Cleavage of Metal–Metal Bonds in Heteronuclear Clusters. The Reaction of $Os_3(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{-}SCH_2)(CO)_8PMe_2Ph$ with Me_3SnH and the Crystal and Molecular Structures of $HOs_3(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{-}SCH_2)(CO)_7(PMe_2Ph)(SnMe_3)$ and $H_2Os_3(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{-}SCH_2)(CO)_7(PMe_2Ph)$

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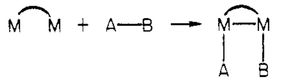
Received September 9, 1981

From the reaction of $Os_3(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{-}SCH_2)(CO)_8(PMe_2Ph)$ (I) with Me_3SnH the compounds $HOs_3(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{-}SCH_2)(CO)_7(PMe_2Ph)(SnMe_3)$ (II) and $H_2Os_3(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{-}SCH_2)(CO)_7(PMe_2Ph)$ (III) have been isolated. Both have been characterized by IR, ^1H NMR, and X-ray crystallographic analyses. For II: space group $P2_1/c$ at 23 °C; $a = 10.426$ (2) Å, $b = 11.421$ (2) Å, $c = 24.563$ (4) Å, $\beta = 95.41$ (2)°; $V = 2912$ Å^3; $Z = 4$, $\rho_{calcd} = 2.68$ g/cm^3. For 3333 reflections ($F_o^2 \geq 3.0\sigma(F_o^2)$) $R_1 = 0.034$ and $R_2 = 0.034$; II contains a cluster of three osmium atoms with two metal–metal bonds. There is a triply bridging sulfide ligand, a triply bridging thioformaldehyde ligand, and a bridging hydride ligand. A trimethyltin group is bonded to one of the exterior osmium atoms of the cluster. In contrast to I the dimethylphenylphosphine ligand is coordinated to the interior osmium atom of the cluster. Mechanisms of formation are proposed and discussed. For III: space group $P\bar{1}$, at 23 °C; $a = 9.169$ (3) Å, $b = 11.157$ (3) Å, $c = 12.359$ (4) Å, $\alpha = 70.50$ (2)°, $\beta = 79.56$ (3)°, $\gamma = 86.75$ (3)°; $V = 1172.0$ (8) Å^3, $Z = 2$, $\rho_{calcd} = 2.97$. g/cm^3. For 3356 reflections ($F_o^2 \geq 3.0\sigma(F_o^2)$) $R_1 = 0.049$ and $R_2 = 0.056$. Like I and II, III also contains a cluster of three osmium atoms with two metal–metal bonds, a triply bridging sulfide ligand, and a triply bridging thioformaldehyde ligand. III is most similar to I but differs in that two bridging hydride ligands have been substituted for one carbonyl ligand.

Introduction

The oxidative addition reaction has now been firmly established as one of the fundamental processes for the activation of small molecules by transition-metal complexes.[1,2] Transition-metal cluster compounds have been discussed as a potentially new class of catalytic agents and as possible models for the types of catalytic processes which occur on surfaces.[3] Oxidative addition reactions in polynuclear metal complexes can occur by the conventional addition to a single metal atom, analogous to those which commonly occur in mononuclear metal complexes, or by addition to a binuclear site which could result in either cleavage (eq 1) or formation (eq 2) of a metal–metal

$$M{-}M + A{-}B \longrightarrow M{-}A + M{-}B \qquad (1)$$



$$M\frown M + A{-}B \longrightarrow \underset{A}{M}{-}\underset{B}{M} \qquad (2)$$

bond.[2] Since metal–metal bonds are frequently the weakest chemical bonds in transition-metal cluster compounds, it seems reasonable to expect that the bond-making and bond-breaking processes could be very important in their chemistry.

In an earlier paper[4] we showed that the oxidative addition of HCl to the molecule $Os_3(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{-}SCH_2)(CO)_8(PMe_2Ph)$ (I) resulted in the cleavage of one of the metal–metal bonds. Group 4 hydrides have also been shown to cleave metal–metal bonds in metal carbonyl cluster compounds.[5] Thus, we decided to investigate the reactivity of I toward Me_3SnH. These results are reported here.

Experimental Section

General Remarks. Although these compounds were generally air stable; reactions and workups were routinely performed under a prepurified nitrogen atmosphere. Purification of heptane solvent involved stirring reagent grade heptane with concentrated sulfuric acid for 2 days and then shaking the heptane layer with anhydrous sodium carbonate. Other solvents were stored over 4-Å molecular sieves and degassed with a dispersed stream of nitrogen gas. The method of preparation of $Os_3(\mu_3\text{-}S)(\mu_3\text{-}SCH_2)(CO)_8(PMe_2Ph)$ has been previously reported.[7] Trimethyltin hydride was prepared according to the method of Birnbaum and Javora.[8] Alumina for chromatography was Baker acid-washed aluminum oxide deactivated with 6% water.

Melting points were determined in evacuated capillary tubes using a Thomas-Hoover apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 237B spectrophotometer calibrated with polystyrene, 1601.4 cm^{-1}. Fourier transform ^1H NMR spectra were obtained at 270 MHz on a Bruker HX270 instrument.

Reaction of $Os_3(\mu_3\text{-}S)(\mu_3\text{-}SCH_2)(CO)_8(PMe_2Ph)$ with Me_3SnH. Trimethyltin hydride (0.134 g, 0.811 mmol) was added to an oxygen-free solution of $Os_3(\mu_3\text{-}S)(\mu_3\text{-}SCH_2)(CO)_8(PMe_2Ph)$ (82 mg, 0.0811 mmol) in 50 mL of heptane solvent in a 100-mL 3-necked flask fitted with a water-cooled reflux condenser and a magnetic stir bar. The reaction was refluxed with stirring for 4 h after which time all volatile components were removed under vacuum. The remaining oily yellow residue was dissolved in a minimum amount of benzene and chromatographed on an alumina column. Three bands were eluted with hexane/benzene (3/1, v/v) solvent. The first band contained a mixture of products. The second band was $H_2Os(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{-}SCH_2)(CO)_7PMe_2Ph$ (III, 29

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0276-7333/82/2301-0460$01.25/0

