According to the skeletal electron pair theory, $Os(CO)_3$ groups donate two electrons for cluster bonding, and $Os(CO)_2$ groups donate zero.[25] With the assumption that the sulfido ligand serves as a four-electron donor, compound II has 14 electrons or seven electron pairs for cluster bonding. Seven electron pairs will provide a filled set of bonding orbitals for a polyhedron with six vertices, the octahedron. Accordingly the five metal atoms Os(1), Os(2), Os(4), Os(6), Os(7) and the sulfido ligand adopt the shape of an octahedron.

The mechanism of the formation of II from I plus III is difficult to predict. Overall, there is a loss of five ligands, two of acetonitrile and three carbonyls, and an increase by five in the number of metal–metal bonds. The sulfido ligand actually serves as a four electron donor both in I and II. The initial link between I and III is probably via formation of a coordinate bond between the sulfido ligand in I and a metal atom in III upon displacement of one of the acetonitrile molecules. Cluster coupling via the formation of sulfur–metal donor bonds has been observed previously[11,12] and most notably in the formation of the cyclotrimer $[(\mu\text{-}H)_2Ru_3(CO)_8(\mu_4\text{-}S)]_3$.[14] One of the sulfido-bridged metal–metal bonds in I is then opened, and the sulfur-coordinated osmium atom in III enters into metal–metal bonding with I. It is not now possible to predict the sequence of the remaining steps which leads to II.

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Registry No. I, 82080-90-8; II, 85442-80-4; III, 61817-93-4; $H_2OS_3(CO)_9(M_3\text{-}S)$, 38979-82-7; $HOS_3(CO)_{10}(OMe)$, 21559-15-9.

Supplementary Material Available: Tables of structure factor amplitudes for each structure (19 pages). Ordering information is given on any current masthead page.

Cleavage of Carbon–Sulfur Bonds in Thiolato Ligands in Osmium Carbonyl Cluster Compounds. The Synthesis and Structural Characterization of $H_2Os_6(CO)_{18}(\mu_4\text{-}S)(\mu_3\text{-}S)$ and Two Isomers of $H_2Os_6(CO)_{17}(\mu_4\text{-}S)(\mu_3\text{-}S)$

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Thermal degradation of $HOs_3(CO)_{10}(\mu\text{-}SCH_2C_6H_5)$, I, at 150 °C leads to cleavage of the carbon–sulfur bond in the phenylmethanethiolato ligand by two competing processes. By one process the cleavage is followed by the elimination of toluene and the formation of the sulfidoosmium carbonyl clusters $Os_3(CO)_9(\mu_3\text{-}S)_2$, $Os_6(CO)_{16}(\mu_4\text{-}S)(\mu_3\text{-}S)$, and $Os_7(CO)_{20}(\mu_4\text{-}S)_2$. The second mechanism involves homolysis of the carbon–sulfur bond and formation of dibenzyl, the red hydride-containing hexanuclear cluster $H_2Os_6(CO)_{17}(\mu_4\text{-}S)(\mu_3\text{-}S)$, III, and its green isomer IV. Both III and IV were characterized by X-ray crystallographic methods. For III: space group $C2/c$, $a = 20.364$ (5) Å, $b = 9.764$ (4) Å, $c = 32.544$ (7) Å, $\beta = 114.01$ (2)°, $V = 5900$ (6) Å^3, $Z = 8$, $\rho_{calcd} = 3.79$ g/cm^3. The structure was solved by direct methods (MULTAN) and refined (2456 reflections, $F^2 \geq 3.0\sigma(F^2)$) to the final values of the residuals $R_F = 0.037$ and $R_{wF} = 0.034$. III contains two triosmium groupings linked by a quadruply bridging sulfido ligand and two metal–metal bonds. The quadruply bridging sulfido ligand has a highly distorted tetrahedral geometry with Os–S–Os bond angles ranging from 72.5 (1)° to 149.4 (2)°. III also contains a triply bridging sulfido ligand, two bridging hydride ligands, and 17 linear terminal carbonyl ligands. For IV: space group $P2_1/n$, $a = 11.124$ (3) Å, $b = 14.090$ (5) Å, $c = 18.694$ (7) Å, $b = 92.00$ (3)°, $V = 2928$ (3) Å^3, $Z = 4$, $\rho_{calcd} = 3.82$ g/cm^3. The structure was solved by direct methods (MULTAN) and refined (2515 reflections, $F^2 \geq 3.0\sigma(F^2)$) to final values of the residuals $R_F = 0.054$ and $R_{wF} = 0.058$. The structure of IV consists of a rhombus of four osmium atoms bridged on opposite sides by quadruply bridging and triply bridging sulfido ligands. Two adjacent edges of the rhombus contain bridging $Os(CO)_4$ groups. The other two edges contain bridging hydride ligands. When exposed to UV radiation at room temperature, I undergoes facile homolysis of the carbon–sulfur bond and yields dibenzyl, compound III, and the new cluster $H_2Os_6(CO)_{18}(\mu_4\text{-}S)(\mu_3\text{-}S)$, V. For V: space group $P\bar{1}$, $a = 9.022$ (2) Å, $b = 11.986$ (4) Å, $c = 14.370$ (3) Å, $\alpha = 89.94$ (2)°, $\beta = 78.23$ (2)°, $\gamma = 83.39$ (3)°, $V = 1511$ (1) Å^3, $Z = 2$, $\rho_{calcd} = 3.76$ g/cm^3. The structure was solved by the heavy-atom method and refined (3407 reflections, $F^2 \geq 3.0\sigma(F^2)$) to final values of the residuals $R_F = 0.044$ and $R_{wF} = 0.044$. Compound V is structurally similar to III. It contains two groups of three osmium atoms which are linked by a quadruply bridging sulfido ligand and one metal–metal bond which also contains a symmetrical bridging carbonyl ligand. The quadruply bridging sulfido ligand contains a highly distorted tetrahedral geometry, Os–S–Os angles range from 74.7 (1)° to 144.5 (2)°. In addition, there is a triply bridging sulfido ligand, two bridging hydride ligands, and 17 linear terminal carbonyl ligands. V can be converted into III both by thermolytic (68 °C) and photolytic decarbonylation.

Introduction

We have recently shown that triosmium carbonyl cluster compounds readily induce carbon–sulfur bond cleavage processes (both inter- and intramolecularly) to yield a variety of new sulfidoosmium carbon cluster compounds.[1-3] In many cases the sulfido ligands contain lone pairs of electrons which are capable of further coordination. In this

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[1] Adams, R. D.; Katahira, D. A.; Yang, L. W. *Organometallics* **1982,** *1,* 235.

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way they can be used for synthesis of larger clusters by either the coupling of suitable reagents[4] or the condensation of monomeric units.[5-8]

In an extension of these studies we have now investigated the thermal and photochemical degradation of the (phenylmethanethiolato)triosmium carbonyl cluster $HOs_3(CO)_{10}(\mu\text{-}SCH_2C_6H_5)$. Compound I like the compounds $HOs_3(CO)_{10}(\mu\text{-}SAr)$, II, Ar = C_6H_5[3] or C_6F_5, eliminates hydrocarbon (toluene) to produce sulfidoosmium carbonyl cluster compounds, but in addition, and unlike the compounds II, I also appears to engage in homolysis of the carbon–sulfur bond. This leads to the formation of hydride-containing sulfidoosmium carbonyl cluster compounds and dibenzyl.

Experimental Section

Although the products are air stable, all the reactions were performed under a prepurified nitrogen atmosphere. Photolysis experiments were made by using an external high-pressure mercury lamp on reaction solutions contained in Pyrex glassware. Solvents were stored over 4-Å molecular sieves and were degassed with a dispersed stream of nitrogen gas before use. Phenylmethanethiol and *n*-decane-d_{22} (99% isotopically enriched) were obtained commercially and were used without further purification. Compound I was made (81% yield) from $Os_3(CO)_{12}$[9] and phenylmethanethiol by a procedure analogous to that used for the preparation of the related compounds $HOs_3(CO)_{10}(\mu\text{-}SR)$.[10] Infrared spectra were recorded on a Nicolet 7199 FT-IR spectrophotometer. A Bruker HX270 FT-NMR spectrometer was used to obtain ^1H NMR spectra at 270 MHz. GC and GC–MS analysis were performed on a Perkin-Elmer 990 gas chromatograph and a Hewlett Packard 5985A GC–MS, respectively, using 2% OV101 on Chromosorb WHP, 6 ft × 0.125 in. stainless-steel columns. For many of the reactions considerable amounts of the starting material were recovered after reaction. The percentage yields of the products were calculated on the basis of the amount of I consumed in the reaction.

Thermolysis of $HOs_3(CO)_{10}SCH_2C_6H_5$, I. In a typical reaction, 425 mg of $HOs_3(CO)_{10}SCH_2C_6H_5$ dissolved in 20 mL of nonane was heated to reflux for 1 h. The solvent was removed in vacuo. GLC analysis of this solvent showed toluene (~8% yield). The red-brown residue was put on silica gel TLC plates. Elution with a mixture of hexane and dichloromethane (85:15) separated the following bands: dibenzyl (16%); a trace of $Os_3(CO)_9(\mu_3\text{-}S)_2$; unreacted I (59%); brown $Os_6(CO)_{16}(\mu_4\text{-}S)(\mu_3\text{-}S)$[3] (7%); green $H_2Os_6(CO)_{17}(\mu_4\text{-}S)(\mu_3\text{-}S)$, IV (2.5%) [IR (hexane) $\nu(CO)$ 2130 (w), 2106 (s), 2097 (s), 2053 (s), 2047 (sh), 2034 (m), 2030 (sh), 2023 (s), 2017 (m), 1999 (w), 1981 (w), 1958 (m), 1943 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ −12.04]; green $Os_7(CO)_{20}(\mu_4\text{-}S)_2$[12] (10%); red $H_2Os_6(CO)_{17}(\mu_4\text{-}S)(\mu_3\text{-}S)$, III (10%) [IR (hexane) $\nu(CO)$ 2133 (w), 2119 (w), 2107 (w), 2096 (m), 2085 (s), 2073 (m), 2059 (w), 2051 (m), 2037 (s), 2028 (w), 2021 (m), 2012 (w), 2003 (w), 1997 (w), 1980 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ −13.20 (s) −15.09 (s). The products were recrystallized from CH_2Cl_2/hexane solvent. Increasing the reaction time did not alter the yields of the products.

Thermolysis of I in Deuterated Solvents. In a sealed tube, the thermolysis was carried out by heating 25 mg of $HOs_3(CO)_{10}SCH_2C_6H_5$ in 1 mL of decane-d_{22} at 150 °C for 3 h. The reaction mixture was allowed to cool, and the red-brown solution was analyzed for toluene and dibenzyl (toluene-d_0 (33%), dibenzyl-d_0 (13%)).

The reaction was performed similarly in toluene-d_8. The dibenzyl so obtained was analyzed by GC–MS and was found to consist of dibenzyl-d_0 (80%) and dibenzyl-d_7 (20%).

