)_{10}(ER_3)_2$.

The structure of $HOs_3(\mu-H)_2(CO)_{10}(SiHPh_2)$ (**1**) was determined by conventional X-ray methods. A view of the molecule is shown in Fig. 1; selected interatomic bond lengths and angles are given in Table 4. Evidence for the gross silicon hydrogen and the hydride ligands were found during the structure determination, but their precise positions did not appear chemically reasonable. They were, therefore, placed at calculated positions for the final refinements of the structure. Other features of the molecular configuration are, however, consistent with the location of the hydrogen ligands as shown in Fig. 1 (The 1H NMR spectrum of **1** was also consistent with this arrangement). The geometry about Os(3) indicates the presence of a terminal hydride substituent in an equatorial site. The Os(1)–Os(3) and Os(2)–Os(3) vectors (3.0369(4), 3.0847(5) Å) show the usual lengthening over normal Os–Os bonds previously observed many times for $Os(\mu-H)Os$ linkages [19].

The unbridged Os(1)–Os(2) bond length of 2.9383(6) Å is somewhat longer than normally found for unbridged Os–Os bonds in triosmium clusters. For example, the average Os–Os distance in $Os_3(CO)_{12}$ is 2.877(3) Å [20]. The lengthening may be

TABLE 3

FINAL ATOMIC COORDINATES AND ISOTROPIC TEMPERATURE FACTORS FOR THE NONHYDROGEN ATOMS OF $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}(\text{SnMe}_3)_2$ (2)

Atom	x	y	z	B_{eq}/B^a
Os(1) ^a	0.23484(16)	0.31472(9)	0.59482(11)	4.34
Os(2) ^a	0.29833(16)	0.21642(9)	0.44979(11)	4.39
Os(3) ^a	0.30095(16)	0.33673(10)	0.37337(11)	4.83
Sn(1) ^a	0.2043(4)	0.4264(2)	0.6687(2)	7.1
Sn(2) ^a	0.2862(3)	0.1095(2)	0.5401(2)	5.7
C(11)	0.032(4)	0.319(2)	0.552(3)	4.9(9)
O(11)	-0.087(3)	0.321(2)	0.526(2)	7.9(8)
C(12)	0.192(5)	0.286(2)	0.727(3)	6.4(11)
O(12)	0.173(3)	0.266(1)	0.801(2)	6.5(7)
C(13)	0.427(4)	0.327(2)	0.644(3)	3.7(8)
O(13)	0.542(3)	0.334(1)	0.677(2)	6.7(7)
C(21)	0.100(5)	0.204(2)	0.420(3)	6.2(11)
O(21)	-0.026(3)	0.194(2)	0.408(2)	7.2(7)
C(22)	0.343(4)	0.175(2)	0.338(3)	5.3(10)
O(22)	0.378(4)	0.152(2)	0.264(3)	9.6(10)
C(23)	0.490(5)	0.216(2)	0.502(3)	6.1(11)
O(23)	0.605(4)	0.219(2)	0.540(2)	7.8(8)
C(31)	0.103(4)	0.319(2)	0.329(3)	4.4(9)
O(31)	-0.012(3)	0.312(2)	0.295(2)	7.3(8)
C(32)	0.308(5)	0.410(3)	0.326(4)	8.0(14)
O(32)	0.293(4)	0.464(2)	0.303(2)	9.1(10)
C(33)	0.499(5)	0.340(2)	0.423(3)	5.8(11)
O(33)	0.617(3)	0.346(2)	0.454(2)	8.0(8)
C(34)	0.358(4)	0.301(2)	0.249(3)	4.9(9)
O(34)	0.381(3)	0.284(1)	0.172(2)	6.8(7)
C(1)	0.013(7)	0.468(3)	0.630(5)	12.8(20)
C(2)	0.247(5)	0.428(3)	0.831(4)	10.0(16)
C(3)	0.355(7)	0.479(3)	0.613(4)	11.6(18)
C(4)	0.183(5)	0.050(3)	0.435(4)	8.4(13)
C(5)	0.162(6)	0.110(3)	0.669(4)	10.8(17)
C(6)	0.487(5)	0.078(3)	0.593(3)	7.9(13)