Table I. Crystallographic Data for X-ray Diffraction Studies

	$Os_3SnS_2PO_8C_{20}H_{23}$ (II)	$Os_3S_2PO_7C_{16}H_{15}$ (III)
(A) Crystal Data		
temp, ±5 °C	23	23
space group	$P2_1/c$, No. 14	$P\bar{1}$, No. 2
a, Å	10.426 (2)	9.169 (3)
b, Å	11.421 (2)	11.157 (3)
c, Å	24.563 (4)	12.359 (4)
α, deg	90.0	70.50 (2)
β, deg	95.41 (2)	79.56 (3)
γ, deg	90.0	86.75 (3)
V, Å^3	2912 (2)	1172.0 (8)
mol wt	1175.8	985.0
Z	4	2
ρ_{calcd}, g/cm^3	2.68	2.79
(B) Measurement of Intensity Data		
radiation	Mo $K\bar{\alpha}$ (0.710 73 Å)	Mo $K\bar{\alpha}$ (0.710 73 Å)
monochromator	graphite	
detector aperture, mm		
horizontal ($A + B \tan\theta$)		
A	3.0	3.0
B	1.0	1.0
vertical	4.0	4.0
crystal faces	001, 00$\bar{1}$, 101 $\bar{1}0\bar{1}$, 010, 0$\bar{1}$0	010, 0$\bar{1}$0, 001, 00$\bar{1}$ 011, 0$\bar{1}\bar{1}$, 111, $\bar{1}\bar{1}\bar{1}$
crystal size:	0.05 × 0.22 × 0.37	0.13 × 0.14 × 0.18
crystal orientation: direction; deg from θ axis	b; 4.3	a^*; 11.9
reflctns measd	$h,k,\pm l$	$h,\pm k,\pm l$
max 2θ	50	52
scan type	moving crystal–stationary counter	
ω-scan width		
$A + 0.347 \tan\theta$	0.80	
background	one-fourth additional scan at each end of scan	
ω-scan rate (variable)		
max, deg/min	10.0	10.0
min, deg/min	1.25	1.25
no. of reflctns measd	5642	4556
data used ($F^2 \geq 3.0\sigma(F)^2$)	3333	3356
(C) Treatment of Data		
absorption correction		
coeff, cm^{-1}	149.6	175.2
grid	14 × 16 × 4	16 × 6 × 8
transmission coeff		
max	0.472	0.21
min	0.044	0.10
P factor	0.005	0.005
final residuals R	0.034	0.049
R_w	0.034	0.056
esd of unit wt	2.11	3.78
largest shift/error value on final cycle	0.03	0.07

mg, 36%) as a mixture of isomers. The third band consisted of small amounts of $HOs_3(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{-}SCH_2)(CO)_7(PMe_2Ph)SnMe_3$ (II <3% yield) and another uncharacterized product.

Both II and III were crystallized from cold hexane solvent (−20 °C) over a period of several days. Pertinent spectra of II and III are indicated below.

II, HOs_3 $(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{-}SCH_2)(CO)_7(PMe_2Ph)(SnMe_3)$: mp 150 °C dec; ^1H NMR ($CDCl_3$ at 298 K) δ 7.58 (m, Ph), 2.28 (d, $^2J_{H\text{-}P}$ = 10.1 Hz, Me), 2.27 (d, $^2J_{H\text{-}P}$ = 10.2 Hz, Me), 2.42 (d, ^2J = 11.0 Hz, SCH_2), 1.37 (ddd, ^2J = 11.0, J = 3.3, $J_{H\text{-}P}$ = 1.3 Hz, SCH_2), 0.43 ($^2J_{^{117,119}Sn\text{-}Me}$ = 50.0, 47.8 Hz, $SnMe_3$), −16.30 (dd, $J_{H\text{-}P}$ = 13.3, J = 3.3 Hz, OsH); IR (hexane, ν_{CO} ±5 cm^{-1}) 2091 (s), 2037 (s), 2000 (vs), 1939 (s).

III, $H_2Os_3(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{-}SCH_2)(CO)_7(PMe_2Ph)$. Isomer **a**: mp 115.5–116.0 °C; ^1H NMR ($CDCl_3$ at 298 K) δ 7.49 (m, Ph), 2.26 (d, $^2J_{H\text{-}P}$ = 7.7 Hz, Me), 2.21 (d, $^2J_{H\text{-}P}$ = 7.6 Hz, Me), 2.75 (d, $^2J_{H\text{-}H}$ = 11.8 Hz, SCH_2), 1.11 (dd, $^2J_{H\text{-}H}$ = 11.8, $^3J_{H\text{-}P}$ = 2.6 Hz, SCH_2), −14.95 (dd, $^2J_{H\text{-}P}$ = 29.4, $^2J_{H\text{-}H}$ = 12.7 Hz, OsH), −16.51 (dd, $^2J_{H\text{-}H}$ = 12.7, $^3J_{H\text{-}P}$ = 2.5 Hz, OsH); IR (hexane, ν_{CO} ±5 cm^{-1}) 2099 (s), 2044 (vs), 2005 (s), 1977 (vs). Isomer **b**: ^1H NMR δ 7.53 (m, Ph), 2.34 (d, $^2J_{H\text{-}P}$ = 9.8 Hz, Me), 2.29 (d, $^2J_{H\text{-}P}$ = 9.7 Hz, Me), 3.06 (dd, $^2J_{H\text{-}H}$ = 11.7, $^4J_{H\text{-}P}$ = 4.8 Hz, SCH_2), 1.77 (ddd, $^2J_{H\text{-}H}$ = 11.6, $^4J_{H\text{-}P}$ = 4.0, $^3J_{H\text{-}H}$ = 2.5 Hz, SCH_2), −15.45 (dd, $^2J_{H\text{-}H}$ = 11.6, $^2J_{H\text{-}P}$ = 7.7 Hz, OsH), −16.61 (dd, $^2J_{H\text{-}H}$ = 11.6, $^3J_{H\text{-}P}$ = 2.4 Hz, OsH). Isomer **c**: ^1H NMR δ 7.68 (m, Ph), 2.15 (d, ^2J = 9.7 Hz, Me), 2.09 (d, ^2J = 9.7 Hz, Me), 2.99 (dd, $^2J_{H\text{-}H}$ = 11.4, $J_{H\text{-}P}$ = 0.6 Hz, SCH_2), 1.63 (dd, $^2J_{H\text{-}H}$ = 11.5, $^3J_{H\text{-}P}$ = 2.4 Hz, SCH_2) −15.65 (dd, $^2J_{H\text{-}H}$ = 11.7, $^3J_{H\text{-}P}$ = 8.8 Hz, OsH), −16.71 (dd, $^2J_{H\text{-}H}$ = 11.7, $^3J_{H\text{-}P}$ = 2.5 Hz, OsH). IR equilibrium mixture of III: 2101 (s), 2043 (s), 2027 (vs), 2011 (s), 1978 (s), 1969 (s) cm^{-1}.