Photolysis of $HOs_3(CO)_{10}(\mu\text{-}SCH_2C_6H_5)$, I. A solution of I (100 mg) in 100 mL of hexane was photolyzed for 2 h under a continuous purge with nitrogen. The solvent was removed in vacuo, and the orange-red residue was put on silica TLC plates. Elution with hexane/CH_2Cl_2 (85:15) separated the dibenzyl (1.5 mg, 16%), from the starting material (11 mg), orange $H_2Os_6(CO)_{18}(\mu_4\text{-}S)(\mu_3\text{-}S)$, V (6 mg, 8%), and red $H_2Os_6(CO)_{17}(\mu_4\text{-}S)(\mu_3\text{-}S)$, III (4.5 mg, 6%). For V: IR (hexane) $\nu(CO)$ 2120 (w), 2101 (w), 2082 (s), 2069 (s), 2058 (w), 2051 (m), 2040 (m), 2033 (m), 2021 (m), 2012 (m), 2005 (m), 1996 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ −13.69 (s), −16.73 (s).

Thermal Decarbonylation of $H_2Os_6(CO)_{18}(\mu_4\text{-}S)(\mu_3\text{-}S)$, V. Compound V (12 mg) was dissolved in hexane (15 mL), and the solution was refluxed for 30 min. The solvent was removed in vacuo, and the residue was placed on TLC plates. Elution with hexane/CH_2Cl_2 (85:15) gave a single red band of III (5 mg, 42%).

Photolysis of $H_2Os_6(CO)_{18}(\mu\text{-}S)(\mu_3\text{-}S)$, V. A solution of V (7 mg) in hexane solvent was irradiated for 30 min. The solvent was then removed in vacuo. Chromatography by TLC on silica yielded only compound III (3 mg, 43%).

Crystallographic Analyses. Crystals of each of the compounds suitable for diffraction analysis were obtained from solutions in CH_2Cl_2/hexane solvent by cooling to 0 °C. All crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on 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. Crystal data and data collection parameters are listed in Table I. All data processing was performed on a Digital PDP 11/45 computer using the Enraf-Nonius SDP program library (Version 18). Absorption corrections of a Gaussian integration type were done for each structure. Neutral atom scattering factors were calculated by the standard procedures.[11a] Anomalous dispersion corrections were applied to all atoms.[11b] Full-matrix least-squares refinements minimized the function $\sum_{hkl} w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_\sigma^2)/2F_o$, and $\sigma(F_\sigma^2) = [\sigma(I_{raw})^2 + (PF_\sigma^2)^2]^{1/2}/Lp$.

Atoms heavier than oxygen were refined anisotropically. All other non-hydrogen atoms were refined isotropically. Hydride ligands were not located in difference Fourier syntheses for any of the structures and were subsequently ignored in the analyses. Estimated standard deviations for the bond distance and angle calculations were obtained by using the inverse matrix obtained on the final cycle of refinement for each structure.

The systematic absences *hkl*, $h + k = 2n + 1$, and *h0l*, $l = 2n + 1$, observed for compound III are consistent with either of the space groups $C2/c$ or Cc. Structure solution was initiated by assuming the space group $C2/c$. The correctness of this choice was confirmed by the successful solution and refinement of the structure. Application of direct methods techniques (MULTAN) to 248 reflections ($E \geq 1.56$) provided phases which subsequently permitted the determination of the coordinates (E map) of the six metal atoms. All remaining non-hydrogen atoms were obtained from a series of ΔF syntheses. Final fractional atomic coordinates, thermal parameters, and bond distance and angles are listed in Tables II–IV, respectively.

For compound IV the space group $P2_1/n$ was established from the systematic absences. For this structure the coordinates of the six metal atoms were determined from 276 reflections ($E \geq 1.33$) phased by application of direct methods procedures (MULTAN). All remaining non-hydrogen atoms were obtained from subsequent ΔF syntheses. Final fractional atomic coordinates and bond distances and angles are given in Tables V–VII, respectively.

For compound V the space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure.

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(11) "International Tables for X-ray Crystallography"; Kynoch Press; Birmingham, England, 1975; Vol. IV: (a) Table 2.2B, pp 99–101; (b) Table 2.3.1, pp 149–150.

Table I. Crystallographic Data for X-ray Diffraction Studies

	III	IV	V
	(A) Crystal Data		
formula	$Os_6S_2O_{17}C_{17}H_2$	$Os_6S_2O_{17}C_{17}H_2$	$Os_6S_2O_{18}C_{18}H_2$
temp, ±5 °C	28	23	23
space group	$C2/c$, No. 15	$P2_1/n$	$P\bar{1}$, No. 2
a, Å	20.364 (5)	11.124 (3)	9.022 (3)
b, Å	9.764 (4)	14.090 (5)	11.986 (4)
c, Å	32.544 (7)	18.694 (7)	14.370 (3)
α, deg	90.00	90.00	89.94 (2)
β, deg	114.01 (2)	92.00 (3)	78.23 (2)
γ, deg	90.00	90.00	83.39 (3)
V, Å^3	5900 (6)	2928 (3)	1511 (1)
M_r	1683.52	1683.5	1711.53
Z	8	4	2
ρ_{calcd}, g/cm^3	3.79	3.82	3.76
	(B) Measurement of Intensity Data		
radiatn	Mo K$\bar{\alpha}$ (0.710 73 Å)	Mo K$\bar{\alpha}$ (0.710 73 Å)	Mo K$\bar{\alpha}$ (0.710 73 Å)
monochromator	graphite	graphite	graphite
detector aperture, mm			
horizontal ($A + B \tan\theta$)			
A	3.0	3.0	3.0
B	1.0	1.0	1.0
vertical	4.0	4.0	4.0
cryst faces	$10\bar{1}$, $\bar{1}01$, 001 $00\bar{1}$, 010, $0\bar{1}0$	$\bar{1}0\bar{1}$, 101, $\bar{1}11$, $1\bar{1}\bar{1}$, $0\bar{1}\bar{2}$ 012, $\bar{1}\bar{1}0$, 110, $02\bar{1}$, $0\bar{2}1$	$01\bar{1}$, $0\bar{1}1$, 011, $0\bar{1}\bar{1}$ $\bar{1}00$, 100
cryst size, mm	0.13 × 0.31 × 0.14	0.12 × 0.20 × 0.17	0.30 × 0.13 × 0.15
cryst orientatn directn, deg from ϕ axis	b, 1.5°	normal to $\bar{1}\bar{2}2$, 3.5	a^*, 12.0
reflctns measd	$h,k,\pm l$	$h,k,\pm l$	$h,\pm k,\pm l$
max 2θ, deg	48	46	50
scan type	moving crystal-stationary counter	moving crystal-stationary counter	moving crystal-stationary counter
ω-scan width (A + 0.347 $\tan\theta$), deg; A =	1.00	0.95	1.10
background	$^1/_4$ additional scan at each end of scan	$^1/_4$ additional scan at each end of scan	$^1/_4$ additional scan at each end of scan
ω-scan rate (variable)			
max, deg/min	10.0	10.0	10.0
min, deg/min	1.33	1.5	1.8
no. of reflctns measd	5208	4455	5246
data used ($F^2 \geqslant 3.0\sigma(F^2)$)	2456	2515	3407
	(C) Treatment of Data		
absorption correctn			
coeff, cm^{-1}	259.9	261.8	253.1
grid	8 × 14 × 8	8 × 8 × 14	14 × 8 × 8
transmissn coeff			
max	0.34	0.17	0.35
min	0.04	0.03	0.05
P factor	0.01	0.015	0.010
final residuals			
R_F	0.037	0.054	0.044
R_{wF}	0.034	0.058	0.044
esd of unit weight observn	1.60	2.79	2.20
largest shift/error value of final cycle	0.03	0.04	0.04
largest peak in final difference Fourier, e/Å^3	2.0	2.5	2.1

The structure was solved by a combination of Patterson and ΔF syntheses. The coordinates of two of the six metal atoms were obtained from a three-dimensional Patterson function. The coordinates of the remaining metal atoms and non-hydrogen atoms were obtained from ΔF syntheses.

Tables of structure factor amplitudes are available for all three structures; see supplementary material.

Results

When refluxed in nonane solvent (150 °C) for periods of 1–2 h, compound I is transformed into a variety of high nuclearity sulfidoosmium carbonyl cluster compounds; see Scheme I. The metal-containing products can be divided into two categories: (1) those which contain hydride ligands and (2) those which do not contain hydride ligands. It is believed that the products in each class are related by common modes of the decomposition of I. None of the products contain benzyl groups indicating that carbon–sulfur bond cleavage in the phenylmethanethiolato ligand is a common feature of each mode. There are two hydrocarbon products, toluene and dibenzyl.

The formation of toluene suggests a RH reductive-elimination process. This is supported by the results of degradation experiments performed in decane-d_{22} solvent which showed no deuterium incorporation in the toluene (eq 1). The elimination of ArH was observed in the

$$HOs_3(CO)_{10}(\mu\text{-}SCH_2C_6H_5) \xrightarrow[\text{decane-}d_{22}]{150\ ^\circ C} CH_3C_6H_5 + [C_6H_5CH_2]_2 + \text{clusters} \quad (1)$$

Table II. Positional and Thermal Parameters and Their Esds for $H_2Os_6(CO)_{17}(\mu_4\text{-}S)(\mu_3\text{-}S)$, III