^a $B_{\text{eq}} = 8\pi^2(U_1 + U_2 + U_3)/3$ where U_n (in \AA^2) are the principal axes of the thermal ellipsoid.

attributed to the *trans* influence of the silyl ligand. A similar influence was observed in the structures $\text{Os}_3(\mu\text{-H})_3(\text{CO})_9(\text{SiXCl}_2)_3$ (X = Me, Cl) [4,5]. In a cluster closely related to 1, $\text{HOs}_3(\mu\text{-H})(\text{CO})_{10}(\text{PPh}_3)$, the unbridged Os–Os bond *trans* to the phosphine is 2.9170(5) Å whereas that *trans* to a carbonyl is 2.8645(7) Å [21].

The Os–Si distance in 1 of 2.455(2) Å may be compared to 2.429(2) Å, the length found for the corresponding bond in $\text{Os}_3(\mu\text{-H})_3(\text{CO})_9(\text{SiPh}_3)$ [6]. Both of these lengths are significantly longer than the Os–Si bonds in $\text{Os}_3(\mu\text{-H})_3(\text{CO})_9(\text{SiMeCl}_2)_3$ (2.420(5), 2.400(6) Å) [4], $\text{Os}_3(\mu\text{-H})_3(\text{CO})_9(\text{SiCl}_3)_3$ (2.389(12), 2.394(14), 2.367(13) Å) [6], and $\text{Os}_3(\text{CO})_{12}(\text{SiCl}_3)_2$ (2.377(3) Å) [5]. As previously discussed [5], this may indicate that the SiXCl_2 (X = Me, Cl) groups are better π -acceptors than SiR_3 (R = H or organic group) ligands. The deviations from the tetrahedral value of the angles about the silicon in 1 is typical and has also been previously discussed [5].

The most novel feature of the structure of 1 is that the terminal hydride ligand occupies an equatorial position in the cluster. Of the numerous triosmium hydride

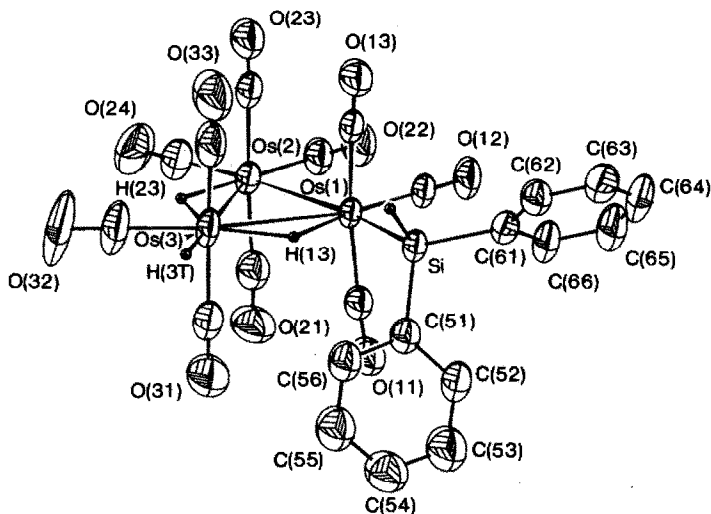


Fig. 1. A thermal ellipsoid diagram of $\text{HOs}_3(\mu\text{-H})_2(\text{CO})_{10}(\text{SiHPh}_2)$ (**1**) with the labelling scheme. Ellipsoids enclose 50% probabilities. Hydrogen atoms of the phenyl groups have been deleted, and others are drawn as small spheres of arbitrary radius.

clusters, only a handful have terminal hydride ligands and in all of these cases they are in axial positions [20–22]. (In $\text{HOs}_3(\mu\text{-H})_3(\mu_3\text{-NCH}_2\text{CF}_3)(\text{CO})_8$ the terminal hydride is disordered over two of the three terminal sites available to it at the osmium [23].)

