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Cluster synthesis. 3. The role of sulfido ligands in the synthesis of high nuclearity metal carbonyl cluster compounds. The crystal and molecular structure of Os4(CO)12(.mu.3-S) and Os7(CO)19(.mu.4-S)

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Cluster Synthesis. 3. The Role of Sulfido Ligands in the Synthesis of High Nuclearity Metal Carbonyl Cluster Compounds. The Crystal and Molecular Structures of $Os_4(CO)_{12}(\mu_3\text{-}S)$ and $Os_7(CO)_{19}(\mu_4\text{-}S)$

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The cluster $Os_7(CO)_{19}(\mu_4\text{-}S)$, II, has been synthesized in 23% yield by the reaction of $Os_4(CO)_{12}(\mu_3\text{-}S)$, I, with $Os_3(CO)_{10}(NCMe)_2$, III, in refluxing octane solvent for 3 h. II can also be made in 4% yield by reaction of $H_2Os_3(CO)_9(\mu_3\text{-}S)$ with $HOs_3(CO)_{10}(OMe)$ in refluxing nonane solvent for 22 h. The crystal and molecular structures of I and II have been determined by single-crystal X-ray diffraction measurements. For I: space group $C2/c$, $a = 29.110$ (13) Å, $b = 8.491$ (2) Å, $c = 16.610$ (6) Å, $\beta = 104.98$ (3)°, $V = 3966$ (4) Å^3, $Z = 8$, $\rho_{calcd} = 3.78$ g/cm^3. The structure was solved by the heavy-atom method and refined (1902 reflections, $F_o^2 \geq 3.0\sigma(F^2)$) to the final residuals $R_1 = 0.031$ and $R_2 = 0.038$. The molecule consists of a tetrahedral cluster of four osmium atoms with a triply bridging sulfido ligand on one of the triangular faces. Each metal atom contains three linear terminal carbonyl ligands. For II: space group $P2_1$, $a = 10.107$ (4) Å, $b = 11.569$ (5) Å, $c = 12.791$ (5) Å, $\beta = 90.38$ (4)°, $V = 1495$ (2) Å^3, $Z = 2$, $\rho_{calcd} = 4.21$ g/cm^3. The structure was solved by a combination of direct methods and difference Fourier techniques and refined (2121 reflections, $F_o^2 \geq 3.0\sigma(F_2)$) to the final residuals $R_1 = 0.036$ and $R_2 = 0.039$. II consists of a cluster of seven osmium atoms and one quadruply bridging sulfido ligand and can be visualized as two deltahedra, one an octahedron consisting of a square pyramid of five metal atoms with the quadruply bridging sulfido ligand spanning the square base and the other a trigonal bipyramid of five osmium atoms, which share one triangular group of three osmium atoms. There are 18 linear terminal carbonyl ligands and one semibridging carbonyl ligand across one of two "formal" donor–acceptor metal–metal bonds in the cluster. It is believed that the combination of I and III is facilitated by formation of a coordinate bond between the sulfido ligand in I and a metal atom in III.

Introduction

The synthesis of high nuclearity transition-metal carbonyl cluster compounds has become a subject of increasing interest and importance in recent years.[1-7] It has been suggested that cluster compounds may serve as models for surfaces and the reactions that occur at polynuclear metal sites in clusters may resemble those that occur on surfaces.[7-9] Presumably, the larger the cluster the more closely it will resemble a surface.

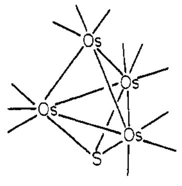
Systematic routes for the synthesis of high nuclearity cluster compounds have been slow to emerge. The more commonly used procedures involve pyrolytic decarbonylation of metal carbonyl compounds and redox condensation of metal complexes in different oxidation sites.[5,10] Clusters can also be made from low nuclearity metal complexes by utilizing ligands which contain uncoordinated pairs of electrons as coupling agents (eq 1). The

$$M_mE{:} + M'_n \rightarrow M_m(\mu\text{-}E)M'_n \qquad (1)$$

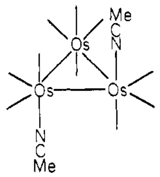
simplest types of such ligands are single atom ligands derived from elements of the main groups, (e.g., P, As, S, Se, etc.).[11]

In recent studies we have synthesized a number of new high nuclearity metal carbonyl cluster compounds by using sulfido ligands to couple small clusters.[12-15]

Herein we report the structural analysis of $Os_4(CO)_{12}(\mu_3\text{-}S)$, I, and the synthesis and structural analysis of the new cluster $Os_7(CO)_{19}(\mu_4\text{-}S)$, II, formed by the reaction of I with $Os_3(CO)_{10}(NCMe)_2$, III.