atom	x	y	z	$B(1,1)$	$B(2,2)$	$B(3,3)$	$B(1,2)$	$B(1,3)$	$B(2,3)$	B(eqv)
Os(1)	0.203 85 (10)	0.054 45 (8)	0.165 87 (6)	2.59 (3)	2.92 (4)	2.52 (3)	0.16 (3)	−0.40 (3)	0.30 (3)	2.73 (2)
Os(2)	−0.061 42 (10)	0.499 79 (8)	0.230 36 (6)	2.99 (4)	3.02 (4)	3.25 (4)	0.57 (3)	−1.04 (3)	0.28 (3)	3.10 (2)
Os(3)	−0.058 34 (9)	0.333 08 (8)	0.383 89 (6)	2.28 (3)	3.20 (4)	2.61 (3)	0.36 (3)	−0.48 (3)	0.09 (3)	2.75 (2)
Os(4)	0.386 04 (10)	−0.034 80 (8)	0.296 70 (6)	2.95 (4)	2.92 (4)	2.90 (4)	0.46 (3)	−0.49 (3)	0.57 (3)	3.01 (2)
Os(5)	0.404 80 (9)	0.191 66 (8)	0.241 62 (6)	1.97 (3)	3.00 (4)	2.98 (3)	0.15 (3)	−0.34 (3)	0.60 (3)	2.71 (2)
Os(6)	0.235 65 (10)	0.389 77 (8)	0.182 33 (6)	2.53 (3)	2.83 (4)	3.24 (4)	−0.17 (3)	−0.52 (3)	0.81 (3)	2.89 (2)
S(1)	0.136 4 (6)	0.229 2 (5)	0.262 1 (4)	2.3 (2)	2.5 (2)	2.9 (2)	0.2 (2)	−0.3 (2)	0.6 (2)	2.6 (1)
S(2)	0.109 3 (6)	0.479 2 (5)	0.337 8 (4)	3.6 (2)	3.3 (3)	3.8 (2)	0.2 (2)	−1.6 (2)	−0.0 (2)	3.5 (1)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
O(1)	0.033 (2)	0.140 (2)	0.012 (1)	6.0 (4)	C(1)	0.098 (3)	0.117 (2)	0.073 (2)	4.1 (5)
O(2)	−0.056 (2)	−0.069 (1)	0.266 (1)	5.6 (4)	C(2)	0.041 (2)	−0.025 (2)	0.228 (2)	3.8 (5)
O(3)	0.350 (2)	−0.143 (1)	0.035 (1)	5.6 (4)	C(3)	0.296 (3)	−0.065 (2)	0.084 (2)	4.0 (5)
O(4)	−0.135 (2)	0.417 (1)	0.046 (1)	5.7 (4)	C(4)	−0.116 (3)	0.451 (2)	0.116 (2)	4.5 (5)
O(5)	−0.367 (2)	0.632 (2)	0.319 (1)	6.9 (5)	C(3)	−0.250 (3)	0.574 (2)	0.283 (2)	5.2 (6)
O(6)	0.037 (2)	0.720 (2)	0.147 (1)	6.9 (5)	C(6)	−0.006 (3)	0.641 (2)	0.178 (2)	4.7 (6)
O(7)	0.092 (2)	0.276 (1)	0.554 (1)	4.9 (4)	C(7)	0.036 (2)	0.294 (2)	0.490 (1)	3.6 (5)
O(8)	−0.320 (2)	0.483 (1)	0.505 (1)	5.6 (4)	C(8)	−0.219 (3)	0.424 (2)	0.460 (2)	4.5 (5)
O(9)	−0.245 (2)	0.136 (2)	0.410 (1)	6.2 (4)	C(9)	−0.177 (3)	0.210 (2)	0.400 (2)	4.0 (5)
O(10)	0.116 (2)	0.061 (1)	0.453 (1)	4.8 (4)	C(10)	0.218 (2)	0.025 (2)	0.396 (1)	3.6 (5)
O(11)	0.618 (2)	−0.079 (2)	0.428 (1)	5.8 (4)	C(11)	0.533 (3)	−0.058 (2)	0.377 (2)	4.0 (5)
O(12)	0.645 (2)	−0.101 (2)	0.123 (1)	6.6 (5)	C(12)	0.544 (3)	−0.077 (2)	0.188 (2)	4.8 (6)
O(13)	0.271 (2)	−0.266 (2)	0.316 (1)	8.2 (6)	C(13)	0.315 (3)	−0.187 (2)	0.307 (2)	5.0 (6)
O(14)	0.749 (2)	0.137 (2)	0.175 (1)	6.2 (4)	C(14)	0.616 (2)	0.151 (2)	0.198 (1)	2.7 (4)
O(15)	0.442 (2)	0.266 (1)	0.436 (1)	5.3 (4)	C(15)	0.424 (3)	0.237 (2)	0.361 (2)	3.9 (5)
O(16)	0.363 (2)	0.604 (2)	0.103 (1)	7.2 (5)	C(16)	0.309 (3)	0.528 (2)	0.132 (2)	4.9 (6)
O(17)	0.271 (2)	0.319 (1)	−0.023 (1)	5.3 (4)	C(17)	0.260 (2)	0.343 (2)	0.060 (1)	3.2 (4)
O(18)	0.562 (3)	0.406 (2)	0.201 (2)	10.5 (7)	C(18)	0.464 (4)	0.353 (3)	0.194 (2)	7.5 (8)

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(h^2a^{*2}B(1,1) + k^2b^{*2}B(2,2) + l^2c^{*2}B(3,3) + 2hka^*b^*B(1,2) + 2hla^*c^*B(1,3) + 2klb^*c^*B(2,3))]$.

Table III. Interatomic Distances (Å) with Esds for $H_2Os_6(CO)_{17}(\mu_4\text{-}S)(\mu_3\text{-}S)$, III

Os(1)-Os(4)	3.028 (1)	Os(3)-C(9)	1.94 (2)
Os(1)-Os(5)	2.829 (1)	Os(4)-C(10)	1.91 (2)
Os(2)-Os(3)	2.990 (1)	Os(4)-C(11)	1.85 (3)
Os(2)-Os(6)	2.810 (1)	Os(4)-C(12)	1.90 (2)
Os(4)-Os(5)	2.850 (1)	Os(5)-C(13)	1.87 (2)
Os(4)-Os(6)	2.828 (1)	Os(5)-C(14)	1.86 (3)
Os(5)-Os(6)	2.933 (1)	Os(5)-C(15)	1.91 (2)
Os(3)···Os(6)	3.588 (1)	Os(6)-C(16)	1.82 (2)
Os(1)···Os(6)	3.944 (1)	Os(6)-C(17)	1.84 (2)
Os(1)···Os(3)	4.671 (1)	C(1)-O(1)	1.19 (2)
Os(3)···Os(5)	4.281 (1)	C(2)-O(2)	1.15 (3)
Os(1)-S(1)	2.386 (4)	C(3)-O(3)	1.14 (3)
Os(2)-S(2)	2.368 (5)	C(4)-O(4)	1.17 (3)
Os(3)-S(1)	2.456 (5)	C(5)-O(5)	1.19 (2)
Os(3)-S(2)	2.437 (5)	C(6)-O(6)	1.15 (2)
Os(5)-S(1)	2.397 (5)	C(7)-O(7)	1.20 (2)
Os(6)-S(1)	2.342 (5)	C(8)-O(8)	1.15 (2)
Os(6)-S(2)	2.466 (4)	C(9)-O(9)	1.12 (2)
Os(1)-C(1)	1.84 (2)	C(10)-O(10)	1.17 (2)
Os(1)-C(2)	1.90 (2)	C(11)-O(11)	1.16 (3)
Os(1)-C(3)	1.91 (3)	C(12)-O(12)	1.15 (2)
Os(2)-C(4)	1.87 (3)	C(13)-O(13)	1.19 (2)
Os(2)-C(5)	1.86 (3)	C(14)-O(14)	1.22 (3)
Os(2)-C(6)	1.89 (2)	C(15)-O(15)	1.12 (3)
Os(3)-C(7)	1.88 (2)	C(16)-O(16)	1.24 (2)
Os(3)-C(8)	1.88 (2)	C(17)-O(17)	1.19 (2)

degradation of compound II.[3] The non-hydride-containing sulfidoosmium carbonyl cluster compounds are believed to be formed via this decomposition pathway. These clusters, plus a few others, were also observed in the degradation of compound II. Details of the mechanism of this mode of decomposition remain to be established; thus, these compounds will not be further described at this time.[3,12,13]

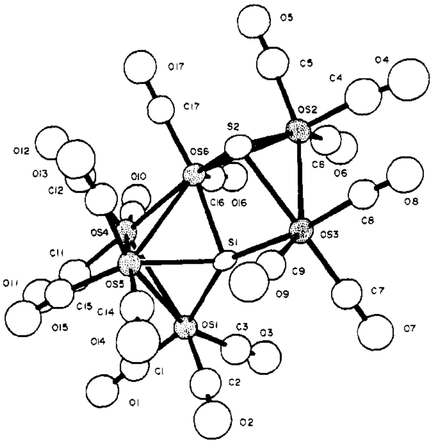

Figure 1. An ORTEP diagram of $H_2Os_6(CO)_{17}(\mu_4\text{-}S)(\mu_3\text{-}S)$, III, showing 50% probability thermal-motion ellipsoids.

The formation of dibenzyl strongly implies a degradation process involving an homolysis of the carbon–sulfur bond in the phenylmethanethiolato ligand with formation of benzyl radicals and $[HOs_3(CO)_{10}(S)]$ radicals. To be sure that the dibenzyl was not somehow derived from the toluene, a sample of compound I was pyrolyzed in a sealed tube in toluene-d_8 solvent. The dibenzyl product was found by mass spectral analysis to consist of dibenzyl-d_0 (80%) and dibenzyl-d_7 (20%) (eq 2). The formation of

$$HOs_3(CO)_{10}(\mu\text{-}SCH_2C_6H_5) \xrightarrow[\text{toluene-}d_8]{150\ °C} \underset{80\%}{[C_6H_5CH_2]_2} + \underset{20\%}{[C_6H_5CH_2CD_2C_6D_5]} + \text{clusters} \quad (2)$$

the small amounts of dibenzyl-d_7 can be attributed to a subsequent slow reaction of benzyl radicals with toluene-d_8 to yield toluene-d_1 and benzyl-d_7 radicals. The latter then

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(12) $Os_7(CO)_{20}(\mu_4\text{-}S)_2$ (not reported previously) is a minor product of the pyrolysis of both I and II: ν(CO) in CH_2Cl_2: 2138 (w), 2112 (s), 2070 (s), 2058 (s), 2023 (s), 2018 (sh), 1950 (w) cm^{-1}.

(13) $Os_7(CO)_{20}(\mu_4\text{-}S)_2$ has been characterized by a single-crystal X-ray diffraction analysis.[14]

(14) Adams, R. D.; Horváth, I. T.; Mathur, P.; Segmüller, B. E.; Yang, L. W. *Organometallics*, in press.

Table IV. Interatomic Angles (deg) with Esds for $H_2Os_6(CO)_{17}(\mu_4\text{-}S)(\mu_3\text{-}S)$, III