Another interesting aspect of **1** is that the terminal, noncarbonyl ligands reside on the same edge of the Os_3 skeleton whereas in $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}(\text{SnMe}_3)_2$, discussed below, they occupy positions on opposite edges of the Os_3 triangle. Also, electron counts at individual osmium atoms in **1** gives $\text{Os}(2)$ $18\frac{1}{2}$ electrons and $\text{Os}(3)$ $17\frac{1}{2}$. There are a number of triosmium clusters that are similar in this respect; some examples are $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}(\text{SnMe}_3)_2$, $\text{Os}_3(\mu\text{-H})_3(\text{CO})_9(\text{SiPh}_3)$ [6], and $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}[\text{Re}(\text{CO})_5]_2$ [24]. The clusters are, of course, electron precise. This probably serves to illustrate that even for these low nuclearity clusters the bonding is best described in terms of molecular orbitals delocalized over all metals in the framework.

$\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}(\text{SnMe}_3)_2$

Clusters of the type $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{12}(\text{ER}_3)_2$ result from the prolonged reaction of $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}$ with excess HER_3 . For the cases studied so far, HSnMe_3 is unique in apparently giving two isomeric forms of $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}(\text{SnMe}_3)_2$. As yet, we have been unable to completely characterize the less-common isomer although there is strong evidence that both SnMe_3 ligands are attached to the same osmium atom in the cluster. Here we report the structure of the common form of $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}(\text{SnMe}_3)_2$ (**2**) was determined by conventional X-ray crystallography. A view of the molecule is shown in Fig. 2, selected bond lengths and angles are recorded in Table 5.

The crystal used was a limiting factor in the precision of the structural determination in that it was not of high quality (though the best we could obtain after an

TABLE 4

SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR $\text{HOs}_3(\mu\text{-H})_2(\text{CO})_{10}(\text{SiHPh}_2)$ (1)