Crystallographic Analyses. Crystals of $HOs_3(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{-}SCH_2)(CO)_7(PMe_2Ph)SnMe_3$ (II) and $H_2Os_3(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{-}SCH_2)(CO)_7(PMe_2Ph)$ (III) suitable for diffraction measurements were obtained by slow crystallization from hexane solutions cooled to −20 °C. All crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on an Enraf-Nonius CAD-4 fully automated four-circle diffractometer using graphite-monochromatized Mo $K\bar{\alpha}$ radiation. Unit cells were determined and refined from 25 randomly selected reflections obtained by using the CAD-4 automatic search, center, index, and least-squares routines. The II the space group $P2_1/c$ was established from the systematic absences observed in the data. For III the space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. Crystal data and data collections parameters are listed in Table I. All data processing was performed on a Digital PDP 11/45 computer using the Enral-Nonius SDP program library (version 16). Absorption corrections of a Gaussian integration type were done for both

Table II. Final Fractional Atomic Coordinates, Thermal Parameters, and Their Esds for $HOs_3(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{-}SCH_2)(CO)_7(PMe_2Ph)SnMe_3$ (II)

atom	*x*	*y*	*z*	*B*(1,1)[b]	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)
Os(1)	0.82697 (4)	0.29918 (4)	0.04349 (2)	2.87 (2)	2.64 (2)	2.44 (2)	−0.16 (2)	−0.02 (2)	0.03 (2)
Os(2)	0.68553 (4)	0.25387 (5)	0.14016 (2)	3.02 (2)	4.12 (2)	2.82 (2)	−0.19 (2)	0.37 (2)	0.30 (2)
Os(3)	1.05877 (4)	0.33029 (5)	0.12018 (2)	2.77 (2)	3.56 (2)	2.74 (2)	−0.11 (2)	−0.12 (2)	0.02 (2)
Sn	1.16603 (8)	0.28459 (9)	0.22017 (4)	4.08 (4)	5.10 (5)	2.88 (4)	0.10 (4)	−0.26 (3)	0.07 (4)
S(1)	0.9515 (3)	0.1491 (3)	0.0974 (1)	3.4 (1)	3.0 (1)	3.6 (2)	0.3 (1)	0.1 (1)	0.5 (1)
S(2)	0.8500 (3)	0.4019 (3)	0.1326 (1)	3.1 (1)	3.9 (2)	2.8 (2)	−0.1 (1)	0.2 (1)	−0.5 (1)
P	0.7529 (3)	0.1663 (3)	−0.0254 (1)	3.9 (1)	3.0 (1)	3.0 (2)	−0.2 (1)	0.0 (1)	−0.4 (1)

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
O(1)	1.0454 (7)	0.3676 (8)	−0.0249 (4)	4.8 (2)	H(171)[a]	0.8887	0.1855	−0.0977	6.0
O(2)	0.6655 (8)	0.4999 (9)	−0.0077 (4)	6.0 (2)	H(172)[a]	0.9434	0.1113	−0.0566	6.0
O(3)	0.4962 (9)	0.0520 (10)	0.1292 (5)	6.5 (3)	H(181)[a]	0.6113	0.0000	−0.0137	6.0
O(4)	0.6894 (10)	0.2686 (11)	0.2629 (5)	8.7 (3)	H(221)[a]	1.0000	0.3691	0.2773	6.0
O(5)	0.4790 (8)	0.4477 (10)	0.1207 (5)	6.4 (2)	H(231)[a]	1.3320	0.4434	0.2910	6.0
O(6)	1.1639 (8)	0.5759 (9)	0.1321 (5)	6.1 (2)	H(173)[a]	0.8124	0.0909	−0.1051	6.0
O(7)	1.3018 (8)	0.2396 (8)	0.0793 (4)	5.4 (2)	H(182)[a]	0.7393	0.0133	0.0392	6.0
C(1)	0.9646 (11)	0.346 (1)	0.0045 (6)	4.3 (3)	H(183)[a]	0.7759	−0.0396	−0.0154	6.0
C(2)	0.7270 (10)	0.423 (1)	0.0117 (6)	3.9 (3)	H(222)[a]	1.0781	0.3036	0.3191	6.0
C(3)	0.5647 (11)	0.133 (1)	0.1348 (6)	4.7 (3)	H(223)[a]	0.9694	0.2451	0.2810	6.0
C(4)	0.6861 (12)	0.261 (1)	0.2164 (7)	5.6 (3)	H(232)[a]	1.3154	0.4706	0.2203	6.0
C(5)	0.5574 (11)	0.375 (1)	0.1273 (6)	4.1 (3)	H(233)[a]	1.4024	0.3656	0.2398	6.0
C(6)	1.1255 (11)	0.480 (1)	0.1272 (6)	4.5 (3)	H(211)[a]	1.2960	0.0895	0.2003	6.0
C(7)	1.2094 (10)	0.276 (1)	0.0956 (5)	3.6 (3)	H(212)[a]	1.2805	0.0910	0.2625	6.0
C(10)	0.8360 (11)	0.123 (1)	0.1479 (6)	4.1 (3)	H(213)[a]	1.1671	0.0503	0.2214	6.0
C(11)	0.6001 (9)	0.209 (1)	−0.0611 (5)	3.0 (2)	H(101)[a]	0.8792	0.1233	0.1841	6.0
C(12)	0.4909 (11)	0.213 (1)	−0.0332 (6)	4.1 (3)	H(102)[a]	0.7983	0.0452	0.1421	6.0
C(13)	0.3714 (12)	0.251 (1)	−0.0594 (6)	4.9 (3)	H(12)[a]	0.4966	0.1877	0.0053	6.0
C(14)	0.3639 (12)	0.283 (1)	−0.1121 (7)	5.6 (3)	H(13)[a]	0.2947	0.2518	−0.0397	6.0
C(15)	0.4698 (13)	0.279 (1)	−0.1408 (7)	6.0 (4)	H(14)[a]	0.2810	0.3132	−0.1287	6.0
C(16)	0.5864 (11)	0.243 (1)	−0.1153 (6)	4.8 (3)	H(15)[a]	0.4622	0.3018	−0.1799	6.0
C(17)	0.8602 (12)	0.138 (1)	−0.0775 (6)	5.4 (3)	H(16)[a]	0.6628	0.2415	−0.1356	6.0
C(18)	0.7220 (13)	0.019 (1)	−0.0005 (7)	5.6 (4)					
C(21)	1.2357 (16)	0.108 (2)	0.2263 (9)	8.6 (5)					
C(22)	1.0356 (16)	0.303 (2)	0.2820 (8)	8.2 (5)					
C(23)	1.3209 (13)	0.403 (1)	0.2445 (7)	6.1 (4)					

[a] Hydrogen atom positions were not refined. [b] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + B_{12}hka^*b^* + B_{13}hla^*c^* + B_{23}klb^*c^*)]$.

structures. Neutral atom scattering factors were calculated by the standard procedures.[9a] Anomalous dispersion corrections were applied to all nonhydrogen atoms.[9b] Full-matrix least-squares refinements minimized the function $\sum_{hkl}w(|F_o| - |F_c|)^2$ where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (PF_o^2)^2]^{1/2}/Lp$. The structure of II was solved by a combination of direct methods and difference Fourier techniques. The three osmium atoms and the tin atom were located in an electron density map based on the phasing (MULTAN) of 197 reflections ($E_{min} \geq 1.80$). All remaining nonhydrogen atoms were located in subsequent difference Fourier syntheses. Hydrogen atom positions were calculated by assuming idealized geometries and staggered threefold rotational conformations for the methyl groups. The hydride ligand was not found, and no attempt to calculate its position was made. All atoms heavier than oxygen were refined with anisotropic thermal parameters. The others were refined with isotropic thermal parameters only. The positions of the hydrogen atoms were not refined.

