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Derivatives of the Type $Os_4(\mu\text{-}H)(CO)_{14}(ER_3)$ (E = Si, Ge, Sn; R = Me, Ph). Structure of $Os_4(\mu\text{-}H)(CO)_{14}(SnMe_3)$

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Addition of EHR_3 (E = Si, Ge, Sn; R = Me, Ph) to $Os_4(CO)_{14}$ in hexane at room temperature readily affords the air-stable derivatives $Os_4(\mu\text{-}H)(CO)_{14}(ER_3)$ in good yield. The structure of $Os_4(\mu\text{-}H)(CO)_{14}(SnMe_3)$ (3) has been determined by X-ray crystallography: space group $P\bar{1}$ with $a = 7.929$ (1) Å, $b = 12.072$ (2) Å, $c = 14.739$ (2) Å, $\alpha = 80.82$ (1)°, $\beta = 81.60$ (1)°, $\gamma = 75.46$ (1)°, $V = 1338$ Å^3, $Z = 2$; $R_1 = 0.041$, $R_2 = 0.046$ for 3113 observed reflections. The osmium atoms in 3 adopt a planar butterfly arrangement with Os(1)–Os(2) = 2.807 (1) Å, Os(1)–Os(3) = 2.875 (1) Å, Os(1)–Os(4) = 2.810 (1) Å, Os(2)–Os(3) = 3.050 (1) Å, and Os(3)–Os(4) = 2.851 (1) Å. The Sn atom lies approximately in the Os_4 plane attached to one of the wingtip Os atoms (Os(2)–Sn = 2.697 (2) Å) and cis to Os(1); Os(1) has only one equatorial carbonyl bonded to it. Surprisingly, calculations with the HYDEX program of Orpen indicate the hydride ligand bridges Os(1)–Os(2) rather than Os(2)–Os(3). (Evidence is presented that the long Os(2)–Os(3) bond is a donor–acceptor metal–metal bond.) ^1H and ^{13}C NMR spectra are also consistent with the hydride bridging the Os(1)–Os(2) bond. In contrast to those of $Os_4(CO)_{14}(PMe_3)$, the carbonyls in 3 are rigid in solution, even at 80 °C.

Introduction

We have recently reported the synthesis and structure of the 62-electron clusters $Os_4(CO)_{14}(PMe_3)$ (**1**) and $Os_4(\mu\text{-}H)_2(CO)_{13}(PMe_3)$ (**2**). The former cluster has an unusual planar Os_4 skeleton with adjacent short and long Os–Os bonds that we have rationalized in terms of three-center, two-electron metal–metal bonds. Furthermore, this cluster exhibits remarkable fluxional character in solution that is apparent even at –89 °C.[1] In contrast, **2** has the more common butterfly structure and is rigid in solution at 0 °C.[2]

Herein, we report the synthesis and characterization of clusters of the type $Os_4(\mu\text{-}H)(CO)_{14}(ER_3)$ (E = Si, Ge, Sn; R = Me, Ph), which are intermediate between **1** and **2** in terms of the number of bridging hydride ligands. Spectroscopic and crystallographic results show that these clusters have a planar Os_4 framework but they are rigid in solution at ambient temperature. Furthermore, evidence is presented that the hydride ligand bridges one of the short Os–Os bonds in the cluster rather than the long Os–Os bond.

Experimental Section

Manipulations of starting materials and products were carried out under a nitrogen atmosphere with the use of Schlenk techniques. Hexane was refluxed over potassium, distilled, and stored under nitrogen before use. Dichloromethane was treated similarly except that P_2O_5 was used as the drying agent. The preparation of $Os_4(CO)_{14}$ was according to the literature synthesis.[3] Solid group 14 hydrides, as obtained commercially, were recrystallized from hexane; liquid and gaseous ($SiHMe_3$) group 14 hydrides were, with the exception of $SnHMe_3$, obtained commercially and used as received. Trimethyltin hydride was prepared by the reduction of $SnMe_3Cl$ with $LiAlH_4$ in diglyme and was distilled twice before use. The ^{13}CO-enriched compounds were obtained from ^{13}CO-enriched $Os_3(CO)_{12}$ (~35% ^{13}C), which was prepared by heating $Os_3(CO)_{12}$ in toluene at 125 °C under ~1.5 atm of ^{13}CO (99% ^{13}C) for 3 days.

Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer; the internal calibration of the instrument was periodically checked against the known absorption frequencies of gaseous CO. NMR spectra were recorded on a Bruker WM400 or a Bruker SY-100 spectrometer. The electron-impact (70 eV) mass spectra were obtained on a Kratos-MS-50 instrument (University of British Columbia, regional facility); the pattern of the envelope of ions at highest mass in each spectrum was compared with that simulated by computer for the species in question and in all cases were found to be in good agreement. Microanalyses were performed by M. K. Yang of the Microanalytical Laboratory of Simon Fraser University. Microanalytical and spectroscopic data for new compounds are given in Table I.