Os(4)-Os(1)-Os(5)	58.12 (3)	Os(2)-Os(3)-C(9)	143.3 (6)	Os(5)-Os(6)-S(1)	52.6 (1)
Os(3)-Os(2)-Os(6)	73.36 (3)	Os(1)-Os(4)-C(10)	119.2 (6)	Os(5)-Os(6)-S(2)	93.0 (1)
Os(1)-Os(4)-Os(5)	57.43 (3)	Os(1)-Os(4)-C(11)	88.3 (8)	Os(5)-Os(6)-C(16)	120.5 (7)
Os(1)-Os(4)-Os(6)	84.61 (3)	Os(1)-Os(4)-C(12)	149.2 (7)	Os(5)-Os(6)-C(17)	116.4 (7)
Os(5)-Os(4)-Os(6)	62.19 (3)	Os(5)-Os(4)-C(10)	172.6 (7)	Os(1)-S(1)-Os(3)	149.4 (2)
Os(1)-Os(5)-Os(4)	64.44 (3)	Os(5)-Os(4)-C(11)	97.4 (7)	Os(1)-S(1)-Os(5)	72.5 (1)
Os(1)-Os(5)-Os(6)	86.39 (3)	Os(5)-Os(4)-C(12)	91.9 (7)	Os(1)-S(1)-Os(6)	113.1 (2)
Os(4)-Os(5)-Os(6)	58.53 (3)	Os(6)-Os(4)-C(10)	111.9 (6)	Os(3)-S(1)-Os(5)	123.8 (2)
Os(2)-Os(6)-Os(4)	150.13 (4)	Os(6)-Os(4)-C(11)	158.9 (8)	Os(3)-S(1)-Os(6)	96.8 (2)
Os(2)-Os(6)-Os(5)	135.30 (4)	Os(6)-Os(4)-C(12)	82.6 (7)	Os(5)-S(1)-Os(6)	76.5 (2)
Os(4)-Os(6)-Os(5)	59.28 (3)	Os(1)-Os(5)-S(1)	53.6 (1)	Os(2)-S(2)-Os(3)	76.9 (2)
Os(4)-Os(1)-S(1)	78.3 (1)	Os(1)-Os(5)-C(13)	161.5 (7)	Os(2)-S(2)-Os(6)	71.1 (1)
Os(4)-Os(1)-C(1)	89.4 (7)	Os(1)-Os(5)-C(14)	100.4 (7)	Os(3)-S(2)-Os(6)	94.1 (1)
Os(4)-Os(1)-C(2)	152.4 (7)	Os(1)-Os(5)-C(15)	95.8 (6)	Os(1)-C(1)-O(1)	178 (2)
Os(4)-Os(1)-C(3)	117.4 (7)	Os(4)-Os(5)-S(1)	81.9 (1)	Os(1)-C(2)-O(2)	173 (2)
Os(5)-Os(1)-S(1)	53.9 (1)	Os(4)-Os(5)-C(13)	102.3 (7)	Os(1)-C(3)-O(3)	174 (2)
Os(5)-Os(1)-C(1)	102.9 (7)	Os(4)-Os(5)-C(14)	163.6 (6)	Os(2)-C(4)-O(4)	173 (2)
Os(5)-Os(1)-C(2)	95.0 (6)	Os(4)-Os(5)-C(15)	83.1 (7)	Os(2)-C(5)-O(5)	176 (2)
Os(5)-Os(1)-C(3)	161.2 (7)	Os(6)-Os(5)-S(1)	50.9 (1)	Os(2)-C(6)-O(6)	177 (2)
Os(3)-Os(2)-S(2)	52.6 (1)	Os(6)-Os(5)-C(13)	75.4 (7)	Os(3)-C(7)-O(7)	178 (2)
Os(3)-Os(2)-C(4)	94.2 (8)	Os(6)-Os(5)-C(14)	129.8 (8)	Os(3)-C(8)-O(8)	175 (2)
Os(3)-Os(2)-C(5)	150.8 (7)	Os(6)-Os(5)-C(15)	136.2 (7)	Os(3)-C(9)-O(9)	173 (2)
Os(3)-Os(2)-C(6)	118.1 (7)	Os(2)-Os(6)-S(1)	90.2 (1)	Os(4)-C(10)-O(10)	175 (2)
Os(6)-Os(2)-S(2)	56.1 (1)	Os(2)-Os(6)-S(2)	52.8 (1)	Os(4)-C(11)-O(11)	171 (2)
Os(6)-Os(2)-C(4)	160.8 (8)	Os(2)-Os(6)-C(16)	85.2 (7)	Os(4)-C(12)-O(12)	179 (2)
Os(6)-Os(2)-C(5)	90.3 (8)	Os(2)-Os(6)-C(17)	95.6 (7)	Os(5)-C(13)-O(13)	172 (2)
Os(6)-Os(2)-C(6)	104.6 (7)	Os(4)-Os(6)-S(1)	83.3 (1)	Os(5)-C(14)-O(14)	174 (2)
Os(2)-Os(3)-S(1)	84.0 (1)	Os(4)-Os(6)-S(2)	152.2 (1)	Os(5)-C(15)-O(15)	170 (2)
Os(2)-Os(3)-S(2)	50.5 (1)	Os(4)-Os(6)-C(16)	67.2 (7)	Os(6)-C(16)-O(16)	166 (2)
Os(2)-Os(3)-C(7)	121.7 (7)	Os(4)-Os(6)-C(17)	97.3 (6)	Os(6)-C(17)-O(17)	177 (2)
Os(2)-Os(3)-C(8)	88.2 (7)				

Table V. Positional and Thermal Parameters and Their for $H_2Os_6(CO)_{17}(\mu_4\text{-}S)(\mu_3\text{-}S)$, IV[a]

atom	*x*	*y*	*z*	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)	*B*(eqv)
Os(1)	1.09971 (5)	0.1041 (1)	0.69022 (3)	2.55 (4)	3.70 (5)	2.56 (3)	−0.04 (5)	0.61 (3)	0.48 (4)	3.08 (2)
Os(2)	0.79620 (5)	0.2185 (1)	0.59766 (3)	2.53 (4)	3.68 (5)	3.12 (8)	0.35 (5)	1.18 (3)	0.17 (4)	3.10 (3)
Os(3)	0.87215 (5)	−0.0338 (1)	0.58788 (3)	2.79 (4)	2.58 (4)	2.43 (3)	−0.16 (4)	1.00 (3)	−0.06 (4)	2.62 (2)
Os(4)	1.07235 (5)	0.4044 (1)	0.66506 (3)	3.28 (4)	3.20 (5)	2.65 (3)	−0.76 (5)	1.23 (3)	−0.42 (4)	3.03 (2)
Os(5)	1.05875 (5)	0.1958 (1)	0.60070 (3)	2.91 (4)	3.03 (5)	2.58 (3)	0.03 (5)	1.39 (3)	−0.02 (4)	2.75 (2)
Os(6)	0.93228 (5)	0.3156 (1)	0.60859 (3)	2.77 (4)	2.44 (4)	2.35 (3)	0.07 (4)	1.07 (3)	−0.06 (4)	2.51 (2)
S(1)	0.9813 (3)	0.0972 (6)	0.6319 (2)	2.9 (2)	1.7 (2)	2.4 (2)	0.2 (3)	0.8 (2)	0.1 (2)	2.5 (1)
S(2)	0.8477 (3)	0.1797 (7)	0.5452 (2)	3.2 (3)	3.2 (3)	2.2 (2)	0.2 (3)	0.7 (2)	0.1 (2)	3.0 (2)

atom	*x*	*y*	*z*	*B*, Å²	atom	*x*	*y*	*z*	*B*, Å²
O(1)	1.2597 (10)	0.162 (2)	0.7317 (5)	6.1 (5)	C(1)	1.197 (1)	0.139 (3)	0.7160 (7)	4.7 (6)
O(2)	1.1299 (11)	−0.187 (2)	0.6679 (6)	6.8 (5)	C(2)	1.116 (1)	−0.081 (3)	0.6780 (8)	4.8 (6)
O(3)	1.0871 (11)	0.023 (2)	0.7772 (6)	6.7 (5)	C(3)	1.094 (2)	0.047 (3)	0.7449 (8)	5.4 (7)
O(4)	0.6511 (11)	0.077 (2)	0.5569 (6)	7.6 (6)	C(4)	0.705 (2)	0.139 (3)	0.5716 (8)	6.1 (8)
O(3)	0.7334 (10)	0.501 (2)	0.5629 (5)	5.6 (4)	C(5)	0.757 (1)	0.390 (3)	0.5776 (8)	5.2 (7)
O(6)	0.7924 (10)	0.271 (2)	0.6887 (5)	6.3 (5)	C(6)	0.792 (1)	0.251 (3)	0.6536 (8)	4.9 (7)
O(7)	0.9103 (9)	−0.266 (2)	0.6577 (5)	5.8 (5)	C(7)	0.896 (1)	−0.177 (3)	0.6299 (7)	4.2 (6)
O(8)	0.7292 (9)	−0.165 (2)	0.5314 (5)	5.0 (4)	C(8)	0.782 (1)	−0.110 (3)	0.5525 (7)	3.6 (5)
O(9)	0.9293 (10)	−0.166 (2)	0.5239 (5)	5.9 (5)	C(9)	0.910 (1)	−0.123 (2)	0.5492 (7)	3.6 (5)
O(10)	1.0661 (9)	0.615 (2)	0.7333 (5)	5.6 (4)	C(10)	1.071 (1)	0.532 (3)	0.7090 (7)	3.9 (5)
O(11)	1.2304 (10)	0.461 (2)	0.6964 (6)	6.9 (5)	C(11)	1.171 (2)	0.429 (3)	0.6860 (8)	5.9 (7)
O(12)	1.0389 (10)	0.628 (2)	0.5939 (5)	6.1 (5)	C(12)	1.051 (1)	0.545 (3)	0.6209 (8)	5.2 (7)
O(13)	0.9870 (10)	0.354 (2)	0.5125 (6)	6.6 (5)	C(13)	1.010 (1)	0.287 (3)	0.5461 (8)	4.7 (6)
O(14)	1.0798 (11)	−0.070 (2)	0.5563 (6)	7.9 (6)	C(14)	1.068 (1)	0.033 (3)	0.5733 (8)	5.1 (7)
O(15)	1.2103 (11)	0.278 (2)	0.6168 (6)	6.5 (5)	C(15)	1.152 (1)	0.258 (3)	0.6087 (7)	4.3 (6)
O(16)	0.9283 (9)	0.412 (2)	0.6964 (5)	5.1 (4)	C(16)	0.938 (1)	0.382 (3)	0.6623 (7)	4.2 (6)
O(17)	0.8767 (10)	0.581 (2)	0.5584 (5)	5.6 (4)	C(17)	0.900 (1)	0.479 (3)	0.5793 (7)	3.9 (6)

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(h^2a^{*2}B(1,1) + k^2b^{*2}B(2,2) + l^2c^{*2}B(3,3) + 2hka^*b^*B(1,2) + 2hla^*c^*B(1,3) + 2klb^*c^*B(2,3))]$.

combine with benzyl-d_0 radicals. It is believed that the hydride-containing clusters $H_2Os_6(CO)_{17}(\mu_4\text{-}S)(\mu_3\text{-}S)$, III, and its isomer IV are formed through this mode of degradation of compound I.

An ORTEP diagram of the molecular structure of compound III is shown in Figure 1. Final positional and thermal parameters are given in Table II. The hexaosmium cluster contains two inorganic sulfido ligands, 17 linear terminal carbonyl ligands, and two hydride ligands which bridge metal–metal bonds. As will become apparent from the structure of compound V and the proposed mechanism for its formation (vide infra), it is probably best to describe the cluster core of III as a combination of two triosmium groupings instead of one extended hexanuclear array.