The structure of III was solved by a combination of Patterson and difference Fourier techniques. Hydrogen atom positions were calculated by assuming idealized geometry. The hydride ligands were not located and were ignored.

Fractional atomic coordinates, thermal parameters, and interatomic distances and angles with errors obtained from the inverse matrix calculated on the final cycle of least-squares refinement are listed in Tables II–VII.

Table III. Interatomic Distances with Esds for $HOs_3(\mu_3\text{-}S)(\mu_3\text{-}SCH_2)(CO)_7(PMe_2Ph)(SnMe_3)$ (II)

atoms	dist, Å	atoms	dist, Å
Os(1)–Os(2)	2.957 (1)	Sn–C(22)	2.143 (13)
Os(1)–Os(3)	2.942 (1)	Sn–C(23)	2.144 (10)
Os(2)···Os(3)	4.063 (1)	S(1)–C(10)	1.833 (9)
Os(1)–S(1)	2.461 (2)	P–C(11)	1.813 (8)
Os(1)–S(2)	2.475 (2)	P–C(17)	1.807 (10)
Os(1)–P	2.349 (2)	P–C(18)	1.833 (11)
Os(1)–C(1)	1.876 (9)	C(11)–C(16)	1.38 (1)
Os(1)–C(2)	1.880 (9)	C(11)–C(12)	1.38 (1)
Os(2)–S(2)	2.428 (2)	C(12)–C(13)	1.42 (1)
Os(2)–C(3)	1.865 (10)	C(13)–C(14)	1.34 (1)
Os(2)–C(4)	1.874 (13)	C(14)–C(15)	1.37 (1)
Os(2)–C(5)	1.931 (9)	C(15)–C(16)	1.38 (1)
Os(2)–C(10)	2.166 (9)	C(1)–O(1)	1.19 (1)
Os(3)–Sn	2.653 (1)	C(2)–O(2)	1.17 (1)
Os(3)–S(1)	2.393 (2)	C(3)–O(3)	1.17 (1)
Os(3)–S(2)	2.372 (2)	C(4)–O(4)	1.14 (1)
Os(3)–C(6)	1.850 (10)	C(5)–O(5)	1.16 (1)
Os(3)–C(7)	1.840 (8)	C(6)–O(6)	1.17 (1)
Sn(1)–C(21)	2.148 (14)	C(7)–O(7)	1.16 (1)
		Os(3)···C(1)	2.92 (1)

Results

Two products, identified as $HOs_3(\mu_3\text{-}S)(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{-}SCH_2)(CO)_7(PMe_2Ph)(SnMe_3)$ (II) and $H_2Os_3(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{-}SCH_2)(CO)_7(PMe_2Ph)$ (III) on the basis of IR and ^1H NMR spectra and X-ray crystallographic analyses, have been isolated from the reaction of Me_3SnH with $Os_3(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{-}SCH_2)(CO)_8(PMe_2Ph)$ (I) in refluxing heptane solvent.

$HOs_3(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{-}SCH_2)(CO)_7(PMe_2Ph)(SnMe_3)$ (II). The molecular structure of II is shown in Figure 1. The molecule consists of an "open" cluster of three osmium atoms with only two metal–metal bonds, Os(1)–Os(2) = 2.957 (1) Å and Os(1)–Os(3) = 2.942 (1) Å. There is a triply

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(9) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1975; Vol. IV: (a) Table 2.2B, pp 99–100; (b) Table 2.3.1, pp 149–150.

Table IV. Interatomic Angles with Esds for $HOs_3(\mu_3\text{-}S)(\mu_3\text{-}SCH_2)(CO)_7(SnMe_3)(PMe_2Ph)$ (II)

atoms	angle, deg	atoms	angle, deg	atoms	angle, deg
Os(2)-Os(1)-Os(3)	87.06 (1)	S(2)-Os(2)-C(10)	88.8 (2)	Os(1)-S(1)-Os(3)	74.62 (7)
Os(2)-Os(1)-S(1)	73.94 (5)	C(3)-Os(2)-C(4)	92.4 (5)	Os(1)-S(1)-C(10)	97.6 (3)
Os(2)-Os(1)-S(2)	52.18 (5)	C(3)-Os(2)-C(5)	93.9 (4)	Os(3)-S(1)-C(10)	107.9 (3)
Os(2)-Os(1)-P	108.10 (6)	C(3)-Os(2)-C(10)	88.4 (4)	Os(1)-S(2)-Os(2)	74.17 (6)
Os(2)-Os(1)-C(1)	157.4 (3)	C(4)-Os(2)-C(5)	94.0 (4)	Os(1)-S(2)-Os(3)	74.71 (6)
Os(2)-Os(1)-C(2)	99.6 (3)	C(4)-Os(2)-C(10)	90.4 (4)	Os(2)-S(2)-Os(3)	115.7 (1)
Os(3)-Os(1)-S(1)	51.64 (5)	C(5)-Os(2)-C(10)	174.9 (4)	Os(2)-C(10)-S(1)	110.0 (5)
Os(3)-Os(1)-S(2)	51.05 (5)	Os(1)-Os(3)-Sn	144.89 (2)	Os(1)-P-C(11)	112.8 (3)
Os(3)-Os(1)-P	137.20 (6)	Os(1)-Os(3)-S(1)	53.74 (5)	Os(1)-P-C(17)	116.3 (3)
Os(3)-Os(1)-C(1)	70.8 (3)	Os(1)-Os(3)-S(2)	54.24 (6)	Os(1)-P-C(18)	114.2 (4)
Os(3)-Os(1)-C(2)	124.4 (3)	Os(1)-Os(3)-C(6)	116.8 (3)	C(11)-P-C(17)	106.3 (5)
S(1)-Os(1)-S(2)	81.47 (8)	Os(1)-Os(3)-C(7)	115.1 (3)	C(11)-P-C(18)	103.8 (4)
S(1)-Os(1)-P	93.38 (8)	Sn-Os(3)-S(1)	101.12 (6)	C(17)-P-C(18)	102.3 (5)
S(1)-Os(1)-C(1)	94.7 (3)	Sn-Os(3)-S(2)	105.10 (6)	P-C(11)-C(12)	119.7 (7)
S(1)-Os(1)-C(2)	172.0 (3)	Sn-Os(3)-C(6)	88.5 (3)	P-C(11)-C(16)	123.3 (5)
S(2)-Os(1)-P	160.28 (8)	Sn-Os(3)-C(7)	86.5 (3)	C(12)-C(11)-C(16)	117 (1)
S(2)-Os(1)-C(1)	107.6 (3)	S(1)-Os(3)-S(2)	85.06 (7)	C(11)-C(12)-C(13)	121 (1)
S(2)-Os(1)-C(2)	90.9 (3)	S(1)-Os(3)-C(6)	170.2 (3)	C(12)-C(13)-C(14)	119 (1)
P-Os(1)-C(1)	91.8 (3)	S(1)-Os(3)-C(7)	91.6 (3)	C(13)-C(14)-C(15)	121 (1)
P-Os(1)-C(2)	93.1 (3)	S(2)-Os(3)-C(6)	90.6 (3)	C(14)-C(15)-C(16)	120 (1)
C(1)-Os(1)-C(2)	89.8 (4)	S(2)-Os(3)-C(7)	168.3 (3)	C(15)-C(16)-C(11)	122 (1)
Os(1)-Os(2)-S(2)	53.65 (6)	C(6)-Os(3)-C(7)	90.9 (4)	Os(1)-C(1)-O(1)	172.5 (8)
Os(1)-Os(2)-C(3)	117.2 (3)	Os(3)-Sn-C(21)	111.1 (4)	Os(1)-C(2)-O(2)	179.5 (6)
Os(1)-Os(2)-C(4)	147.2 (3)	Os(3)-Sn-C(22)	113.4 (4)	Os(2)-C(3)-O(3)	174.5 (9)
Os(1)-Os(2)-C(5)	97.6 (3)	Os(3)-Sn-C(23)	112.0 (3)	Os(2)-C(4)-O(4)	178.0 (10)
Os(1)-Os(2)-C(10)	77.3 (3)	C(21)-Sn-C(22)	106.1 (5)	Os(2)-C(5)-O(5)	178.3 (9)
S(2)-Os(2)-C(3)	170.8 (3)	C(21)-Sn-C(23)	109.3 (4)	Os(3)-C(6)-O(6)	177.9 (8)
S(2)-Os(2)-C(4)	96.4 (3)	C(22)-Sn-C(23)	104.6 (5)	Os(3)-C(7)-O(7)	177.8 (7)
S(2)-Os(2)-C(5)	88.3 (3)				