Scheme I

$$Os_4(CO)_{14} + EHR_3 \xrightarrow[\text{hexane}]{25\ ^\circ C} Os_4(\mu\text{-}H)(CO)_{14}(ER_3)$$

E = Si, Ge, Sn **3**: $ER_3 = SnMe_3$
R = Me, Ph

Preparation of $Os_4(\mu\text{-}H)(CO)_{14}(SnMe_3)$ (3). A solution of $Os_4(CO)_{14}$ (40 mg; 0.035 mmol) in hexane (40 mL) was prepared by heating the components with stirring at ~50 °C for 15 min. The solution was cooled to room temperature and $SnHMe_3$ (8 mg, 0.05 mmol) in hexane was added with stirring. There was an immediate color change to red-brown. The solvent and excess $SnHMe_3$ were removed on the vacuum line, and the residue was recrystallized from toluene to yield $Os_4(\mu\text{-}H)(CO)_{14}(SnMe_3)$ (40 mg, 91%) as red, air-stable crystals.

The preparation of the other derivatives followed the same procedure except that reaction times of up to 1 h were employed (in the case of the $SiHPh_3$ derivative); the progress of the reaction may be conveniently monitored by infrared spectroscopy. The preparation of $Os_4(\mu\text{-}H)(CO)_{14}(SiMe_3)$ was carried out in a small sealed flask under 1 atm of $SiHMe_3$ (the reaction time was 30 min). Yields ranged from 30% to 90%.

X-ray Structure Determination for 3. A crystal of suitable size (Table SIII) was cut from one that had been grown from toluene and mounted on an Enraf-Nonius CAD4F diffractometer and a data set (Table II) collected. Background measurements were made by extending the scan range by 25% on each side of the scan. Two standard reflections were monitored every hour during data collection. The data did not show any significant decay during the data collection. The unit cell was determined on the basis of 23 accurately centered reflections that were widely separated in reciprocal space and with $32° < 2\theta < 45°$. The choice of $P\bar{1}$ for the space group of **3** was confirmed by the successful solution and refinement of the structure. Intensity data were corrected for Lorentz, polarization, and absorption effects (an analytical absorption correction was applied).

The osmium atoms were located by direct methods. All other non-hydrogen atoms were located from Fourier difference maps alternated with least-squares refinement of the partial model. After anisotropic refinement of the Os, Sn, and O atoms, the methyl hydrogen atoms were included as fixed atoms at calculated positions (d(C–H) = 0.96 Å). Upon convergence of the model, the bridging hydride atom was placed at the position calculated by the HYDEX program of Orpen.[4] The model was refined to convergence by full-matrix least squares (no hydrogen atoms were refined). A weighting scheme based on counting statistics was adopted in the final stages of refinement to remove systematic trends in the error analysis. Crystallographic data and details of the data collection and refinement are given in Table II, atomic coordinates in Table III, and bond length and angle data in Table IV. Neutral-atom

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Table I. Analytical and Spectroscopic Data for New $Os_4(\mu\text{-}H)(CO)_{14}(L)$ Compounds

	anal., %						^1H NMR[b]	
	calcd		found					
L	C	H	C	H	mass spectrum	$\nu(CO)$,[a] cm^{-1}	δ(Me)	δ(H)
$SiMe_3$	16.60	0.82	16.72	0.99	M^+	2121, 2083, 2063, 2052, 2041, 2019, 2012, 1994, 1978	0.66	−13.70
$SiMe_2Ph$	20.48	0.93	20.70	0.99	$M^+ - CO$	2125, 2084, 2064, 2053, 2041, 2019, 2012, 1996, 1978	0.94	−13.51
$SiMePh_2$	23.93	1.04	24.03	1.08	*c*	2125, 2085, 2064, 2054, 2042, 2019, 2014, 1997, 1978, 1950	1.24	−13.27
$SiPh_3$	27.19	1.14	27.32	1.29	$M^+ - CO$	2126, 2086, 2066, 2056, 2043, 2020, 2016, 1997, 1979		−13.18
$SiHPh_2$	23.33	0.90	23.25	1.07	*c*	2127, 2087, 2065, 2055, 2043, 2020, 2016, 1999, 1979	5.82[d]	−13.32
$GePh_3$	26.36	1.11	26.41	1.31	$M^+ - CO$	2126, 2085, 2065, 2055, 2043, 2021, 2016, 1997, 1978, 1950		−13.39
$SnMe_3$	15.50	0.76	15.54	0.78	$M^+ - Me$	2124, 2079, 2061, 2051, 2041, 2020, 2013, 1996, 1990, 1977	0.58[e]	−14.11[f]
$SnPh_3$	25.56	1.07	25.76	1.12	*g*	2125, 2082, 2064, 2054, 2042, 2021, 2016, 2004, 1996, 1988, 1980		−13.69

[a] Hexane solution (see Figure 1 for intensities). [b] CD_2Cl_2 solution. [c] Not determined. [d] Si–*H*. [e] J_{Sn-H} = 50.2 Hz. [f] J_{Sn-H} = 34.5 Hz. [g] $M^+ - CO - Ph$.