Os(1)–Os(2)	2.9383(6)	Os(2)–Os(3)	3.0847(5)
Os(1)–Os(3)	3.0369(4)	Os(1)–Si	2.455(2)
Os(1)–C(11)	1.925(7)	C(11)–O(11)	1.147(8)
Os(1)–C(12)	1.895(6)	C(12)–O(12)	1.129(8)
Os(1)–C(13)	1.946(7)	C(13)–O(13)	1.135(9)
Os(2)–C(21)	1.955(9)	C(21)–O(21)	1.130(10)
Os(2)–C(22)	1.928(7)	C(22)–O(22)	1.133(9)
Os(2)–C(23)	1.952(8)	C(23)–O(23)	1.140(9)
Os(2)–C(24)	1.919(8)	C(24)–O(24)	1.130(10)
Os(3)–C(31)	1.950(8)	C(31)–O(31)	1.124(10)
Os(3)–C(32)	1.887(8)	C(32)–O(32)	1.131(10)
Os(3)–C(33)	1.914(9)	C(33)–O(33)	1.156(11)
Si–C(51)	1.871(7)	Si–C(61)	1.875(7)
C(51)–C(52)	1.400(10)	C(61)–C(62)	1.395(10)
C(52)–C(53)	1.392(12)	C(62)–C(63)	1.368(11)
C(53)–C(54)	1.361(15)	C(63)–C(64)	1.374(13)
C(54)–C(55)	1.365(15)	C(64)–C(65)	1.357(13)
C(55)–C(56)	1.390(12)	C(65)–C(66)	1.371(11)
C(56)–C(51)	1.396(10)	C(66)–C(61)	1.392(9)
Os(2)–Os(1)–Os(3)	62.14(1)	Os(3)–Os(1)–Si	105.06(4)
Os(2)–Os(1)–Si	167.17(4)	Os(3)–Os(1)–C(11)	93.8(2)
Os(2)–Os(1)–C(11)	95.0(2)	Os(3)–Os(1)–C(12)	158.9(2)
Os(2)–Os(1)–C(12)	96.8(2)	Os(3)–Os(1)–C(13)	89.8(2)
Os(2)–Os(1)–C(13)	94.3(2)	C(11)–Os(1)–C(12)	89.3(3)
Si–Os(1)–C(11)	86.3(2)	C(11)–Os(1)–C(13)	170.6(3)
Si–Os(1)–C(12)	96.0(2)	C(12)–Os(1)–C(13)	90.5(3)
Si–Os(1)–C(13)	84.3(2)		
Os(1)–Os(2)–Os(3)	60.50(1)	Os(3)–Os(2)–C(21)	85.7(2)
Os(1)–Os(2)–C(21)	84.5(2)	Os(3)–Os(2)–C(22)	147.6(2)
Os(1)–Os(2)–C(22)	87.1(2)	Os(3)–Os(2)–C(23)	87.4(2)
Os(1)–Os(2)–C(23)	87.2(2)	Os(3)–Os(2)–C(24)	115.4(2)
Os(1)–Os(2)–C(24)	175.6(2)	C(22)–Os(2)–C(23)	91.2(3)
C(21)–Os(2)–C(22)	91.6(3)	C(22)–Os(2)–C(24)	97.1(3)
C(21)–Os(2)–C(23)	171.1(3)	C(23)–Os(2)–C(24)	94.3(3)
C(21)–Os(2)–C(24)	93.7(3)		
Os(1)–Os(3)–Os(2)	57.36(1)	Os(2)–Os(3)–C(31)	95.7(2)
Os(1)–Os(3)–C(31)	91.9(2)	Os(2)–Os(3)–C(32)	108.1(3)
Os(1)–Os(3)–C(32)	165.5(3)	Os(2)–Os(3)–C(33)	95.8(2)
Os(1)–Os(3)–C(33)	90.0(2)	C(31)–Os(3)–C(32)	90.3(4)
C(32)–Os(3)–C(33)	91.0(4)	C(31)–Os(3)–C(33)	167.4(4)
Os(1)–Si–C(51)	110.4(2)	C(51)–Si–C(61)	108.0(3)
Os(1)–Si–C(61)	117.0(2)		
Os(1)–C(11)–O(11)	175.8(6)	Os(2)–C(23)–O(23)	177.4(6)
Os(1)–C(12)–O(12)	179.5(6)	Os(2)–C(24)–O(24)	179.5(7)
Os(1)–C(13)–O(13)	175.1(6)	Os(3)–C(31)–O(31)	174.4(8)
Os(2)–C(21)–O(21)	177.2(7)	Os(3)–C(32)–O(32)	179.2(8)
Os(2)–C(22)–O(22)	179.2(7)	Os(3)–C(33)–O(33)	176.3(7)

extensive search) and furthermore the shape led to an extreme variation in the absorption. Although the hydrogen atoms were not located, there is no doubt that one bridges the Os(1), Os(2) edge and the other the Os(1), Os(3) edge. These Os–Os

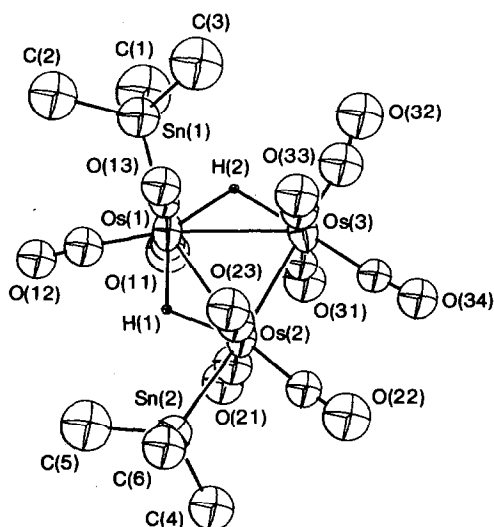


Fig. 2. Thermal ellipsoid diagram of $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}(\text{SnMe}_3)_2$ (**2**). Ellipsoids enclose 50% probabilities. Hydrides are shown as small spheres and methyl hydrogen atoms have been deleted for clarity. In the carbonyl groups, only the oxygen atoms have been labelled; the carbon atom is identified with the same numerals as the respective oxygen.