Table V. Final Fractional Atomic Coordinates and Thermal Parameters and Their Estimated Standard Deviations for $H_2Os_3(\mu_3\text{-}S)(\mu_3\text{-}SCH_2)(CO)_7PMe_2Ph$ (III)

atom	*x*	*y*	*z*	*B*(1,1)[b]	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)
Os(1)	0.10791 (7)	0.68100 (7)	0.16254 (6)	2.54 (3)	2.72 (3)	3.53 (2)	0.39 (2)	−0.80 (2)	−0.89 (2)
Os(2)	0.34722 (8)	0.66494 (7)	0.29161 (5)	2.59 (3)	3.05 (3)	3.06 (2)	0.14 (2)	−0.63 (2)	−0.90 (2)
Os(3)	0.16063 (7)	0.43197 (6)	0.15613 (5)	2.56 (3)	2.75 (3)	2.68 (2)	0.10 (2)	−0.23 (2)	−0.83 (2)
S(1)	0.0630 (5)	0.4866 (4)	0.3281 (3)	2.9 (2)	3.3 (2)	3.0 (2)	−0.2 (2)	0.3 (1)	−0.9 (1)
S(2)	0.3516 (5)	0.5863 (4)	0.1296 (3)	2.5 (2)	3.4 (2)	2.5 (1)	0.2 (2)	−0.1 (1)	−0.6 (1)
P	0.2917 (6)	0.2484 (5)	0.2334 (4)	3.9 (2)	3.0 (2)	3.4 (2)	0.6 (2)	0.1 (2)	−0.7 (2)

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
O(1)	0.178 (2)	0.908 (2)	−0.057 (1)	7.6 (4)	C(14)	0.192 (3)	0.064 (2)	0.632 (2)	6.1 (5)
O(2)	−0.207 (2)	0.767 (2)	0.212 (1)	7.3 (4)	C(15)	0.337 (3)	0.086 (2)	0.573 (2)	6.1 (5)
O(3)	0.524 (2)	0.899 (1)	0.112 (1)	6.4 (4)	C(16)	0.371 (2)	0.138 (2)	0.453 (2)	4.9 (4)
O(4)	0.284 (2)	0.772 (2)	0.491 (1)	7.1 (4)	C(17)	0.491 (3)	0.263 (2)	0.191 (2)	5.8 (5)
O(5)	0.618 (2)	0.512 (1)	0.372 (1)	5.9 (3)	C(18)	0.258 (3)	0.117 (2)	0.185 (2)	6.0 (5)
O(6)	−0.122 (2)	0.283 (1)	0.190 (1)	5.9 (3)	H(12)[a]	0.0292	0.1802	0.4072	6.0
O(7)	0.273 (1)	0.428 (1)	−0.089 (1)	4.8 (3)	H(13)[a]	−0.0227	0.0900	0.6117	6.0
C(1)	0.150 (2)	0.821 (2)	0.028 (2)	4.5 (4)	H(14)[a]	0.1697	0.0214	0.7161	6.0
C(2)	−0.087 (2)	0.735 (2)	0.194 (2)	4.6 (4)	H(15)[a]	0.4168	0.0634	0.6200	6.0
C(3)	0.457 (2)	0.811 (2)	0.177 (1)	4.3 (4)	H(16)[a]	0.4737	0.1480	0.4134	6.0
C(4)	0.309 (2)	0.730 (2)	0.413 (2)	4.3 (4)	H(81)[a]	0.2730	0.4257	0.4165	6.0
C(5)	0.519 (2)	0.577 (2)	0.343 (1)	3.8 (4)	H(82)[a]	0.1737	0.5113	0.4758	6.0
C(6)	−0.013 (2)	0.337 (2)	0.176 (1)	3.7 (4)	H(171)[a]	0.5273	0.3047	0.2207	6.0
C(7)	0.231 (2)	0.429 (2)	0.004 (1)	3.3 (3)	H(172)[a]	0.5273	0.2773	0.0820	6.0
C(8)	0.213 (2)	0.503 (2)	0.402 (1)	3.3 (3)	H(173)[a]	0.5504	0.1903	0.2264	6.0
C(11)	0.254 (2)	0.178 (2)	0.390 (1)	3.4 (3)	H(181)[a]	0.1660	0.1094	0.1934	6.0
C(12)	0.112 (2)	0.157 (2)	0.451 (2)	4.6 (4)	H(182)[a]	0.2943	0.0385	0.2311	6.0
C(13)	0.080 (2)	0.102 (2)	0.572 (2)	5.9 (5)	H(183)[a]	0.2973	0.1320	0.1054	6.0

[a] Hydrogen atom positions were not refined. [b] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + B_{12}hka^*b^* + B_{13}hla^*c^* + B_{23}klb^*c^*)]$.