Table II. Crystallographic Data for $Os_4(\mu\text{-}H)(CO)_{14}(SnMe_3)$ (**3**)

$C_{17}H_{10}O_{14}Os_4Sn$	fw 1317.7
a = 7.929 (1) Å	space group $P\bar{1}$
b = 12.072 (2) Å	T = 21 °C
c = 14.739 (2) Å	λ = 0.70926 Å
α = 80.82 (1)°	ρ_{calcd} = 3.55 g cm^{-3}
β = 81.60 (1)°	μ = 216.45
γ = 75.46 (1)°	transm coeff = 0.05416 − 0.29885
V = 1338 $Å^3$	R = 0.041
Z = 2	R_w = 0.046

Table III. Fractional Coordinates for **3**

atom	*x*	*y*	*z*
Os(1)	0.15506 (8)	0.26126 (6)	0.68998 (4)
Os(2)	0.40872 (8)	0.07587 (6)	0.77988 (4)
Os(3)	0.29973 (8)	0.31334 (6)	0.84557 (4)
Os(4)	0.04068 (9)	0.48528 (6)	0.74059 (5)
Sn	0.43652 (18)	−0.11488 (12)	0.70034 (10)
O(11)	0.4464 (18)	0.3275 (14)	0.5447 (9)
O(12)	−0.1426 (15)	0.1722 (11)	0.8098 (9)
O(13)	−0.0443 (17)	0.2726 (14)	0.5271 (9)
O(21)	0.7129 (17)	0.1187 (14)	0.6347 (10)
O(22)	0.1265 (18)	−0.0243 (15)	0.9073 (11)
O(23)	0.6846 (19)	−0.0602 (14)	0.9033 (11)
O(31)	0.5977 (16)	0.3746 (13)	0.7039 (8)
O(32)	0.0085 (17)	0.2247 (13)	0.9770 (9)
O(33)	0.5736 (16)	0.1793 (14)	0.9736 (8)
O(34)	0.2476 (25)	0.5250 (15)	0.9454 (12)
O(41)	0.3429 (20)	0.5686 (16)	0.6108 (13)
O(42)	−0.2569 (17)	0.4129 (14)	0.8726 (10)
O(43)	−0.1890 (19)	0.5469 (15)	0.5839 (11)
O(44)	−0.0481 (24)	0.7079 (18)	0.8263 (16)
C(11)	0.3350 (23)	0.3058 (16)	0.6022 (12)
C(12)	−0.0331 (23)	0.2082 (16)	0.7678 (12)
C(13)	0.0299 (23)	0.2684 (16)	0.5874 (12)
C(21)	0.5998 (24)	0.1076 (16)	0.6871 (12)
C(22)	0.2288 (27)	0.0188 (18)	0.8642 (14)
C(23)	0.5797 (28)	−0.0113 (20)	0.8555 (14)
C(31)	0.4880 (25)	0.3531 (16)	0.7526 (12)
C(32)	0.1124 (24)	0.2600 (16)	0.9262 (12)
C(33)	0.4725 (26)	0.2252 (18)	0.9239 (13)
C(34)	0.2588 (27)	0.4469 (19)	0.9039 (14)
C(41)	0.2342 (28)	0.5316 (19)	0.6581 (14)
C(42)	−0.1406 (25)	0.4344 (17)	0.8263 (13)
C(43)	−0.1022 (27)	0.5249 (19)	0.6426 (14)
C(44)	−0.0166 (33)	0.6252 (24)	0.7927 (17)
C(1)	0.2015 (38)	−0.1042 (27)	0.6409 (20)
C(2)	0.4749 (31)	−0.2736 (22)	0.7983 (16)
C(3)	0.6530 (40)	−0.1424 (29)	0.5959 (21)
H[a]	0.271	0.110	0.683

[a] Position calculated with the HYDEX program.[4]

scattering factors with anomalous dispersion corrections were employed.[5] The computer programs used were from "The CRYSTALS Program Suite" and "The VAX 750/780 Crystal Structure System", except that the SNOOPI program was used to draw the atomic thermal ellipsoid diagrams.[6]