vectors are elongated (3.021(3) and 3.070(2) Å respectively) as expected for $\text{Os}(\mu\text{-H})\text{Os}$ linkages [19]. The unbridged $\text{Os}\text{-Os}$ bond, $\text{Os}(2)\text{-Os}(3)$, has a length (2.896(3) Å) that is typical for such bonds in triosmium clusters.

The $\text{Os}\text{-Sn}$ distances in **2** (2.726(5), 2.696(4) Å) are similar to the terminal $\text{Os}\text{-Sn}$ lengths reported in the literature: 2.653(1) Å in $\text{Os}_3(\mu\text{-H})(\mu_3\text{-S})(\mu_3\text{-SCH}_2)(\text{CO})_7(\text{PMe}_2\text{Ph})(\text{SnMe}_3)$ [25], and 2.711(1) and 2.712(1) Å in *trans*- $\text{Os}(\text{CO})_4(\text{SnPh}_3)_2$ [26]. These lengths may also be compared to $\text{Os}\text{-Sn}$ distances found for molecules in which the tin ligand bridges two osmium atoms [8].

Group IV derivatives of $\text{Os}_3(\text{CO})_{12}$ with the formulation $\text{Os}_3(\mu\text{-H})(\text{CO})_{11}(\text{ER}_3)$ [9] and $\text{Os}_3(\mu\text{-H})_3(\text{CO})_9(\text{ER}_3)_3$ [4,5] have been described in the literature. We have briefly reported the synthesis of $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}(\text{SiPh}_3)_2$ [6], a member of the intermediate series of compounds, $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}(\text{ER}_3)_2$. The structure of **2** represents the first of a member of this series. The structure does, however, have its analogue amongst transition metal hydride derivatives of $\text{Os}_3(\text{CO})_{10}$ in $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}[\text{Re}(\text{CO})_5]_2$ [24]. It is interesting that the $\text{Os}\text{-Os}$ bond lengths in the rhenium derivative are similar to the corresponding distances in **2**. This probably indicates that the *trans* influences of the isolobal fragments, $\text{Re}(\text{CO})_5$ and SnMe_3 , are comparable.

Additional material. Tables of observed and calculated structure factors for **1** and **2** are available on request (from F.W.B.E.).

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TABLE 5

SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR Os₃(μ-H)₂(CO)₁₀(SnMe₃)₂ (2)