bridging η^2-thioformaldehyde ligand in which the sulfur atom bridges the Os(1)–Os(3) bond and the carbon atom is coordinated solely to Os(2), Os(2)–C(10) = 2.166 (9) Å. The carbon–sulfur distance, S(1)–C(10), at 1.833 (9) Å is similar to that found in I, 1.869 (6) Å,[8] $Os_3(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{-}SCH_2)(CO)_7(PMe_2Ph)P(OMe)_3$ (IV), 1.837 (7) Å,[4] and $HOs_3(\mu_3\text{-}S)(\mu_3\text{-}SCH_2)(CO)_8(PMe_2Ph)Cl$ (V), 1.872 (12) Å,[4] and is indicative of a carbon–sulfur single bond. The hydrogen atoms on C(10) were not observed crystallographically but were confirmed by a characteristic AB quartet resonance pattern (δ_A 1.37, δ_B 2.42 (J_{AB} = 11.0 Hz)) in its ^{1}H NMR spectrum. There is also a triply bridging sulfide ligand, S(2). The ^{1}H NMR spectrum shows a resonance δ −16.30 indicative of a bridging hydride ligand. This was not detected crystallographically, but there is a large cavity along the Os(1)–Os(2) bond which is circumscribed by the phosphine ligand and the three carbonyls C(2)–O(2), C(3)–O(3), and C(5)–O(5) which could signify its location. A trimethylstannyl group is coordinated to atom Os(3)–Sn = 2.653 (1) Å, and as far as we can ascertain, this is the first crystallographic characterization of an osmium–tin bonding distance.[10] Unlike I the di-

Table VI. Interatomic Distances with Esds for $H_2Os_3(\mu_3\text{-}S)(\mu_3\text{-}SCH_2)(CO)_7PMe_2Ph$ (III)

atoms	dist, Å	atoms	dist, Å
Os(1)-Os(2)	2.903 (1)	S(1)-C(8)	1.828 (8)
Os(1)-Os(3)	2.818 (1)	P-C(11)	1.807 (9)
Os(2)···Os(3)	4.115 (1)	P-C(17)	1.81 (1)
Os(1)-S(1)	2.428 (2)	P-C(18)	1.82 (1)
Os(1)-S(2)	2.442 (2)	C(11)-C(12)	1.37 (1)
Os(1)-C(1)	1.86 (1)	C(12)-C(13)	1.40 (1)
Os(1)-C(2)	1.87 (1)	C(13)-C(14)	1.34 (2)
Os(2)-S(2)	2.432 (2)	C(14)-C(15)	1.38 (2)
Os(2)-C(3)	1.95 (1)	C(15)-C(16)	1.38 (1)
Os(2)-C(4)	1.85 (1)	C(16)-C(11)	1.41 (1)
Os(2)-C(5)	1.90 (1)	C(1)-O(1)	1.16 (1)
Os(2)-C(8)	2.155 (9)	C(2)-O(2)	1.14 (1)
Os(3)-S(1)	2.409 (2)	C(3)-O(3)	1.16 (1)
Os(3)-S(2)	2.428 (2)	C(4)-O(4)	1.19 (1)
Os(3)-P	2.320 (3)	C(5)-O(5)	1.16 (1)
Os(3)-C(6)	1.90 (1)	C(6)-O(6)	1.16 (1)
Os(3)-C(7)	1.88 (1)	C(7)-O(7)	1.15 (1)

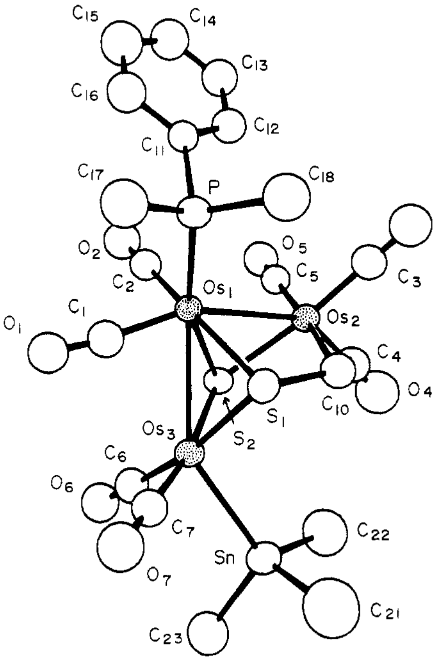

Figure 1. A perspective ORTEP diagram of $HOs_3(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{-}SCH_2)(CO)_7(PMe_2Ph)SnMe_3$ (II) showing 50% electron density probability ellipsoids.

methylphenylphosphine ligand is coordinated to the interior osmium atom of the cluster. The mechanistic implications of this result are discussed below. There are seven carbonyl ligands. Six of these are clearly linear terminal ligands; however, C(1)-O(1), which is principally bonded to Os(1), is also leaning significantly toward Os(3). The Os(3)-Os(1)-C(1) angle is acute at 70.8 (3)° and the Os(3)$\cdots$C(1) internuclear separation is 2.92 (1) Å. This ligand may be involved in a slight semibridging interaction to Os(3). The Os(1)-C(1)-O(1) angle at 172.5 (8)° is the most nonlinear of the seven carbonyl ligands. The shortest intermolecular contact was between carbonyl oxygen atoms O(2)$\cdots$O(5) at 3.09 (1) Å.

$H_2Os_3(\mu_3\text{-}\eta^2\text{-}SCH_2)(CO)_7(PMe_2Ph)$ (III). The molecular structure of III is shown in Figure 2. This molecule also contains an open cluster of three osmium atoms with two metal-metal bonds, Os(1)-Os(2) = 2.903 (1) Å and Os(1)-Os(3) = 2.818 (1) Å. The Os(2)$\cdots$Os(3) distance at 4.115 (1) Å is clearly nonbonding. There is a triply bridging thioformaldehyde ligand, C(8)-S(1), with the sulfur atom bridging the Os(1)-Os(3) bond and the carbon atom coordinated to Os(2). As in I,[8] II, IV,[4] and V,[4] the C(8)-S(1) distance of 1.828 (9) Å is indicative of a carbon-sulfur single bond. The two hydrogen atoms of C(8) were not observed crystallographically but were identified by a characteristic AB quartet resonance pattern (δ_A 1.11, δ_B 2.75 ($^2J_{AB}$ = 11.8 Hz)) in the ^1H NMR spectrum. The molecule also contains a triply bridging sulfide ligand, S(2), and two bridging hydride ligands, presumably one on each metal-metal bond. The hydride ligands were not observed crystallographically but were confirmed in the ^1H NMR spectrum (δ -14.95 and -16.51 (J = 12.7 Hz)). As in I the dimethylphenylphosphine ligand is coordinated to the exterior osmium atom of the cluster which is also coordinated to the two sulfur atoms. There are seven linear terminal carbonyl groups arranged such that Os(1) and Os(3) have two each and Os(2) has three. The shortest intermolecular contact is between the carbonyl oxygen atoms O(2)$\cdots$O(3) at 3.05 (1) Å. III is structurally very similar to I but differs in that one carbonyl ligand on the interior osmium atom of the cluster has been replaced with two hydride ligands which bridge the metal-metal bonds.