Table IV. Interatomic Distances (Å) and Selected Angles (deg) for **3**

Distances			
Os(1)–Os(2)	2.807 (1)	Os(4)–C(43)	1.84 (2)
Os(1)–Os(3)	2.875 (1)	Os(4)–C(44)	1.89 (3)
Os(1)–Os(4)	2.810 (1)	Sn–C(1)	2.00 (3)
Os(2)–Os(3)	3.050 (1)	Sn–C(2)	2.19 (3)
Os(3)–Os(4)	2.851 (1)	Sn–C(3)	2.04 (3)
Os(1)–C(11)	1.82 (2)	C(11)–O(11)	1.13 (2)
Os(1)–C(12)	1.83 (2)	C(12)–O(12)	1.07 (2)
Os(1)–C(13)	1.85 (2)	C(13)–O(13)	1.10 (2)
Os(1)–H	1.82[a]	C(21)–O(21)	1.06 (2)
Os(2)–C(21)	1.87 (2)	C(22)–O(22)	1.07 (2)
Os(2)–C(22)	1.86 (2)	C(23)–O(23)	1.11 (2)
Os(2)–C(23)	1.81 (2)	C(31)–O(31)	1.05 (2)
Os(2)–Sn	2.697 (2)	C(32)–O(32)	1.10 (2)
Os(2)–H	1.80[a]	C(33)–O(33)	1.10 (2)
Os(3)–C(31)	1.89 (2)	C(34)–O(34)	1.18 (2)
Os(3)–C(32)	1.84 (2)	C(41)–O(41)	1.11 (2)
Os(3)–C(33)	1.84 (2)	C(42)–O(42)	1.07 (2)
Os(3)–C(34)	1.88 (2)	C(43)–O(43)	1.10 (2)
Os(4)–C(41)	1.86 (2)	C(44)–O(44)	1.14 (3)
Os(4)–C(42)	1.84 (2)		
Bond Angles			
Os(2)–Os(1)–Os(3)	64.93 (3)	C(33)–Os(3)–C(34)	94.3 (9)
Os(2)–Os(1)–Os(4)	125.12 (3)	C(31)–Os(3)–C(32)	172.1 (8)
Os(2)–Os(1)–C(13)	130.2 (6)	Os(3)–Os(4)–Os(1)	61.04 (2)
C(11)–Os(1)–C(12)	173.3 (7)	Os(3)–Os(4)–C(44)	109.6 (7)
Os(1)–Os(2)–Os(3)	58.62 (2)	C(44)–Os(4)–C(43)	102 (1)
Os(1)–Os(2)–Sn	108.86 (4)	C(41)–Os(4)–C(42)	176.8 (8)
Sn–Os(2)–C(23)	87.7 (7)	Os(1)–H–Os(2)	102[a]
C(21)–Os(2)–C(22)	169.8 (9)	Os(2)–Sn–C(1)	111.2 (9)
Os(2)–Os(3)–Os(1)	56.45 (2)	Os(2)–Sn–C(2)	113.4 (6)
Os(2)–Os(3)–Os(4)	115.21 (3)	Os(2)–Sn–C(3)	114.6 (9)
Os(2)–Os(3)–C(33)	75.6 (6)		

[a] Calculated position.

Results

Addition of EHR_3 to $Os_4(CO)_{14}$ in hexane at room temperature gives the clusters $Os_4(\mu\text{-}H)(CO)_{14}(ER_3)$ (Scheme I); the yields ranged from 30 to 90%.

The compounds are red, air-stable crystalline solids. They all give a similar pattern in the CO stretching region of the infrared spectrum (Table I; see also Figure 1), which indicates they probably have the same structure. The ^1H NMR data for the derivatives are reported in Table I. The position of the hydride resonance shows little variation when the ER_3 is changed. The ^1H-coupled and -decoupled ^{13}C NMR spectra of **3** are shown in Figure 4. The spectroscopic data are discussed in more detail

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(5) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2B and 2.3.1.

(6) (a) Watkin, D. J.; Carruthers, J. R.; Betteridge, P. W. *CRYSTALS User Guide*; Chemical Crystallography Laboratory, University of Oxford: Oxford, England, 1985. (b) Gabe, E. J.; Larson, A. C.; Lee, F. L.; Le Page, Y. *NRC Crystal Structure System*; National Research Council of Canada: Ottawa, 1984. (c) Davies, E. K. *SNOOPI Plot Program*; Chemical Crystallography Laboratory, University of Oxford: Oxford, England, 1984.

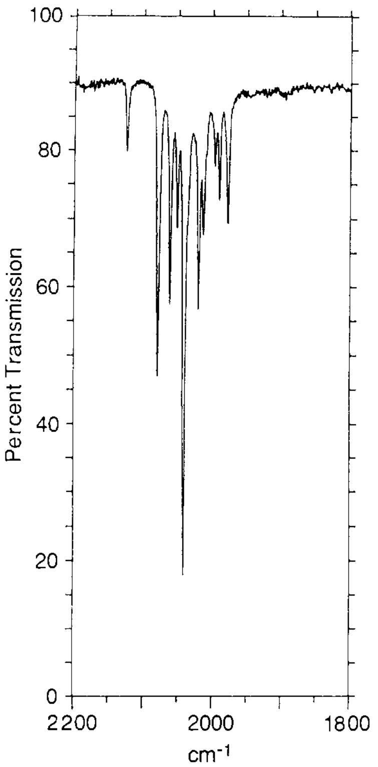


Figure 1. Carbonyl stretching region of the infrared spectrum of $Os_4(\mu\text{-}H)(CO)_{14}(SnMe_3)$ (**3**) in hexane solution.