I



III

Experimental Section

All reactions were performed under a prepurified nitrogen atmosphere. $Os_3(CO)_{10}(NCMe)_2$,[16] $Os_4(CO)_{12}(\mu_3\text{-}S)$,[17] $H_2Os_3(CO)_9S$,[18] and $HOs_3(CO)_{10}(OCH_3)$[19] were prepared as previously

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Table I. Crystallographic Data for X-ray Diffraction Studies

	I	III
	(A) Crystal Data	
formula	$Os_4SO_{12}C_{12}$	$Os_7SO_{19}C_{19}$
temp, ±3 °C	25	23
space group	$C2/c$, No. 15	$P2_1$, No. 4
a, Å	29.110 (13)	10.107 (4)
b, Å	8.491 (2)	11.569 (5)
c, Å	16.610	12.791 (5)
α, deg	90.00	90.00
β, deg	104.93 (3)	90.38 (4)
γ, deg	90.00	90.00
V, Å^3	3966 (4)	1495 (2)
M_r		1895.7
Z	8	2
ρ_{calcd}, g cm^3	3.78	4.21
	(B) Measurement of Intensity Data	
radiation	Mo K$\bar{\alpha}$ (0.71073 Å)	Mo K$\bar{\alpha}$ (0.71073 Å)
monochromator	graphite	graphite
detector aperture (mm)		
horizontal (A + B tan θ)		
A	3.0	3.0
B	1.0	1.0
vertical	4.0	4.0
cryst faces	$10\bar{1}$, $\bar{1}01$, $\bar{4}0\bar{1}$, 401 111, $\bar{1}\bar{1}\bar{1}$, $01\bar{1}$, $0\bar{1}1$	$\bar{1}0\bar{2}$, 102, $\bar{1}\bar{2}\bar{1}$ 121, $1\bar{2}2$, 102 $\bar{1}02$, 100, $\bar{1}00$
cryst size, mm	0.04 × 0.11 × 0.32	0.08 × 0.14 × 0.14
cryst orientatn directn, deg from ϕ axis	b, 3.76	normal to $\bar{2}01$, 6.85
reflctns measd	$h, k, \pm l$	$h, k, \pm l$
max 2θ, deg	46	48
scan type	moving crystal-stationary counter	moving crystal-stationary counter
ω-scan width		
(A + 0.347 tan θ), deg; A =	0.75	0.95
background	$^1/_4$ additional scan at each end of scan	$^1/_4$ additional scan at each end of scan
ω-scan rate (variable)		
max deg/min	10.00	10.0
min, deg/min	1.25	1.4
no. of reflctns measd	2738	2914
data used ($F^2 \geqslant 3.0\sigma(F^2)$)	1902	2121
	(C) Treatment of Data	
abs correctn		
coeff, cm^{-1}	257.48	298.1
grid	14 × 8 × 8	10 × 12 × 8
transmissn coeff		
max	0.340	0.200
min	0.060	0.019
P factor	0.01	0.02
final residuals		
R_1	0.031	0.036
R_2	0.038	0.039
esd of unit weight	2.21	1.65
largest shift/error value of final cycle	0.13	0.25

reported. Infrared spectra were recorded on a Nicolet 7199 FT-IR spectrophotometer.

Preparation of $Os_7(CO)_{19}(\mu_4\text{-}S)$, II. Method a. To $Os_4(CO)_{12}(\mu_3\text{-}S)$ (20 mg, 0.02 mmol) dissolved in 30 mL of octane was added $Os_3(CO)_{10}(NCMe)_2$ (28 mg, 0.03 mmol), and the mixture was heated to reflux for 3 h. The solvent was removed in vacuo, and the yellow-brown residue was placed on silica TLC plates. Elution with CH_2Cl_2/hexane (10/40) separated the unreacted I (1 mg, 5%) from the orange-brown $Os_7(CO)_{19}(\mu_4\text{-}S)$ (9 mg, 23%): IR ν(CO) (hexane) 2074 (s), 2065 (s), 2037 (s), 2014 (w), 2005 (w), 1992 (w) cm^{-1}.