One group consists of the metal atoms Os(2), Os(3), and Os(6). It contains a triply bridging sulfido ligand S(2) and eight linear terminal carbonyl ligands arranged such that Os(2) and Os(3) contain three each and Os(6) contains two. Tables III and IV list selected interatomic distances and

Scheme I

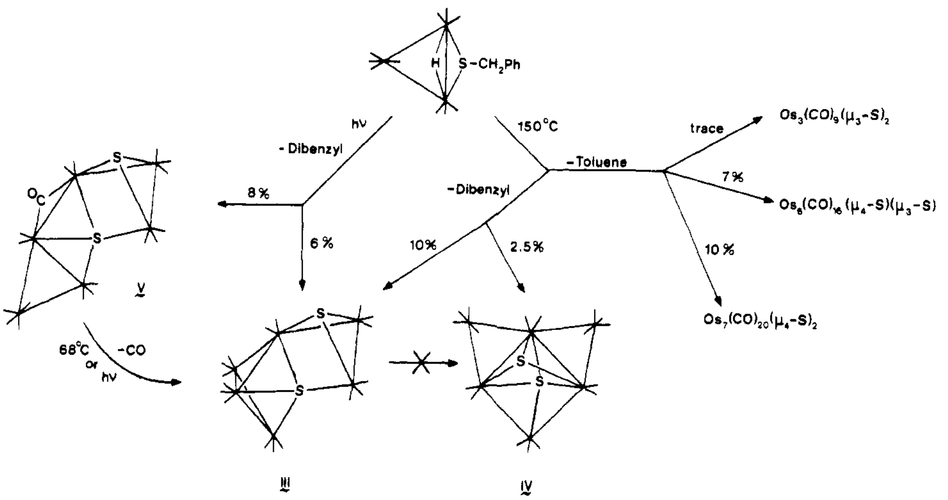

Table VI. Interatomic Distances (Å) with Esds for $H_2Os_6(CO)_{17}(\mu_4\text{-}S)(\mu_3\text{-}S)$, IV

Os(1)-Os(2)	2.883 (1)	Os(5)-C(11)	1.86 (3)
Os(1)-Os(4)	2.959 (1)	Os(5)-C(12)	1.83 (2)
Os(1)-Os(5)	2.844 (1)	Os(5)-C(13)	1.78 (2)
Os(2)-Os(3)	2.854 (1)	Os(6)-C(14)	1.88 (3)
Os(2)-Os(5)	2.786 (1)	Os(6)-C(15)	1.97 (2)
Os(2)-Os(6)	2.789 (1)	Os(6)-C(16)	1.79 (3)
Os(3)-Os(4)	2.970 (1)	Os(6)-C(17)	1.91 (2)
Os(3)-Os(6)	2.850 (1)	C(1)-O(1)	1.11 (3)
Os(1)-S(1)	2.489 (6)	C(2)-O(2)	1.19 (3)
Os(1)-S(2)	2.461 (5)	C(3)-O(3)	1.19 (3)
Os(2)-S(1)	2.558 (6)	C(4)-O(4)	1.22 (3)
Os(2)-S(2)	2.351 (6)	C(5)-O(5)	1.14 (2)
Os(3)-S(1)	2.484 (6)	C(6)-O(6)	1.17 (3)
Os(3)-S(2)	2.452 (6)	C(7)-O(7)	1.22 (3)
Os(4)-S(1)	2.411 (6)	C(8)-O(8)	1.19 (3)
Os(1)-C(1)	1.95 (3)	C(9)-O(9)	1.18 (2)
Os(1)-C(2)	1.84 (2)	C(10)-O(10)	1.23 (3)
Os(2)-C(3)	1.91 (2)	C(11)-O(11)	1.21 (3)
Os(2)-C(4)	1.81 (2)	C(12)-O(12)	1.11 (3)
Os(3)-C(5)	1.87 (2)	C(13)-O(13)	1.27 (3)
Os(3)-C(6)	1.89 (2)	C(14)-O(14)	1.15 (4)
Os(4)-C(7)	1.85 (3)	C(15)-O(15)	1.11 (3)
Os(4)-C(8)	1.83 (3)	C(16)-O(16)	1.29 (3)
Os(4)-C(9)	1.89 (2)	C(17)-O(17)	1.13 (3)
Os(5)-C(10)	1.87 (2)		

angles. The two internuclear separations Os(2)–Os(3) = 2.990 (1) Å and Os(2)–Os(6) = 2.810 (1) Å are sufficiently short to imply a significant degree of metal–metal bonding. The Os–Os separation in $Os_3(CO)_{12}$ is 2.877 (3) Å.[15] The comparative shortness of the Os(2)–Os(6) distance can be attributed to the effects of the bridging sulfido ligand. One the other hand the longer length of the Os(2)–Os(3) distance is probably due to the presence of a bridging hydride ligand (not observed crystallographically).[16] These three metal atoms are linked to the second group of three metal atoms Os(1), Os(4), and Os(5) by the quadruply bridging sulfido ligand S(1) and metal–metal bonds between Os(4) and Os(6) and Os(5) and Os(6).

The three Os–Os internuclear separations Os(1)–Os(4) = 3.028 (1) Å, Os(1)–Os(5) = 2.829 (1) Å, and Os(4)–Os(5) = 2.850 (1) Å are sufficiently short to imply significant bonding interactions; however, the longer Os(1)–Os(4) bond probably contains a bridging hydride ligand.[15] The Os(4)–Os(6) and Os(5)–Os(6) lengths at 2.828 (1) and 2.933 (1) Å, respectively, do not differ greatly from the value

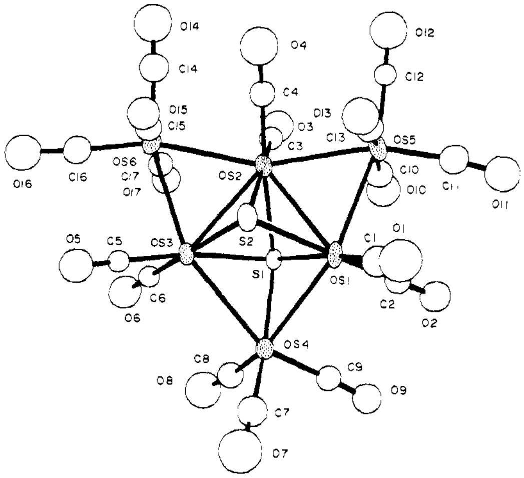

Figure 2. An ORTEP diagram of $H_2Os_6(CO)_{17}(\mu_4\text{-}S)(\mu_3\text{-}S)$, IV, showing 50% probability thermal-motion ellipsoids.

2.877 (3) Å found in $Os_3(CO)_{12}$[15] but are significantly different from each other. The reason for this is not apparent at present. Each metal atom in this second group contains three linear terminal carbonyl ligands.

The osmium–sulfur bonding distances span a considerable range. To the triple bridge S(2) the range is 2.368 (5)–2.466 (4) Å, while to the quadruple bridge S(1) it is 2.342 (5)–2.456 (5) Å. However, these values do not differ greatly from those found in other sulfidoosmium carbonyl clusters.[2–5,17,18] Interestingly, the shortest and longest Os–S bond distances both involve atom Os(6), Os(6)–S(1) = 2.342 (5) Å and Os(6)–S(2) = 2.466 (4) Å. This seems to suggest that one bond is influencing the other. The geometry of the quadruply bridging sulfido ligand could be described as highly distorted tetrahedral since the bond angles range from 72.5 (1)° across mutally bonded metal atoms to 149.4 (2)° across metal atoms that are not bonded. These distortions probably influence the Os–S bonding. If S(2) serves as a six-electron donor, then each metal atom in the cluster can achieve an 18-electron configuration. ^1H NMR spectroscopy indicated that the molecule contains two bridging hydride ligands: δ −13.20 (s) and −15.09 (s). As indicated above, these probably bridge the Os(1)–Os(4) and Os(2)–Os(3) separations. The shortest intermolecular

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Table VII. Interatomic Angles (deg) with Esds for $H_2Os_6(CO)_{17}(\mu_4\text{-}S)(\mu_3\text{-}S)$, IV