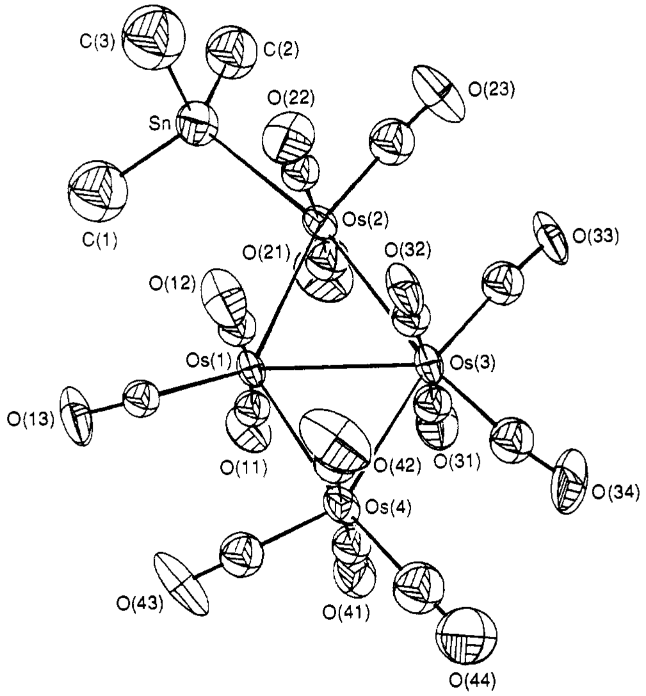


Figure 2. Molecular structure of **3**.

below, as are the structural results.

Discussion

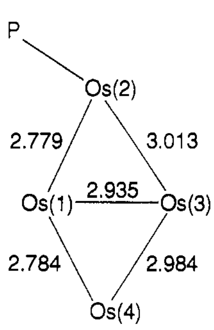
The structure of the $SnHMe_3$ derivative, $Os_4(\mu\text{-}H)(CO)_{14}(SnMe_3)$ (**3**), was determined by X-ray crystallography; a view of the molecule is shown in Figure 2; bond length and angle data are given in Table IV. The Os_4Sn unit is essentially planar: the dihedral angle between the planes Os(1)–Os(2)–Os(3) and Os(1)–Os(3)–Os(4) is 179.73 (3)°, with the Sn atom 0.150 (2) Å from the best plane through the four osmium atoms. Planar tetranuclear clusters were, until recently, quite rare; the tetrahedral and butterfly are the common arrangments found for this class of clusters.[7] There have, however, been a number of recent reports from our laboratory and others of planar M_4 clusters. These include $Os_4(CO)_{15}$ (**4**),[8] $Os_4(CO)_{12}(O_2CCF_3)_2$ (**5**),[9] $Ru_4(CO)_{13}(\mu\text{-}PPh_2)_2$ (**6**),[10] and $Ru_4(CO)_{10}(\mu\text{-}PPh_2)_4$ (**7**).[10] These clusters may also be compared to $Os_3(SnCl_2)(CO)_{11}(\mu\text{-}CH_2)$, which has a planar Os_3Sn core[11] (the $SnCl_2$ unit may be considered as isolobal with $Os(CO)_4$).

Table V. Calculated Site Energies for the Hydride Ligand in Various Positions in **3**

	site energy[a]		site energy[a]
	Bridging Positions		
Os(1)–Os(2)	2.4	Os(1)–Os(4)	33.9
Os(2)–Os(3)	29.9	Os(3)–Os(4)	53.8
Os(1)–Os(3)	45.5		
	Terminal Positions		
Os(1)	11.5	Os(2)	21.8

[a] Calculated from the HYDEX program.[4]

Although the Os_4 skeleton in **3** resembles that in **1** (and **4**), the metal–metal bond lengths within each compound show significant differences:



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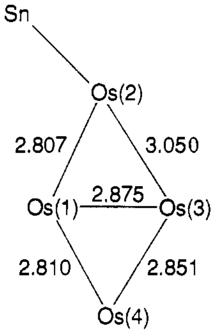

3

The bond lengths may also be compared to 2.877 (3) Å, the average Os–Os bond length found for $Os_3(CO)_{12}$.[12] Evidence is presented below that the hydride ligand bridges Os(1) and Os(2). We have rationalized the long and short bond lengths in **1** and **4** in terms of three-center, two-electron metal–metal bonds so that the short bonds were assigned a bond order of 1.5 and the long bonds an order of 0.5. In this way each osmium atom in the cluster achieves an 18-electron configuration.[1,8] The application of this idea to **3** (and, indeed, to clusters **5**–**7**) is not obvious, and the correct electronic description of the bonding in these molecules must await a more detailed analysis.

The Os–Sn distance in **3** (2.697 (2) Å) is similar to the terminal Os–Sn lengths reported in the literature: 2.726 (5) and 2.696 (4) Å in $Os_3(\mu\text{-}H)_2(CO)_{10}(SnMe_3)_2$,[13] 2.653 (1) Å in $Os_3(\mu\text{-}H)(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{-}SCH_2)(CO)_7(PMe_2Ph)(SnMe_3)$,[14] and 2.711 (1) and 2.712 (1) Å in *trans*-$Os(CO)_4(SnPh_3)_2$.[15]

Location of the Hydride Ligand. As expected, the hydride ligand was not located in the crystallographic study. It is well-known that in trinuclear clusters a single bridging hydride ligand causes a lengthening of the metal–metal vector with which it is associated.[16,17] From the bond lengths in **3** it might therefore be