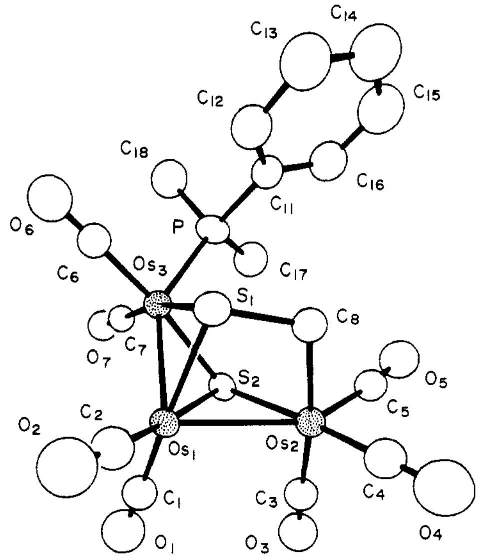

Figure 2. A perspective ORTEP diagram of $H_2Os_3(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{-}SCH_2)(CO)_7(PMe_2Ph)$ (III) showing 50% electron density probability ellipsoids.

A molecule which is structurally very similar to III is $H_2Os_3(\mu_3\text{-}S)_2(CO)_7CS$.[11] It has two triply bridging sulfide ligands, one on either side of an "open" cluster of three osmium atoms, one hydride ligand bridging each of metal-metal bonds, and only two carbonyl ligands on the interior osmium atom.

In solution III exists as a mixture of three isomers. IIIa is the isomer found in the solid state. All isomers exhibit the same general ^1H NMR spectral pattern (see ^1H NMR data in Experimental Section). At equilibrium, the distribution of isomers is (**a**/**b**/**c**, 15%/62%/23%). The half-life for the disappearance of isomer IIIa is approximately 70 min at 298 K.

Discussion

Stoichiometrically, the formation of II requires the loss

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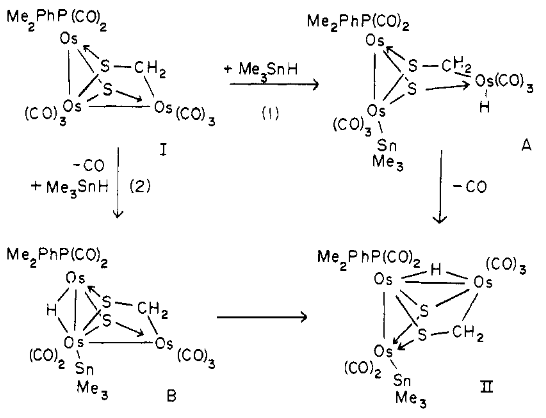
(11) Broadhurst, P. V.; Johnson, B. F. G.; Lewis, J.; Orpen, A. G.; Raithby, P. R.; Thornback, J. R. *J. Organomet. Chem.* **1980**, *187*, 141.

Table VII. Interatomic Angles with Esds for $H_2Os_3(\mu_3\text{-}S)(\mu_3\text{-}SCH_2)(CO)_7PMe_2Ph$ (III)

atoms	angle, deg	atoms	angle, deg	atoms	angle, deg
Os(2)-Os(1)-Os(3)	92.00 (1)	C(3)-Os(2)-C(5)	94.7 (4)	Os(2)-S(2)-Os(3)	115.69 (8)
Os(2)-Os(1)-S(1)	74.35 (6)	C(3)-Os(2)-C(8)	173.3 (4)	Os(3)-P-C(11)	115.8 (3)
Os(2)-Os(1)-S(2)	53.31 (5)	C(4)-Os(2)-C(5)	93.1 (4)	Os(3)-P-C(17)	115.1 (4)
Os(2)-Os(1)-C(1)	106.3 (3)	C(4)-Os(2)-C(8)	89.7 (4)	Os(3)-P-C(18)	114.7 (4)
Os(2)-Os(1)-C(2)	128.6 (3)	C(5)-Os(2)-C(8)	89.6 (4)	C(11)-P-C(17)	106.8 (5)
Os(3)-Os(1)-S(1)	54.06 (6)	Os(1)-Os(3)-S(1)	54.67 (6)	C(11)-P-C(18)	102.4 (5)
Os(3)-Os(1)-S(2)	54.42 (6)	Os(1)-Os(3)-S(2)	54.88 (5)	C(17)-P-C(18)	100.3 (6)
Os(3)-Os(1)-C(1)	120.7 (3)	Os(1)-Os(3)-P	142.48 (7)	Os(2)-C(8)-S(1)	108.7 (4)
Os(3)-Os(1)-C(2)	119.4 (3)	Os(1)-Os(3)-C(6)	114.5 (3)	C(11)-C(12)-C(13)	123 (1)
S(1)-Os(1)-S(2)	83.02 (7)	Os(1)-Os(3)-C(7)	112.3 (3)	C(12)-C(13)-C(14)	119 (1)
S(1)-Os(1)-C(1)	174.7 (3)	S(1)-Os(3)-S(2)	83.69 (8)	C(13)-C(14)-C(15)	120 (1)
S(1)-Os(1)-C(2)	91.7 (3)	S(1)-Os(3)-P	101.35 (8)	C(14)-C(15)-C(16)	122 (1)
S(2)-Os(1)-C(1)	93.2 (3)	S(1)-Os(3)-C(6)	90.7 (3)	C(15)-C(16)-C(11)	119 (1)
S(2)-Os(1)-C(2)	173.6 (3)	S(1)-Os(3)-C(7)	166.9 (3)	C(16)-C(11)-C(12)	118 (1)
C(1)-Os(1)-C(2)	91.9 (5)	S(2)-Os(3)-P	98.33 (9)	P-C(11)-C(12)	121.7 (7)
Os(1)-Os(2)-S(2)	53.60 (5)	S(2)-Os(3)-C(6)	169.3 (3)	P-C(11)-C(16)	120.5 (7)
Os(1)-Os(2)-C(3)	95.5 (3)	S(2)-Os(3)-C(7)	89.5 (3)	Os(1)-C(1)-O(1)	179.7 (7)
Os(1)-Os(2)-C(4)	116.4 (3)	P-Os(3)-C(6)	91.7 (3)	Os(1)-C(2)-O(2)	179 (1)
Os(1)-Os(2)-C(5)	147.2 (3)	P-Os(3)-C(7)	90.7 (3)	Os(2)-C(3)-O(3)	178.4 (9)
Os(1)-Os(2)-C(8)	78.2 (2)	C(6)-Os(3)-C(7)	94.2 (2)	Os(2)-C(4)-O(4)	179.5 (8)
S(2)-Os(2)-C(3)	85.9 (3)	Os(1)-S(1)-Os(3)	71.26 (6)	Os(2)-C(5)-O(5)	173.2 (9)
S(2)-Os(2)-C(4)	169.9 (3)	Os(1)-S(1)-C(8)	98.3 (3)	Os(3)-C(6)-O(6)	177.2 (9)
S(2)-Os(2)-C(5)	96.3 (3)	Os(3)-S(1)-C(8)	110.6 (3)	Os(3)-C(7)-O(7)	179.5 (7)
S(2)-Os(2)-C(8)	88.5 (2)	Os(1)-S(2)-Os(2)	73.09 (6)		
C(3)-Os(2)-C(4)	97.1 (4)	Os(1)-S(2)-Os(3)	70.70 (6)		

Scheme I



of 1 mol of carbon monoxide from I and the addition of 1 mol of Me_3SnH. However, a more subtle result is the repositioning of the phosphine ligand from an exterior osmium atom of the cluster in I to the interior osmium atom in II.