Method b. A mixture of $HOs_3(CO)_{10}(OCH_3)$ (100 mg, 0.11 mmol) and $H_2Os_3(CO)_9S$ (98 mg, 0.11 mmol) in 30 mL of nonane was heated to reflux for 22 h. The solution turned yellow-brown, and the solvent was removed in vacuo. The orange-brown product III was isolated by TLC using CH_2Cl_2/hexane (15/85) and crystallized from benzene/hexane at 5 °C: yield 8 mg (4%); mp 226 °C dec.

Crystallographic Analyses. Crystals of I suitable for X-ray diffraction measurements were grown from hexanes solutions by cooling to −20 °C by Dr. Li-Wu Yang. Crystals of II suitable for diffraction measurements were obtained by cooling benzene/hexane solutions to 5 °C. The crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on an Enraf-Nonius CAD-4 fully automated diffractometer using graphite-monochromated 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.

For I the systematic absences for hkl, $h + k = 2n + 1$, and for $h0l$, $l = 2n + 1$, are indicative of either of the space groups $C2/c$ or Cc. The structure was solved and satisfactorily refined in the space group $C2/c$. An attempted solution in the space group Cc yielded a poor quality structure that did not refine well.

For II the space group $P2_1$ was chosen on the basis of the systematic absences $0k0$, $k = 2n + 1$, observed in the data. II

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Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Os_4(CO)_{12}(\mu_3\text{-}S)$, I[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)	0.106 47 (3)	0.0301 (1)	0.157 01 (5)	3.11 (3)	2.36 (3)	2.14 (3)	0.24 (3)	0.72 (3)	0.04 (3)	2.53 (2)
Os(2)	0.069 72 (3)	−0.2828 (1)	0.160 73 (5)	2.63 (3)	2.99 (4)	2.81 (4)	−0.39 (3)	0.85 (3)	−0.19 (4)	2.78 (2)
Os(3)	0.157 47 (3)	−0.1954 (1)	0.274 94 (5)	3.01 (3)	2.67 (4)	1.68 (3)	−0.01 (3)	0.58 (3)	0.07 (3)	2.46 (2)
Os(4)	0.150 92 (2)	−0.2279 (1)	0.105 61 (5)	2.82 (3)	2.56 (4)	1.87 (3)	−0.04 (3)	0.78 (3)	−0.21 (3)	2.39 (2)
S	0.080 8 (2)	−0.0890 (7)	0.268 0 (3)	3.6 (2)	3.6 (3)	2.7 (2)	0.2 (2)	1.5 (2)	0.1 (2)	3.2 (1)

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
O(1)	0.1546 (5)	0.314 (2)	0.2600 (9)	4.9 (4)	C(1)	0.1357 (7)	0.209 (3)	0.219 (1)	3.7 (5)
O(2)	0.0088 (5)	0.183 (2)	0.0929 (10)	5.9 (4)	C(2)	0.0462 (7)	0.130 (3)	0.114 (1)	4.0 (5)
O(3)	0.1398 (5)	0.145 (2)	0.0063 (10)	5.1 (4)	C(3)	0.1278 (6)	0.094 (3)	0.063 (1)	3.8 (5)
O(4)	0.0526 (5)	−0.557 (2)	0.2731 (11)	6.8 (4)	C(4)	0.0571 (7)	−0.452 (3)	0.232 (1)	4.0 (5)
O(5)	0.0624 (5)	−0.513 (2)	0.0182 (11)	6.5 (4)	C(5)	0.0665 (7)	−0.422 (3)	0.071 (1)	4.2 (5)
O(6)	−0.0336 (5)	−0.186 (2)	0.0857 (10)	5.8 (4)	C(6)	0.0042 (7)	−0.226 (3)	0.114 (1)	3.7 (5)
O(7)	0.2086 (5)	0.055 (2)	0.3990 (10)	5.3 (4)	C(7)	0.1905 (6)	−0.044 (3)	0.353 (1)	3.4 (4)
O(8)	0.1512 (5)	−0.448 (2)	0.4062 (9)	5.1 (4)	C(8)	0.1540 (6)	−0.354 (3)	0.359 (1)	3.9 (5)
O(9)	0.2526 (5)	−0.337 (2)	0.2672 (10)	5.0 (4)	C(9)	0.2155 (6)	−0.282 (3)	0.266 (1)	3.7 (5)
O(10)	0.1878 (5)	−0.565 (2)	0.1028 (10)	5.5 (4)	C(10)	0.1745 (6)	−0.430 (3)	0.101 (1)	3.4 (4)
O(11)	0.1085 (5)	−0.211 (2)	−0.0843 (9)	4.8 (3)	C(11)	0.1259 (7)	−0.220 (3)	−0.011 (1)	4.2 (5)
O(12)	0.2446 (5)	−0.086 (2)	0.0921 (9)	4.9 (4)	C(12)	0.2092 (6)	−0.138 (3)	0.097 (1)	3.5 (5)

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}\{h^2a^{*2}B(1,1) + k^2b^{*2}B(2,2) + l^2c^{*2}B(3,3) + 2hka^*b^*B(1,2) + 2hla^*c^*B(1,3) + 2klb^*c^*B(2,3)\}]$.