Os(2)-Os(1)-Os(4)	98.55 (4)	Os(6)-Os(2)-C(3)	86.8 (7)	Os(2)-Os(5)-C(13)	90.1 (8)
Os(2)-Os(1)-Os(5)	58.21 (3)	Os(6)-Os(2)-C(4)	79.7 (8)	C(10)-Os(5)-C(11)	88 (1)
Os(4)-Os(1)-Os(5)	148.13 (5)	S(1)-Os(2)-S(2)	83.4 (2)	C(10)-Os(5)-C(12)	94 (1)
Os(1)-Os(2)-Os(3)	78.28 (4)	S(1)-Os(2)-C(3)	87.5 (7)	C(10)-Os(5)-C(13)	172 (1)
Os(1)-Os(2)-Os(5)	60.20 (3)	S(1)-Os(2)-C(4)	175.1 (8)	C(11)-Os(5)-C(12)	94 (1)
Os(1)-Os(2)-Os(6)	137.44 (5)	S(2)-Os(2)-C(3)	169.5 (7)	C(11)-Os(5)-C(13)	95 (1)
Os(3)-Os(2)-Os(5)	138.48 (4)	S(2)-Os(2)-C(4)	100.2 (7)	C(12)-Os(5)-C(13)	93 (1)
Os(3)-Os(2)-Os(6)	60.64 (3)	C(3)-Os(2)-C(4)	89 (1)	Os(2)-Os(6)-C(14)	100.5 (8)
Os(5)-Os(2)-Os(6)	159.19 (5)	Os(2)-Os(3)-S(1)	56.8 (1)	Os(2)-Os(6)-C(15)	85.2 (7)
Os(2)-Os(3)-Os(4)	98.92 (4)	Os(2)-Os(3)-S(2)	51.9 (1)	Os(2)-Os(6)-C(16)	161.1 (8)
Os(2)-Os(3)-Os(6)	58.55 (3)	Os(2)-Os(3)-C(5)	129.4 (6)	Os(2)-Os(6)-C(17)	88.3 (7)
Os(4)-Os(3)-Os(6)	155.17 (4)	Os(2)-Os(3)-C(6)	121.9 (7)	Os(3)-Os(6)-C(14)	161.2 (8)
Os(1)-Os(4)-Os(3)	75.30 (3)	Os(4)-Os(3)-S(1)	51.5 (1)	Os(3)-Os(6)-C(15)	87.8 (7)
Os(1)-Os(5)-Os(2)	61.59 (3)	Os(4)-Os(3)-S(2)	86.2 (1)	Os(3)-Os(6)-C(16)	100.9 (8)
Os(2)-Os(6)-Os(3)	60.81 (3)	Os(4)-Os(3)-C(5)	119.6 (6)	Os(3)-Os(6)-C(17)	84.2 (7)
Os(2)-Os(1)-S(1)	56.3 (1)	Os(4)-Os(3)-C(6)	92.7 (6)	C(14)-Os(6)-C(15)	93 (1)
Os(2)-Os(1)-S(2)	51.5 (1)	Os(6)-Os(3)-S(1)	104.0 (1)	C(14)-Os(6)-C(16)	98 (1)
Os(2)-Os(1)-C(1)	126.2 (7)	Os(6)-Os(3)-S(2)	86.7 (1)	C(14)-Os(6)-C(17)	94 (1)
Os(2)-Os(1)-C(2)	127.6 (7)	Os(6)-Os(3)-C(5)	84.9 (6)	C(15)-Os(6)-C(16)	88 (1)
Os(4)-Os(1)-S(1)	51.7 (1)	Os(6)-Os(3)-C(6)	91.6 (6)	C(15)-Os(6)-C(17)	174.0 (8)
Os(4)-Os(1)-S(2)	86.3 (2)	S(1)-Os(3)-S(2)	83.0 (2)	C(16)-Os(6)-C(17)	95 (1)
Os(4)-Os(1)-C(1)	119.2 (8)	S(1)-Os(3)-C(5)	171.1 (6)	Os(1)-S(1)-Os(2)	69.7 (2)
Os(4)-Os(1)-C(2)	94.9 (7)	S(1)-Os(3)-C(6)	91.2 (7)	Os(1)-S(1)-Os(3)	93.5 (2)
Os(5)-Os(1)-S(1)	96.6 (1)	S(2)-Os(3)-C(5)	96.5 (7)	Os(1)-S(1)-Os(4)	74.3 (2)
Os(5)-Os(1)-S(2)	93.1 (2)	S(2)-Os(3)-C(6)	173.4 (7)	Os(2)-S(1)-Os(3)	69.0 (1)
Os(5)-Os(1)-C(1)	92.7 (8)	C(5)-Os(3)-C(6)	89.7 (9)	Os(2)-S(1)-Os(4)	126.0 (3)
Os(5)-Os(1)-C(2)	85.5 (7)	Os(1)-Os(4)-S(1)	54.1 (1)	Os(3)-S(1)-Os(4)	74.7 (2)
S(1)-Os(1)-S(2)	82.7 (2)	Os(1)-Os(4)-C(7)	117.4 (8)	Os(1)-S(2)-Os(2)	73.6 (2)
S(1)-Os(1)-C(1)	169.4 (8)	Os(1)-Os(4)-C(8)	146.3 (8)	Os(1)-S(2)-Os(3)	95.0 (2)
S(1)-Os(1)-C(2)	97.6 (7)	Os(1)-Os(4)-C(9)	88.3 (7)	Os(2)-S(2)-Os(3)	72.9 (2)
S(2)-Os(1)-C(1)	91.8 (8)	Os(3)-Os(4)-S(1)	53.8 (1)	Os(1)-C(1)-O(1)	173 (2)
S(2)-Os(1)-C(2)	178.6 (8)	Os(3)-Os(4)-C(7)	115.1 (8)	Os(1)-C(2)-O(2)	177 (2)
C(1)-Os(1)-C(2)	88 (1)	Os(3)-Os(4)-C(8)	94.3 (7)	Os(2)-C(3)-O(3)	174 (2)
Os(1)-Os(2)-S(1)	54.1 (1)	Os(3)-Os(4)-C(9)	115.1 (7)	Os(2)-C(4)-O(4)	172 (2)
Os(1)-Os(2)-S(2)	55.0 (1)	S(1)-Os(4)-C(7)	165.8 (8)	Os(3)-C(5)-O(5)	177 (2)
Os(1)-Os(2)-C(3)	122.8 (7)	S(1)-Os(4)-C(8)	93.7 (8)	Os(3)-C(6)-O(6)	175 (2)
Os(1)-Os(2)-C(4)	125.5 (7)	S(1)-Os(4)-C(9)	97.4 (7)	Os(4)-C(7)-O(7)	173 (2)
Os(3)-Os(2)-S(1)	54.3 (1)	C(7)-Os(4)-C(8)	96 (1)	Os(4)-C(8)-O(8)	170 (2)
Os(3)-Os(2)-S(2)	55.2 (2)	C(7)-Os(4)-C(9)	93 (1)	Os(4)-C(9)-O(9)	178 (2)
Os(3)-Os(2)-C(3)	114.9 (7)	C(8)-Os(4)-C(9)	86 (1)	Os(5)-C(10)-O(10)	177 (2)
Os(3)-Os(2)-C(4)	130.5 (8)	Os(1)-Os(5)-C(10)	85.9 (8)	Os(5)-C(11)-O(11)	172 (2)
Os(5)-Os(2)-S(1)	96.5 (1)	Os(1)-Os(5)-C(11)	100.9 (8)	Os(5)-C(12)-O(12)	176 (2)
Os(5)-Os(2)-S(2)	97.1 (2)	Os(1)-Os(5)-C(12)	164.6 (4)	Os(5)-C(13)-O(13)	176 (2)
Os(5)-Os(2)-C(3)	89.2 (7)	Os(1)-Os(5)-C(13)	86.3 (8)	Os(6)-C(14)-O(14)	175 (2)
Os(5)-Os(2)-C(4)	79.8 (8)	Os(2)-Os(5)-C(10)	84.9 (8)	Os(6)-C(15)-O(15)	173 (2)
Os(6)-Os(2)-S(1)	103.7 (1)	Os(2)-Os(5)-C(11)	161.4 (8)	Os(6)-C(16)-O(16)	176 (2)
Os(6)-Os(2)-S(2)	90.1 (1)	Os(2)-Os(5)-C(12)	103.8 (7)	Os(6)-C(17)-O(17)	176 (2)

contact is between oxygen atoms of the carbonyl ligands, O(4)⋯O(13) = 2.88 (2) Å.

Compound IV was obtained in low yield (~2.5%) and was shown by an X-ray crystallographic analysis to be an isomer of compound III. An ORTEP diagram of the molecular structure of IV is shown in Figure 2. Table V contains a list of final positional and thermal parameters. Interatomic distances and angles are given in Tables VI and VII, respectively. The hexaosmium cluster consists of a central group of four metal atoms, Os(1), Os(2), Os(3), and Os(4), which are arranged in the shape of a slightly nonplanar rhombus, Os(1)–Os(2) = 2.883 (1) Å and Os(2)–Os(3) = 2.854 (1) Å, and are similar to those in $Os_3(CO)_{12}$, Os–Os = 2.877 (3) Å.[15] However, the Os(1)–Os(4) and Os(3)–Os(4) lengths at 2.959 (1) and 2.970 (1) Å, respectively are significantly longer. This is probably due to the presence of bridging hydride ligands.[16] The angle between the planes defined by Os(1)–Os(2)–Os(3) and Os(1)–Os(3)–Os(4) is 16.3°. $Os(CO)_4$ groups bridge the Os(1)–Os(2) and Os(2)–Os(3) edges of the rhombus.

The sulfido ligand S(1) is a quadruple bridge bonded to all four metal atoms of the central rhombus, while sulfido ligand S(2) serves as triple bridge on the opposite side of the Os_4 rhombus and is bonded to Os(1), Os(2), and Os(3) only. As in III the osmium–sulfur bond distances span a considerable range from Os(2)–S(2) at 2.351 (6) Å to Os(2)–S(1) at 2.558 (6) Å. Curiously, the longest and shortest osmium–sulfur bond distances involve the same metal atom Os(2). Although a detailed nature of the osmium–sulfur bonding is not clear, it seems likely that there is a correlation between these two osmium–sulfur bonds. As found in other compounds, the osmium–sulfur bond lengths to the quadruply bridging sulfido ligands are on the average (Os–μ_4-S = 2.485 Å) significantly longer than those to the triply bridging sulfido ligand (Os–μ_3-S = 2.421 Å).[3] In compound IV both sulfido ligands serve as four electron donors and each metal has an 18-electron configuration. This is different from I where the quadruply bridging sulfido ligand serves as a six-electron donor. This difference is compensated for in IV by the existence of an additional metal–metal bond. Compound IV contains two equivalent hydride ligands (δ −12.04) which are believed to bridge the Os(1)–Os(4) and Os(3)–Os(4) internuclear separations (vide supra). The shortest intermolecular contact is between oxygen atoms of the carbonyl ligands, O(11)⋯O(14) = 2.88 (3) Å.

Although compounds III and IV are isomers, we have not been able to interconvert them under the reaction conditions. Thus, it is possible that they are formed by different mechanisms.

Evidence concerning the mechanism of formation of compound III was obtained from a product obtained from

Table VIII. Positional and Thermal Parameters and Their Esds for $H_2Os_6(CO)_{18}(\mu_4\text{-}S)(\mu_3\text{-}S)$, V[a]

atom	*x*	*y*	*z*	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)	*B*eqv)
Os(1)	0.9638 (1)	0.7084 (1)	0.927 94 (8)	1.93 (6)	2.54 (6)	2.82 (6)	−0.27 (6)	1.26 (5)	0.13 (6)	2.40 (3)
Os(2)	0.9827 (1)	0.8608 (1)	0.826 07 (8)	1.48 (6)	3.08 (7)	2.30 (6)	0.16 (7)	0.55 (5)	−0.02 (6)	2.27 (3)
Os(3)	1.2294 (1)	0.8135 (1)	0.854 07 (8)	1.42 (6)	2.79 (6)	2.31 (6)	−0.07 (6)	0.63 (5)	0.12 (6)	2.16 (3)
Os(4)	1.2071 (1)	0.7224 (1)	0.996 29 (8)	1.92 (7)	3.66 (7)	2.72 (6)	0.47 (7)	0.76 (6)	0.99 (6)	2.75 (3)
Os(5)	0.7571 (1)	0.8033 (1)	0.869 59 (8)	1.44 (6)	4.01 (8)	3.21 (7)	−0.29 (7)	0.67 (6)	−0.71 (7)	2.87 (4)
Os(6)	1.1577 (1)	0.9356 (1)	0.738 81 (8)	2.34 (7)	2.95 (7)	2.31 (6)	−0.28 (7)	0.59 (6)	0.46 (6)	2.52 (3)
S(1)	1.0883 (9)	0.8530 (7)	0.949 7 (5)	1.5 (4)	3.3 (4)	2.5 (4)	−0.6 (4)	0.2 (3)	0.8 (4)	2.4 (2)
S(2)	1.0653 (9)	0.7084 (7)	0.813 1 (5)	2.3 (4)	3.4 (5)	2.2 (4)	0.3 (4)	1.0 (3)	−0.8 (4)	2.6 (2)