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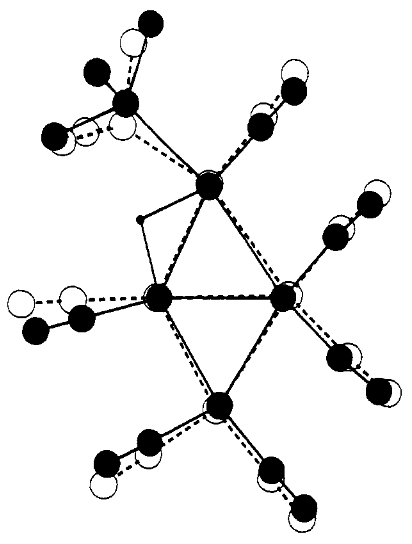

Figure 3. Superimposition of the structure of 3 (filled circles) on that of $Os_4(CO)_{14}(PMe_3)$ (open circles). Axial ligands have been omitted, and as far as possible, Os(1) and Os(2) have been directly superimposed.

expected that the hydride ligand bridges Os(2) and Os(3) since the Os(2)–Os(3) distance is much longer than any other bonding Os–Os distance in the molecule (see structure 3). However, in view of the presence of long, unbridged Os–Os bonds in 1, the HYDEX program of Orpen[4] was used to locate the position of the hydride. The program gave the surprising result that this ligand should be positioned between Os(1) and Os(2) (the Os(1)–Os(2) length at 2.807 (1) Å is the second shortest Os–Os length in the cluster). The program was unequivocal in this location. It gave a "site energy"[4] of 2.4 for this position whereas all other positions tried gave values greater than 11 (Table V). In his original study Orpen estimated the site energies for 41 bridging hydrides and found them to occur in the range 0.2–10.6 with an average value of 2.76.[4]

The reasonableness of this location for the hydride ligand is further illustrated in Figure 3, where the diagrams of the molecular structures of 1 and 3 are superimposed (the axial carbonyls on each molecule have been omitted). As can be seen, the geometry of the carbonyls bonded to Os(2) and Os(3) are virtually identical for both clusters. On the other hand, the equatorial carbonyl on Os(1) and the $SnMe_3$ ligand in 3 show a significant displacement from the corresponding positions of CO(13) and the PMe_3 group in 1. The displacement is entirely consistent with the location of the hydride ligand between Os(1) and Os(2) in 3.

Spectroscopic Properties of 3. The ^1H and ^{13}C NMR spectroscopic properties of 3 are also consistent with the location of the hydride ligand between Os(1) and Os(2). The ^1H NMR spectrum of 3 in CD_2Cl_2 at room temperature exhibits resonances at δ 0.58 and −14.11, as expected for $Os_4(\mu\text{-}H)(CO)_{14}(SnMe_3)$. The hydride signal exhibits $^{117,119}Sn$ coupling of 34.5 Hz, consistent with a cis arrangement of the hydride and trimethyltin ligands. We observe a tin–hydrogen coupling of 30.2 Hz for the resonance of the hydride ligand that is cis to the $SnMe_3$ group in $HOs_3(\mu\text{-}H)_2(CO)_{10}(SnMe_3)$.[18] Furthermore, irradiation of the methyl signal in the ^1H NMR spectrum of 3 caused a nuclear Overhauser enhancement of the hydride signal of about 18%. This is in good agreement with the enhancement expected if the methyl hydrogens come within 2.6 Å of the hydride ligand, the closest distance calculated from the coordinates given for these atoms.

The Orpen program also quite clearly favored the hydride ligand in the bridging position rather than a terminal position on either Os(1) or Os(2) (Table V). The chemical shift of the hydride resonance of 3 is, however, in the region normally associated with terminal hydride ligands. In saturated trinuclear osmium clusters the ^1H NMR resonances of bridging hydrides usually occur in the range δ −15 to −23 whereas those of terminal ligands usually appear in the region δ 0 to −15.[19] That the hydride resonance in 3 has an unusual chemical shift can probably be attributed to the unusual bonding in the cluster. In formally unsaturated clusters such as $Os_3(\mu\text{-}H)_2(CO)_9L$ (L = CO, PR_3,[20] $CNBu^t$ [21,22]) and $Os_3(\mu\text{-}H)_3(CO)_9(SiPh_3)$,[23] the resonances of the bridging hydride ligands all occur downfield of δ −15.

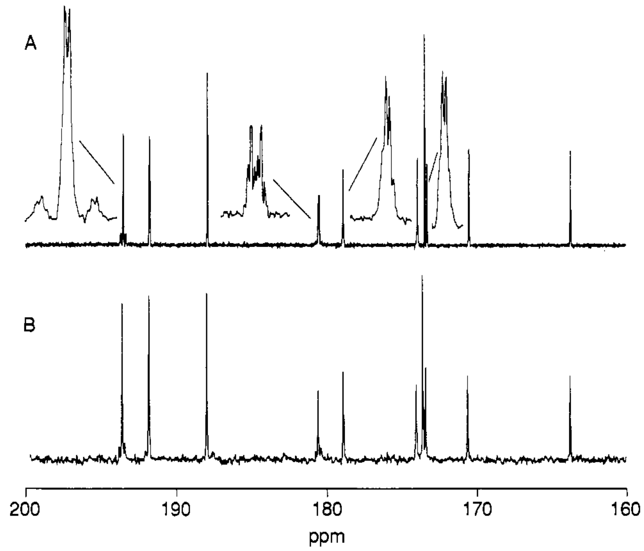

Figure 4. ^1H-Coupled (A) and -decoupled (B) ^{13}C NMR spectra of 3 (^{13}CO-enriched) in CD_2Cl_2 solution at room temperature.