Table III. Interatomic Distances (Å) with Esds for $Os_4(CO)_{12}(\mu_3\text{-}S)$, I

Os(1)-Os(2)	2.870 (1)	Os(4)-C(10)	1.855 (15)
Os(1)-Os(3)	2.864 (1)	Os(4)-C(11)	1.880 (16)
Os(2)-Os(3)	2.858 (1)	Os(4)-C(12)	1.899 (14)
Os(1)-Os(4)	2.788 (1)	C(1)-O(1)	1.171 (16)
Os(2)-Os(4)	2.786 (1)	C(2)-O(2)	1.143 (15)
Os(3)-Os(4)	2.783 (1)	C(3)-O(3)	1.173 (17)
Os(1)-S	2.386 (4)	C(4)-O(4)	1.152 (18)
Os(2)-S	2.386 (4)	C(5)-O(5)	1.154 (18)
Os(3)-S	2.383 (3)	C(6)-O(6)	1.133 (14)
Os(1)-C(1)	1.906 (16)	C(7)-O(7)	1.166 (16)
Os(1)-C(2)	1.915 (14)	C(8)-O(8)	1.135 (17)
Os(1)-C(3)	1.899 (17)	C(9)-O(9)	1.171 (20)
Os(2)-C(4)	1.957 (17)	C(10)-O(10)	1.207 (17)
Os(2)-C(5)	1.880 (17)	C(11)-O(11)	1.199 (16)
Os(2)-C(6)	1.925 (14)	C(12)-O(12)	1.143 (15)
Os(3)-C(7)	1.899 (15)	Os(4)···C(3)	2.860 (16)
Os(3)-C(8)	1.965 (17)	Os(4)···C(5)	2.891 (15)
Os(3)-C(9)	1.885 (14)	Os(4)···C(9)	2.872 (14)

was found to crystallize in a second crystallographic modification: space group $P2_12_12_1$, $a = 11.426$ (5) Å, $b = 15.985$ (9) Å, $c = 16.688$ (7) Å. A preliminary structural analysis revealed a molecular structure of II identical with that found in the space group $P2_1$ which was the one completed and reported here. Crystal data and data collection parameters are listed in Table I. All data processing was performed on a Digital Equipment Corp. PDP 11/45 computer using the Enraf-Nonius SDP program library (version 18). An absorption correction of a Gaussian integration type was applied to all data. Neutral atom scattering factors were calculated by the standard procedures.[20a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[20b] 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 I was solved by a combination of Patterson and difference Fourier techniques. The coordinates of two of the four metal atoms were obtained from a three-dimensional Patterson function. The coordinates of all the remaining atoms were obtained from subsequent difference Fourier syntheses. Only the osmium and sulfur atoms were refined anisotropically. Table II lists final fractional atomic coordinates and thermal parameters. Tables III and IV list interatomic distances and angles with esds obtained from the inverse matrix obtained on the final cycle of refinement.

The structure of II was solved by a combination of direct methods and differences Fourier techniques. The seven metal atoms were located in an electron-density map based on the phasing (MULTAN) of 288 reflections ($E \geq 1.40$). Only the osmium atoms were refined anisotropically. The enantiomorph corresponding to positive fractional coordinates was selected originally and with this model the values of residuals R_1 and R_2 upon convergence of the refinement were 0.038 and 0.041, respectively. At this point the other enantiomorph was tested by transforming all atomic coordinates to their negative values and

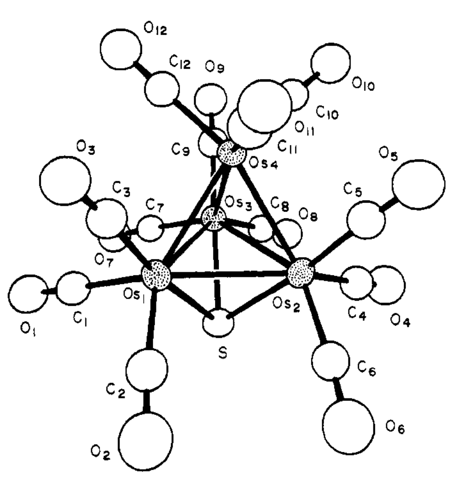

Figure 1. An ORTEP diagram of $Os_4(CO)_{12}(\mu_3\text{-}S)$, I, showing 50% probability thermal-motion ellipsoids.