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
O(1)	0.855 (3)	0.515 (2)	0.892 (2)	7.3 (9)	C(1)	0.895 (4)	0.583 (3)	0.909 (2)	4.1 (10)
O(2)	0.837 (3)	0.714 (2)	1.068 (1)	4.6 (7)	C(2)	0.885 (4)	0.710 (3)	1.013 (2)	3.2 (8)
O(3)	0.915 (3)	1.066 (2)	0.867 (1)	5.5 (7)	C(3)	0.941 (4)	0.989 (3)	0.848 (2)	2.9 (8)
O(4)	0.845 (3)	0.867 (2)	0.684 (2)	6.5 (8)	C(4)	0.897 (4)	0.871 (3)	0.742 (2)	3.0 (8)
O(5)	1.411 (3)	0.736 (2)	0.753 (1)	4.9 (7)	C(5)	1.344 (3)	0.768 (2)	0.791 (2)	2.2 (7)
O(6)	1.418 (3)	0.955 (2)	0.911 (2)	5.5 (7)	C(6)	1.342 (3)	0.904 (2)	0.890 (2)	2.3 (7)
O(7)	1.348 (4)	0.536 (3)	1.010 (2)	8.3 (10)	C(7)	1.293 (4)	0.611 (3)	1.009 (2)	4.2 (10)
O(8)	1.401 (3)	0.849 (2)	1.062 (2)	7.0 (9)	C(8)	1.319 (4)	0.800 (3)	1.041 (2)	3.5 (9)
O(9)	1.093 (3)	0.706 (2)	1.143 (1)	4.5 (6)	C(9)	1.135 (3)	0.714 (3)	1.086 (2)	3.1 (8)
O(10)	0.794 (3)	0.948 (2)	0.993 (2)	6.2 (8)	C(10)	0.782 (4)	0.891 (3)	0.944 (2)	3.9 (9)
O(11)	0.569 (3)	0.707 (2)	0.961 (2)	5.8 (8)	C(11)	0.637 (4)	0.750 (3)	0.923 (2)	4.0 (10)
O(12)	0.590 (3)	0.924 (2)	0.784 (2)	6.7 (9)	C(12)	0.652 (3)	0.880 (2)	0.818 (2)	2.4 (7)
O(13)	0.759 (3)	0.648 (2)	0.756 (2)	5.5 (7)	C(13)	0.753 (4)	0.713 (3)	0.803 (2)	3.4 (9)
O(14)	1.010 (3)	1.064 (2)	0.640 (2)	7.1 (9)	C(14)	1.062 (4)	1.012 (3)	0.678 (2)	4.2 (10)
O(15)	1.113 (3)	0.762 (2)	0.641 (1)	4.2 (6)	C(15)	1.129 (4)	0.821 (3)	0.680 (2)	3.0 (8)
O(16)	1.397 (3)	0.971 (2)	0.665 (2)	6.0 (8)	C(16)	1.298 (4)	0.953 (3)	0.697 (2)	3.8 (9)
O(17)	1.202 (3)	1.089 (2)	0.851 (1)	4.4 (6)	C(17)	1.183 (4)	1.034 (3)	0.808 (2)	3.2 (8)

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(h^2a^{*2}B(1,1) + k^2b^{*2}B(2,2) + l^2c^{*2}B(3,3) + 2hka^*b^*B(1,2) + 2hla^*c^*B(1,3) + 2klb^*c^*B(2,3))]$.

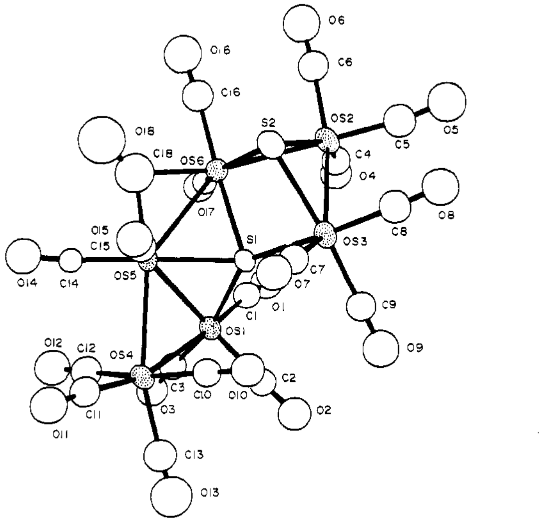

Figure 3. An ORTEP diagram of $H_2Os_6(CO)_{18}(\mu_4\text{-}S)(\mu_3\text{-}S)$, V, showing 50% probability thermal-motion ellipsoids.

Table IX. Interatomic Distances (Å) with Esds for $H_2Os_6(CO)_{18}(\mu_4\text{-}S)(\mu_3\text{-}S)$, V

Os(1)–Os(4)	2.869 (1)	Os(5)–S(1)	2.369 (4)
Os(1)–Os(5)	2.945 (1)	Os(5)–C(14)	1.89 (1)
Os(2)–Os(3)	2.977 (1)	Os(5)–C(15)	1.85 (2)
Os(2)–Os(6)	2.799 (1)	Os(5)–C(18)	2.13 (3)
Os(4)–Os(5)	2.841 (1)	Os(6)–S(1)	2.407 (4)
Os(5)–Os(6)	2.896 (1)	Os(6)–S(2)	2.475 (4)
Os(1)···Os(3)	4.663 (1)	Os(6)–C(16)	1.94 (2)
Os(1)···Os(6)	4.073 (1)	Os(6)–C(17)	1.81 (1)
Os(3)···Os(5)	4.405 (1)	Os(6)–C(18)	2.10 (2)
Os(3)···Os(6)	3.628 (1)	C(1)–O(1)	1.17 (2)
Os(4)···Os(6)	5.454 (1)	C(2)–O(2)	1.13 (2)
Os(1)–S(1)	2.458 (3)	C(3)–O(3)	1.16 (2)
Os(1)–C(1)	1.90 (2)	C(4)–O(4)	1.15 (2)
Os(1)–C(2)	1.91 (2)	C(5)–O(5)	1.21 (2)
Os(1)–C(3)	1.86 (2)	C(6)–O(6)	1.13 (2)
Os(2)–S(2)	2.387 (4)	C(7)–O(7)	1.14 (2)
Os(2)–C(4)	1.91 (2)	C(8)–O(8)	1.17 (2)
Os(2)–C(5)	1.84 (2)	C(9)–O(9)	1.13 (2)
Os(2)–C(6)	1.93 (2)	C(10)–O(10)	1.15 (2)
Os(3)–S(1)	2.438 (3)	C(11)–O(11)	1.17 (2)
Os(3)–S(2)	2.448 (5)	C(12)–O(12)	1.18 (2)
Os(3)–C(7)	1.93 (2)	C(13)–O(13)	1.06 (2)
Os(3)–C(8)	1.87 (2)	C(14)–O(14)	1.17 (2)
Os(3)–C(9)	1.91 (2)	C(15)–O(15)	1.18 (2)
Os(4)–C(10)	1.93 (2)	C(16)–O(16)	1.12 (2)
Os(4)–C(11)	1.92 (2)	C(17)–O(17)	1.21 (2)
Os(4)–C(12)	1.91 (2)	C(18)–O(18)	1.17 (3)
Os(4)–C(13)	2.00 (2)		

the photolysis of compound I (Scheme I). This product has the formula $H_2Os_6(CO)_{18}(\mu_4\text{-}S)(\mu_3\text{-}S)$, V, and was characterized by IR, ^1H NMR, and a single-crystal X-ray diffraction analysis. An ORTEP diagram of its structure is shown in Figure 3. Table VIII lists final positional and thermal parameters. Tables IX and X list interatomic distances and angles, respectively. Structurally, compound V is similar to III except that it contains one additional carbonyl ligand and one less metal–metal bond. The three metal atoms Os(2), Os(3), and Os(6) are joined by a triply bridging sulfido ligand S(2) and two metal–metal bonds, Os(2)–Os(3) = 2.977 (1) Å and Os(2)–Os(6) = 2.799 (1) Å. The longer length of the Os(2)–Os(3) bond is probably due to the presence of one of the bridging hydride ligands.[16] These three metal atoms contain eight linear terminal carbonyl groups arranged such that Os(2) and Os(3) contain three each and Os(6) contains two. These metal atoms are linked to a second group of three metal atoms Os(1), Os(4), and Os(5) by the quadruply bridging sulfido ligand S(1) and the metal–metal bond Os(5)–Os(6) = 2.896 (1) Å. The three Os–Os internuclear separations Os(1)–Os(4) = 2.869 (1) Å, Os(1)–Os(5) = 2.945 (1) Å, and Os(5)–Os(6) = 2.896 (1) Å are similar to those found in $Os_3(CO)_{12}$.[15] The longest separation Os(1)–Os(5) probably contains a bridging hydride ligand. This group of three metal atoms contains nine linear terminal carbonyl groups arranged such that Os(4) contains four, Os(1) contains three, and Os(5) contains two. One carbonyl ligand C(18)–O(18)

Table X. Interatomic Angles (deg) with Esds for $H_2Os_6(CO)_{18}(\mu_4\text{-}S)(\mu_3\text{-}S)$, V

Os(4)-Os(1)-Os(5)	58.48 (2)	Os(1)-Os(4)-C(12)	86.8 (5)	Os(1)-S(1)-Os(5)	75.2 (1)
Os(3)-Os(2)-Os(6)	77.76 (2)	Os(1)-Os(4)-C(13)	97.2 (5)	Os(1)-S(1)-Os(6)	113.7 (1)
Os(1)-Os(4)-Os(5)	62.09 (2)	Os(5)-Os(4)-C(10)	85.7 (5)	Os(3)-S(1)-Os(5)	132.8 (2)
Os(1)-Os(5)-Os(4)	59.43 (2)	Os(5)-Os(4)-C(11)	102.7 (5)	Os(3)-S(1)-Os(6)	97.0 (1)
Os(1)-Os(5)-Os(6)	88.42 (2)	Os(5)-Os(4)-C(12)	87.3 (6)	Os(5)-S(1)-Os(6)	74.7 (1)
Os(4)-Os(5)-Os(6)	143.87 (3)	Os(5)-Os(4)-C(13)	159.2 (5)	Os(2)-S(2)-Os(3)	76.0 (1)
Os(2)-Os(6)-Os(5)	136.94 (3)	Os(1)-Os(5)-S(1)	53.80 (9)	Os(2)-S(2)-Os(6)	70.3 (1)
Os(4)-Os(1)-S(1)	89.48 (9)	Os(1)-Os(5)-C(14)	115.9 (4)	Os(3)-S(2)-Os(6)	95.0 (1)
Os(4)-Os(1)-C(1)	175.3 (5)	Os(1)-Os(5)-C(15)	135.8 (5)	Os(1)-C(1)-O(1)	170 (1)
Os(4)-Os(1)-C(2)	89.8 (5)	Os(1)-Os(5)-C(18)	126.8 (6)	Os(1)-C(2)-O(2)	179 (1)
Os(4)-Os(1)-C(3)	87.5 (5)	Os(4)-Os(5)-S(1)	91.99 (10)	Os(1)-C(3)-O(3)	177 (2)
Os(5)-Os(1)-S(1)	51.04 (9)	Os(4)-Os(5)-C(14)	87.4 (5)	Os(2)-C(4)-O(4)	174 (2)
Os(5)-Os(1)-C(1)	118.6 (5)	Os(4)-Os(5)-C(15)	92.8 (5)	Os(2)-C(5)-O(5)	173 (2)
Os(5)-Os(1)-C(2)	131.4 (4)	Os(4)-Os(5)-C(18)	169.3 (6)	Os(2)-C(6)-O(6)	175 (2)
Os(5)-Os(1)-C(3)	117.5 (5)	Os(6)-Os(5)-S(1)	53.27 (10)	Os(3)-C(7)-O(7)	177 (1)
Os(3)-Os(2)-S(2)	52.92 (11)	Os(6)-Os(5)-C(14)	124.1 (5)	Os(3)-C(8)-O(8)	178 (2)
Os(3)-Os(2)-C(4)	117.0 (6)	Os(6)-Os(5)-C(15)	101.1 (5)	Os(3)-C(9)-O(9)	178 (2)
Os(3)-Os(2)-C(5)	95.3 (6)	Os(6)-Os(5)-C(18)	46.2 (6)	Os(4)-C(10)-O(10)	179 (1)
Os(3)-Os(2)-C(6)	148.9 (5)	Os(2)-Os(6)-S(1)	86.95 (8)	Os(4)-C(11)-O(11)	175 (2)
Os(6)-Os(2)-S(2)	56.34 (9)	Os(2)-Os(6)-S(2)	53.40 (9)	Os(4)-C(12)-O(12)	177 (1)
Os(6)-Os(2)-C(4)	93.7 (5)	Os(2)-Os(6)-C(16)	90.2 (5)	Os(4)-C(13)-O(13)	177 (2)
Os(6)-Os(2)-C(5)	169.8 (6)	Os(2)-Os(6)-C(17)	105.4 (5)	Os(5)-C(14)-O(14)	173 (1)
Os(6)-Os(2)-C(6)	94.2 (5)	Os(2)-Os(6)-C(18)	155.5 (6)	Os(5)-C(15)-O(15)	177 (1)
Os(2)-Os(3)-S(1)	82.48 (9)	Os(5)-Os(6)-S(1)	52.07 (8)	Os(6)-C(16)-O(16)	175 (2)
Os(2)-Os(3)-S(2)	51.08 (9)	Os(5)-Os(6)-S(2)	101.18 (10)	Os(6)-C(17)-O(17)	176 (1)
Os(2)-Os(3)-C(7)	142.0 (5)	Os(5)-Os(6)-C(16)	128.9 (5)	Os(5)-C(18)-O(18)	135 (2)
Os(2)-Os(3)-C(8)	88.9 (6)	Os(5)-Os(6)-C(17)	95.5 (5)	Os(6)-C(18)-O(18)	135 (2)
Os(2)-Os(3)-C(9)	124.2 (5)	Os(5)-Os(6)-C(18)	47.3 (7)	Os(5)-C(18)-Os(6)	86 (1)
Os(1)-Os(4)-C(10)	86.1 (5)	Os(1)-S(1)-Os(3)	144.5 (2)		
Os(1)-Os(4)-C(11)	164.5 (5)				