The ^{13}C and $^{13}C\{^1H\}$ NMR spectra of 3 (^{13}CO-enriched) in CD_2Cl_2/CH_2Cl_2 at room temperature are shown in Figure 4. The spectra are consistent with the solid-state structure found for 3 and that the hydride bridges Os(1)–Os(2). In particular, the signal at δ 180.5, which can be assigned to C(23) (see below), shows the largest hydrogen coupling (J_{HC} = 6.7 Hz), consistent with the location of the hydride ligand in a position trans to this carbon.

The H-coupled ^{13}C NMR spectrum showed small couplings that we have rarely observed before in spectra of this type (Figure 4). These couplings especially aided the assignment of the signals, which can be a difficult task for the ^{13}C NMR spectra of asymmetric clusters. The assignment is as follows. The signal at δ 193.6 is assigned to C(21) and C(22) on the basis of signal intensity and because of the fact that the signal exhibits coupling to $^{117,119}Sn$ (J_{SnC} = 36.1 Hz); the signal also exhibits a small hydrogen coupling (J_{HC} = 3.0 Hz). The resonance at δ 191.8 is attributed to C(11) and C(12) on the basis that it has an intensity of 2 and shows unresolved coupling to the hydride proton. The peak at δ 187.9 is assigned to C(41) and C(42) since it also has an intensity of 2 and appears in the region of the spectrum expected for axial carbonyls of $Os(CO)_4$ groups in saturated triosmium clusters[24-26] (e.g., in the ^{13}C NMR spectrum of $Os_3(CO)_{12}$ the signal due to the axial carbonyls occurs at δ 182.3[27]). The signal at δ 180.5 is attributed to C(23) because it exhibits coupling to Sn (J_{SnC} = 32.0 Hz) and has a peak height of 1. As previously mentioned, it shows the largest coupling to the hydrogen atom. The resonance at δ 178.9 is assigned to C(13) since it has an intensity of 1 and shows a small coupling to the hydrogen atom

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(17) See also papers in the series "Structural Studies on Polynuclear Osmium Carbonyl Hydrides", e.g.: Park, J. T.; Shapley, J. R.; Bueno, C.; Ziller, J. W.; Churchill, M. R. *Organometallics* **1988**, *7*, 2307.

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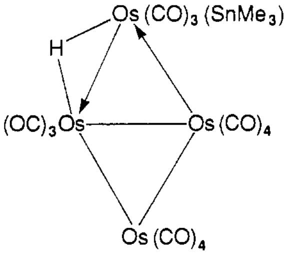
(J_{HC} = 2.4 Hz) and because it is expected that due to the chemical environment of C(13) the signal will be shifted downfield in a manner similar to that of the axial carbonyls attached to Os(1). The peak at δ 174.0 is thought due to C(43) since it has an intensity 1, does not exhibit coupling to hydrogen, and occurs in the region for resonances of equatorial carbonyls in $Os(CO)_4$ units in saturated triosmium compounds$^{24-26}$ (e.g., for $Os_3(CO)_{12}$ this resonance occurs at δ 170.4^{27}). The signal at δ 173.5, which has an intensity of 2, is assigned to the axial carbonyls on Os(3) (i.e., C(31) and C(32)) on the basis that this is an unusual region for the signals of axial carbonyls of an $Os(CO)_4$ unit to appear and is in agreement with the unusual chemical environment about Os(3) in **3**. The peaks of axial carbonyls of $Os(CO)_4$ groups in formally unsaturated triosmium clusters can also occur at high fields.^{22,23} In the ^{13}C NMR spectrum of **1** the signal assigned to C(31) and C(32), analogous to those in **3**, occurs at δ 171.9.^{1} The resonance at δ 173.4 is assigned to C(44) since it has an intensity of 1, exhibits a three-bond coupling to the hydride proton, and occurs in the region found for the signals of equatorial carbonyls in trinuclear osmium clusters.$^{24-27}$ The peaks at δ 170.6 and 163.7 are believed due to C(33) and C(34). We have assigned that at δ 163.7 to C(34) since it is trans to the unusual, long Os–Os bond and is most likely to show an unusual chemical shift.