A simple rearrangement could be dissociation of the phosphine from the exterior osmium atom and reattachment at the interior one, but if this were occurring, one would also expect that in the presence of uncoordinated donor ligands, phosphine ligand substitution would be an important reaction. However, we believe that this can be ruled out since we have shown that the reaction of I with trimethyl phosphite yields CO substitution, and no products of replacement of the dimethylphenylphosphine ligand were observed.[4]

Scheme I shows two other possible routes to II. By route 1 the Me_3SnH molecule oxidatively cleaves one osmium–osmium bond to give an intermediate like A which might be very similar to the known molecule V. Decarbonylation and formation of a new osmium–osmium bond between the former exterior osmium atoms of the cluster in I could lead to II.

By route 2 we envisage a dissociation of a carbonyl ligand from the interior osmium atom in I. Oxidative addition of Me_3SnH to that metal atom could produce an intermediate like B which subsequently undergoes a relocation of the metal–metal bond to give II. At present we have no evidence which distinguishes between them, but we favor route 1 because of mitigating evidence concerning route 2. If carbon monoxide were being dissociated readily from the interior osmium atom, one might expect that in the presence of uncoordinated donor ligands CO substitution at the interior osmium atom would occur. However, we have shown,[4] as mentioned earlier, that although the reaction of trimethyl phosphite with I does lead to CO substitution, the substitution occurs at the exterior phosphine-substituted osmium atom, although admittedly this does not prove that CO loss originated at the metal atom. It is well-known that trialkyltin hydrides react characterisically via radical chain processes.[12] Mechanistically, it is probable that the intermediates proposed in Scheme I are formed via radical processes, probably, via additional and even more elusive intermediates.

At present we have no attractive mechanisms to explain the formation of III and do not wish to advance speculation at this time.

As mentioned earlier the general features of the ^1H NMR spectra of the isomers of III are similar. However, in the splitting patterns there is a striking difference between the hydride–phosphorus coupling in these isomers. In isomer IIIa the phosphorus coupling to the δ −14.95 hydride (J = 29.4 Hz) is more than twice that observed for the corresponding coupling in either isomer **b** or **c**. This could be attributed to differences in stereochemistry about Os(3). In IIIa the phosphine and one hydride should be approximately trans to one another about Os(3). Two other isomers would be formed by placing the phosphine ligand in sites cis to the bridging hydride ligand. It is well-known that trans-hydride–phosphorus couplings are much larger than cis couplings.[13]

Acknowledgment. This work was supported by the National Science Foundation under Grant CHE-8019041 and the Alfred P. Sloan Foundation through a fellowship to R.D.A. We wish to thank Engelhard Industries for a loan of osmium tetroxide and Dr. B. F. G. Johnson,

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University Chem. Labs, Cambridge, for converting it into $Os_3(CO)_{12}$ for us. NMR studies were supported by Grant No. CHE-7916210 from the National Science Foundation. We wish to thank the reviewers for their thoughtful comments.

Registry No. I, 71903-66-7; II, 79953-70-1; III, 79953-71-2; Me_3SnH, 1631-73-8.

Supplementary Material Available: Listings of structure factor amplitudes for both crystallographic analyses (30 pages). Ordering information is given on any current masthead page.

Absolute Rate Constants for the Reactions of *tert*-Butoxyl Radicals and Some Ketone Triplets with Silanes[1]

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Received September 22, 1981

Absolute rate constants for the reactions of *tert*-butoxyl radicals and some ketone triplets with a variety of silanes have been measured by a laser flash technique. At 300 K rate constants, k_a, for H atom abstraction by *tert*-butoxyl from, e.g., Et_3SiH, $n\text{-}C_5H_{11}SiH_3$, $C_6H_5SiH_3$, and Cl_3SiH are 5.7, 10.6, 7.5, and $\sim 40 \times 10^6$ M^{-1} s^{-1}, respectively, and for quenching the benzophenone triplet, 9.6, 8.8, 5.0, and $\sim 7.6 \times 10^6$ M^{-1} s^{-1}, respectively, the principal reaction in all these cases being abstraction of an H atom bound to silicon. With $(EtO)_3SiH$, however, *tert*-butoxyl abstracts hydrogen, $k_a = 2.0 \times 10^6$ M^{-1} s^{-1}, from the methylene positions rather than from the silicon. The effect (or lack of it) produced by neighboring phenyl, alkoxy, and chlorine substituents on the ease of formation of silyl radicals is discussed in relation to formation of the analogous carbon-centered radicals. Additional kinetic data are presented together with the UV absorption spectra of some silicon-centered radicals.

Silanes which contain silicon–hydrogen bonds are known to react with a variety of free-radicals to form silyl radicals.[3,4] Although these are important intermediates in many chemical reactions, absolute rate data regarding their formation from silanes are extremely limited.[5,6] Utilizing the techniques of kinetic EPR spectroscopy and laser flash photolysis, we have recently embarked upon a research program which will provide a reliable body of quantitative kinetic data for many of the important reactions of group 4 centered organometallic radicals in solution.[7,8] For such studies, the preferred method for generating the organometallic radical is hydrogen atom abstraction from an appropriate precursor in a very fast (essentially "instantaneous") photoinitiated process. The preferred hydrogen atom abstracting agents will be *tert*-butoxyl radicals or ketone triplets. Although the *tert*-butoxyl/silane reaction has been very extensively used for silyl radical generation,[9] only for triethylsilane has a rate constant been measured (6×10^6 M^{-1} s^{-1} at 300 K, as reported in our preliminary communication).[7] For ketone triplets the literature contains one report indicating that the reaction does take place when ketone/organosilane systems are examined by EPR spectroscopy,[10] plus a gas-phase study of the acetone/SiH_4 system.[11] In addition, a semiempirical calculation based on the bond energy bond order (BEBO) method predicted that the photoreduction of benzophenone triplets by trimethylsilane should occur with a rate constant of 3×10^6 M^{-1} s^{-1} at 298 K and an activation energy of 3.05 kcal/mol.[12]

Experimental Section

Materials. All the reagents and solvents used in this work were commercial materials which were purified by standard methods before use.

Procedure. The experiments were carried out under oxygen-free conditions using the pulses (337.1 nm, ~8 ns, up to 10 mJ) from a Molectron UV 24 nitrogen laser for excitation. The experimental system has been interfaced with a PDP-11/03L computer that controls the experiment and provides suitable data gathering, storage, and hardcopy facilities. Complete details have been given elsewhere.[13]

Results

Reactions with *tert*-Butoxyl Radicals. The rates of reaction of *tert*-butoxyl radicals with various silanes were measured by using the technique described previously,[14]

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[1] Issued as N.R.C.C. No. 19985.

[2] N.R.C.C. Research Associate, 1979–1981.

[3] For a concise general review, see: Sakurai, H. *Free Radicals* **1973**, *2*, 741–808.

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