serves as a symmetrical bridge across Os(5)–Os(6) bond, ν(CO) 1844 cm^{-1}.

As in III, the metal–sulfur bond distances in V span a considerable range, 2.369 (4)–2.475 (4) Å. Similarly, the quadruply bridging sulfido ligand contains a highly distorted tetrahedral geometry with bond angles ranging from 74.7 (1) to 144.5 (2)°. If the quadruply bridging sulfido ligand serves as a six-electron donor, each atom can obtain an 18-electron configuration. Compound V contains two hydride ligands, δ −13.69 (s) and −16.73 (s). These are believed to bridge the Os(2)–Os(3) and Os(1)–Os(5) bonds (vide supra).

Dibenzyl was also observed as a product of the photolysis reaction, suggesting that a carbon–sulfur bond homolysis mechanism is involved. However, attempts to observe radicals by photolysis of a sample at low temperature in an EPR spectrometer were unsuccessful.

Discussion

The formation of toluene and non-hydride-containing sulfidoosmium carbonyl clusters and dibenzyl and hydride-containing sulfidoosmium carbonyl clusters suggests that two modes of decomposition occur in the pyrolysis of I at 150 °C.

In this report we have described the reaction that appears to involve homolysis of the carbon–sulfur bond and formation of benzyl radicals and $[HOs_3(CO)_{10}S]\cdot$ radicals. The product, dibenzyl, was apparently formed by the combination of benzyl radicals. To eliminate the possibility that the dibenzyl was formed from a metal-induced transformation of the toluene product, the pyrolysis of I was also performed in toluene-d_8 solvent. The dibenzyl obtained from this reaction was found to be predominantly dibenzyl-d_0 (80%). However, there was also formed significant amounts of dibenzyl-d_7 (20%). This product could be formed by deuterium abstraction from the toluene-d_8 solvent by the benzyl radicals and a subsequent combination of the benzyl-d_7 radical with a benzyl-d_0 radical. In this regard, the dibenzyl-d_7 product is still further evidence for radical intermediates. Under photolytic conditions the carbon–sulfur bond homolysis reaction is the dominant one.

All the hydride-containing clusters contain two hydride ligands, six osmium atoms, and two sulfido ligands. These products are apparently formed by the coupling of two $[HOs_3(CO)_{10}(S)]\cdot$ fragments. None of the hexaosmium clusters contain more than 18 carbonyl ligands, and thus, it is possible that two carbonyl ligands are lost rapidly. Although no evidence is available, it is possible that this may occur before the triosmium units couple. For example, loss of CO from $[HOs_3(CO)_{10}(S)]\cdot$ to give $[HOs_3(CO)_9(S)]\cdot$ would be favored by formation a triply bridging sulfido ligand. This could be a facile process since it is known that carbonyl ligands are readily displaced in metal carbonyl radical complexes.[19] Details of the process which would lead to the coupling two $[HOs_3(CO)_9(S)]\cdot$ fragments to yield compound V are not clear, but formation of a coordinate bond between a sulfido ligand in one cluster and a metal atom in the second cluster seems most likely. This would be followed by conversion of the sulfido ligand into an edge-bridging ligand in the first cluster and formation of a second metal-sulfur bond to the second cluster. This could cleave a metal–metal bond in the second cluster, induce formation of the metal-metal bond between the clusters, and shift one carbonyl ligand from the second cluster toward the first (i.e., formation of the carbonyl bridge). The precise sequence of these events cannot be predicted at this time, but it should be pointed out that a similar series of transformations has been observed in the decarbonylation and coupling of the two clusters of the compound $HOs_3(CO)_9(\mu_3\text{-}S)(\mu\text{-}HC{=}NPh)$.[6]

The formation of compound III from V involves simple decarbonylation, probably from the $Os(CO)_4$ unit, and formation of a metal–metal bond between atoms Os(4) and Os(6); see Figure 3. A simple mechanism for the formation

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of compound IV is not apparent, and we do not wish to speculate upon this at this time.

The formation of the organic product, toluene, and the non-hydride containing cluster compounds could also proceed via radical intermediates. This could involve hydrogen atom abstraction either from I or the $[HOs_3(CO)_9(S)]\cdot$ radicals by the benzyl radicals. Alternatively, the toluene could be formed via an intramolecular reductive elimination involving metal-induced cleavage of the carbon–sulfur bond. Evidence supporting such a mechanism was obtained from the compound $HRu_3(CO)_9(\mu\text{-}PPh_2)$ which eliminates benzene at 80 °C.[20] Studies focusing on the mechanism of toluene elimination from I are currently in progress.

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Registry No. I, 85442-97-3; III, 85442-98-4; IV, 85442-99-5; V, 85443-00-1; dibenzyl, 103-29-7.

Supplementary Material Available: Tables of structure factor amplitudes for all three structures (37 pages). Ordering information is given on any current masthead page.

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Synthesis and Molecular and Crystal Structure of 2,2′,5,5′-Tetramethylbiarsolyl

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2,2′,5,5′-Tetramethylbiarsolyl has been prepared by treating 1-phenyl-2,5-dimethylarsole with lithium followed by iodine. Yellow crystals of the nonthermochromic diarsine form in the $P2/c$ space group with $Z = 4$, $a = 13.247$ (6) Å, $b = 7.271$ (3) Å, $c = 14.534$ (5) Å, and $\beta = 114.79$ (3)°. The full structure has been determined and has been compared with that of the thermochromic 2,2′,5,5′-tetramethylbistibolyl.

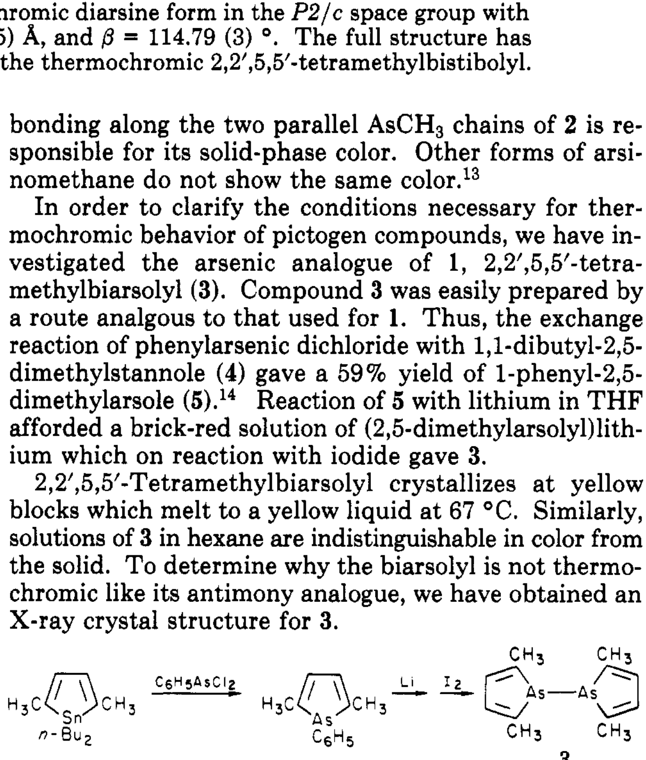
Introduction

We recently reported on the synthesis of 2,2′,5,5′-tetramethylbistibolyl (1), which displays interesting thermochromic behavior.[1] Crystals of 1 appear purple-blue to reflected light but melt reversibly to a pale yellow oil. Similarly, solutions of 1 are pale yellow. The crystal structure of 1 shows that all of the antimony atoms are aligned in a linear chain with very short intermolecular Sb–Sb···Sb–Sb separation as illustrated in Figure 1. Evidently the solid-phase color is associated with intermolecular interaction along this chain.[2]

Thermochromic behavior similar to that of 1 has been found for several other distibines[3-5] and dibismuthines,[3,6-8] although little structural data are yet available.[9,10] On the other hand, the blue-black ladder polymer of arsinomethane 2 has a solid-phase structure strikingly similar to that of 1 (see Figure 1).[11,12] Apparently extended bonding along the two parallel $AsCH_3$ chains of 2 is responsible for its solid-phase color. Other forms of arsinomethane do not show the same color.[13]

In order to clarify the conditions necessary for thermochromic behavior of pictogen compounds, we have investigated the arsenic analogue of 1, 2,2′,5,5′-tetramethylbiarsolyl (3). Compound 3 was easily prepared by a route analgous to that used for 1. Thus, the exchange reaction of phenylarsenic dichloride with 1,1-dibutyl-2,5-dimethylstannole (4) gave a 59% yield of 1-phenyl-2,5-dimethylarsole (5).[14] Reaction of 5 with lithium in THF afforded a brick-red solution of (2,5-dimethylarsolyl)lithium which on reaction with iodide gave 3.

2,2′,5,5′-Tetramethylbiarsolyl crystallizes at yellow blocks which melt to a yellow liquid at 67 °C. Similarly, solutions of 3 in hexane are indistinguishable in color from the solid. To determine why the biarsolyl is not thermochromic like its antimony analogue, we have obtained an X-ray crystal structure for 3.



4 5 3

X-ray Crystallography

Crystals of 2,2′,5,5′-tetramethyl-1,1′-biarsolyl were obtained by sublimation at 40 °C. A crystal was mounted on a Syntex $P2_1$

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