The resonance at δ 163.7 is at an unusually low field for a carbonyl group in an osmium cluster compound. We have observed resonances in this region in osmium complexes where the CO is trans to a halogen (X) (i.e., OC—Os—X)^{28,29} or trans to a donor–acceptor metal–metal bond (i.e., OC—Os→M).^{28,30,31} In both cases the osmium atom is believed to carry a partial positive charge since the Os—X or Os→M bond is polarized in the sense Os(δ+)—X(δ−) or Os(δ+)→M(δ−). It might be expected that this should cause a deshielding of the carbon atom. It is, however, well-known that the change in the chemical shift of the ^{13}C NMR signals of metal carbonyls is contrary to that expected from simple arguments based on changes in electron density about the carbon. This has been rationalized in terms of changes to the ΔE parameter in the paramagnetic contribution to the chemical shift.^{32}

The ^{13}C NMR spectrum therefore suggests the Os(3) atom in **3** carries a partial positive charge. Note one of the carbonyl stretches in the infrared spectrum of **3** occurs at a high frequency (Figure 1), consistent with the view that there is less back-bonding to the carbonyl or carbonyls involved in this vibration.

The above evidence further suggests that the Os(3)–Os(2) bond may be a weak donor–acceptor interaction. A possible formulation for the bonding in **3** is therefore



which achieves an 18-electron configuration for each osmium atom. It is noted here that Bruce and co-workers have observed a long Ru–Ru bond (3.009 (1) Å) in one of the isomers of $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{15}$ that is of the donor–acceptor type.^{33} It is also relevant to note here that the reaction of **3** with PMe_3 gives as one of the major products $Os_3(CO)_{11}(PMe_3)$ (identified by IR and ^1H NMR spectroscopy). This indicates the $Os(CO)_3(SnMe_3)(H)$ group is easily displaced from the $Os_3(CO)_{11}$ unit.

The ^{13}C NMR spectrum of **3** indicates the carbonyls are rigid at room temperature, as did a spectrum of **3** (in toluene-d_8) at 80 °C. (The sample underwent decomposition at the higher temperature as evidenced by the appearance of new peaks in the latter spectrum.) The rigidity of **3** is in remarkable contrast to **1**, which undergoes a fluxional process in solution that is rapid on the NMR time scale even at −89 °C. Two possible processes were proposed to account for nonrigidity in **1**; both involved an intermediate in which a carbonyl group bridges Os(1)–Os(2). It may be that the presence of the bridging hydride ligand along this bond prevents the formation of such a carbonyl bridge in **3** and stops carbonyl exchange from occurring.

It is also interesting that carbonyls CO(31), CO(33), CO(32), CO(42), CO(43), and CO(41) do not undergo exchange by a terminal–bridge carbonyl rearrangment in the plane that is perpendicular to the Os_4 plane and also passes through Os(3) and Os(4). This is the presumed low-energy process that gives rise to carbonyl exchange in clusters of the type $Os_3(CO)_{11}(L)$,^{26,34} including $(Me_3P)(OC)_4OsOs_3(CO)_{11}$.^{1}

The silyl derivative, $Os_4(\mu\text{-H})(CO)_{14}(SiMe_2Ph)$, was also studied by ^{13}C NMR spectroscopy and found to exhibit behavior similar to that of **3**: resonances in the spectrum in CD_2Cl_2/CH_2Cl_2 at room temperature were observed at δ 193.1, 191.2, 187.3, 180.4, 179.8, 174.3, 174.2, 173.3, 170.6, and 164.3 in the same intensity ratio as observed for **3** (Figure 4). These signals also remained sharp in the spectrum of the sample in toluene-d_8 at 80 °C (two signals at δ 174.0 were, however, degenerate in this solvent). In contrast to the case of **3**, there was no decomposition of the sample observed in the spectrum at the higher temperature.

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Registry No. **3**, 123264-47-1; $Os_4(\mu\text{-H})(CO)_{14}(SiMe_3)$, 123264-45-9; $Os_4(\mu\text{-H})(CO)_{14}(SiMe_2Ph)$, 123264-46-0; $Os_4(\mu\text{-H})(CO)_{14}(SiMe_2Ph_2)$, 123264-48-2; $Os_4(\mu\text{-H})(CO)_{14}(SiPh_3)$, 123264-49-3; $Os_4(\mu\text{-H})(CO)_{14}(SiHPh_2)$, 123264-50-6; $Os_4(\mu\text{-H})(CO)_{14}(GePh_3)$, 123264-51-7; $Os_4(\mu\text{-H})(CO)_{14}(SnPh_3)$, 123264-52-8; $SiMe_3H$, 993-07-7; $SiMe_2PhH$, 766-77-8; $SiMePh_2H$, 776-76-1; $SiPh_3H$, 789-25-3; SiH_2Ph_2, 775-12-2; $GePh_3H$, 2816-43-5; $SnMe_3H$, 1631-73-8; $SnPh_3H$, 892-20-6; $SnMe_3Cl$, 1066-45-1; $Os_4(CO)_{14}$, 115227-28-6.

Supplementary Material Available: Hydrogen atom coordinates (Table SI), anisotropic thermal parameters (Table SII), and full crystal data (Table SIII) for **3** (5 pages); observed and calculated structure factors for **3** (Table SIV) (22 pages). Ordering information is given on any current masthead page.

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