Os(1)–Os(2)	3.021(3)	Os(2)–Os(3)	2.896(3)
Os(1)–Os(3)	3.070(2)		
Os(1)–Sn(1)	2.726(5)	Os(2)–Sn(2)	2.696(4)
Os(1)–C(11)	1.95(4)	Os(2)–C(21)	1.90(4)
Os(1)–C(12)	1.92(5)	Os(2)–C(22)	1.82(4)
Os(1)–C(13)	1.90(4)	Os(2)–C(23)	1.88(4)
Os(3)–C(31)	1.95(4)	Os(3)–C(33)	1.93(4)
Os(3)–C(32)	1.78(6)	Os(3)–C(34)	1.94(4)
Sn(1)–C(1)	2.05(7)	Sn(2)–C(4)	2.09(5)
Sn(1)–C(2)	2.13(5)	Sn(2)–C(5)	2.15(6)
Sn(1)–C(3)	2.05(7)	Sn(2)–C(6)	2.09(5)
C(11)–O(11)	1.15(5)	C(21)–O(21)	1.20(5)
C(12)–O(12)	1.11(6)	C(22)–O(22)	1.18(6)
C(13)–O(13)	1.14(5)	C(23)–O(23)	1.15(5)
C(31)–O(31)	1.14(5)	C(33)–O(33)	1.15(5)
C(32)–O(32)	1.26(8)	C(34)–O(34)	1.11(5)
Os(2)–Os(1)–Os(3)	56.78(6)	Os(1)–Os(3)–Os(2)	60.74(6)
Os(1)–Os(2)–Os(3)	62.48(6)		
Os(2)–Os(1)–Sn(1)	159.65(10)	Os(3)–Os(1)–Sn(1)	102.99(10)
Os(2)–Os(1)–C(11)	95.9(12)	Os(3)–Os(1)–C(11)	90.0(11)
Os(2)–Os(1)–C(12)	113.2(16)	Os(3)–Os(1)–C(12)	169.8(16)
Os(2)–Os(1)–C(13)	94.7(11)	Os(3)–Os(1)–C(13)	91.5(10)
Sn(1)–Os(1)–C(11)	85.5(13)	C(11)–Os(1)–C(12)	90(2)
Sn(1)–Os(1)–C(12)	87.1(16)	C(11)–Os(1)–C(13)	168(2)
Sn(1)–Os(1)–C(13)	82.7(12)	C(12)–Os(1)–C(13)	91(2)
Os(1)–Os(2)–Sn(2)	111.20(9)	Os(3)–Os(2)–Sn(2)	173.65(10)
Os(1)–Os(2)–C(21)	89.5(14)	Os(3)–Os(2)–C(21)	96.3(15)
Os(1)–Os(2)–C(22)	163.7(14)	Os(3)–Os(2)–C(22)	101.2(14)
Os(1)–Os(2)–C(23)	90.9(14)	Os(3)–Os(2)–C(23)	95.3(15)
Sn(2)–Os(2)–C(21)	82.8(15)	C(21)–Os(2)–C(22)	93(2)
Sn(2)–Os(2)–C(22)	85.1(14)	C(21)–Os(2)–C(23)	167(2)
Sn(2)–Os(2)–C(23)	85.1(15)	C(22)–Os(2)–C(23)	90(2)
Os(1)–Os(3)–C(31)	88.5(10)	Os(2)–Os(3)–C(31)	82.4(12)
Os(1)–Os(3)–C(32)	119.8(16)	Os(2)–Os(3)–C(32)	178.5(17)
Os(1)–Os(3)–C(33)	87.9(12)	Os(2)–Os(3)–C(33)	87.8(14)
Os(1)–Os(3)–C(34)	145.5(13)	Os(2)–Os(3)–C(34)	84.8(13)
C(31)–Os(3)–C(32)	99(2)	C(32)–Os(3)–C(33)	91(2)
C(31)–Os(3)–C(33)	170(2)	C(32)–Os(3)–C(34)	95(2)
C(31)–Os(3)–C(34)	90(2)	C(33)–Os(3)–C(34)	88(2)
Os(1)–Sn(1)–C(1)	117(2)	Os(2)–Sn(2)–C(4)	109(2)
Os(1)–Sn(1)–C(2)	111(2)	Os(2)–Sn(2)–C(5)	113(2)
Os(1)–Sn(1)–C(3)	108(2)	Os(2)–Sn(2)–C(6)	112(1)
C(1)–Sn(1)–C(2)	109(2)	C(4)–Sn(2)–C(5)	105(2)
C(1)–Sn(1)–C(3)	106(2)	C(4)–Sn(2)–C(6)	110(2)
C(2)–Sn(1)–C(3)	106(2)	C(5)–Sn(2)–C(6)	107(2)
Os(1)–C(11)–O(11)	179(4)	Os(2)–C(21)–O(21)	175(3)
Os(1)–C(12)–O(12)	174(4)	Os(2)–C(22)–O(22)	174(4)
Os(1)–C(13)–O(13)	178(3)	Os(2)–C(23)–O(23)	175(4)
Os(3)–C(31)–O(31)	174(3)	Os(3)–C(33)–O(33)	176(4)
Os(3)–C(32)–O(32)	169(4)	Os(3)–C(34)–O(34)	172(4)

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