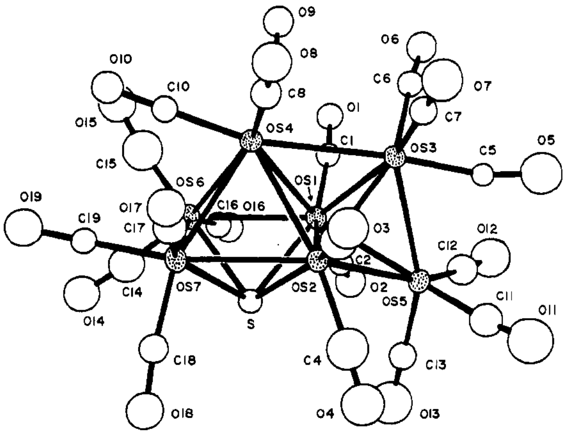

Figure 2. An ORTEP diagram of $Os_7(CO)_{19}(\mu_4\text{-}S)$, III showing 50% probability thermal-motion ellipsoids. Atom C(9) is hidden behind O(8).

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(20) "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 IV. Interatomic Angles (deg) with Esds for $Os_4(CO)_{12}(\mu_3\text{-}S)$, I

(A) Between Metal Atoms			
Os(2)-Os(1)-Os(3)	59.79 (2)	Os(1)-Os(3)-Os(2)	60.21 (2)
Os(2)-Os(1)-Os(4)	58.97 (2)	Os(1)-Os(3)-Os(4)	59.14 (2)
Os(3)-Os(1)-Os(4)	58.98 (2)	Os(2)-Os(3)-Os(4)	59.16 (2)
Os(1)-Os(2)-Os(3)	60.00 (2)	Os(1)-Os(4)-Os(2)	62.00 (2)
Os(1)-Os(2)-Os(4)	59.04 (2)	Os(1)-Os(4)-Os(3)	61.88 (2)
Os(3)-Os(2)-Os(4)	59.08 (2)	Os(2)-Os(4)-Os(3)	61.76 (2)
(B) Involving Metal-Metal-Ligand			
Os(2)-Os(1)-S	53.0 (1)	Os(4)-Os(2)-C(6)	131.3 (5)
Os(2)-Os(1)-C(1)	147.6 (5)	Os(1)-Os(3)-S	53.1 (1)
Os(2)-Os(1)-C(2)	96.2 (5)	Os(1)-Os(3)-C(7)	95.5 (4)
Os(2)-Os(1)-C(3)	119.0 (5)	Os(1)-Os(3)-C(8)	146.4 (4)
Os(3)-Os(1)-S	53.0 (1)	Os(1)-Os(3)-C(9)	121.6 (5)
Os(3)-Os(1)-C(1)	94.9 (4)	Os(2)-Os(3)-S	53.2 (1)
Os(3)-Os(1)-C(2)	144.6 (5)	Os(2)-Os(3)-C(7)	146.7 (4)
Os(3)-Os(1)-C(3)	122.1 (4)	Os(2)-Os(3)-C(8)	95.4 (4)
Os(4)-Os(1)-S	99.6 (1)	Os(2)-Os(3)-C(9)	120.7 (4)
Os(4)-Os(1)-C(1)	127.8 (4)	Os(4)-Os(3)-S	99.8 (1)
Os(4)-Os(1)-C(2)	133.6 (5)	Os(4)-Os(3)-C(7)	130.4 (4)
Os(4)-Os(1)-C(3)	72.4 (5)	Os(4)-Os(3)-C(8)	130.6 (5)
Os(1)-Os(2)-S	53.0 (1)	Os(4)-Os(3)-C(9)	73.1 (5)
Os(1)-Os(2)-C(4)	145.4 (4)	Os(1)-Os(4)-C(10)	161.0 (5)
Os(1)-Os(2)-C(5)	120.6 (5)	Os(1)-Os(4)-C(11)	101.6 (5)
Os(1)-Os(2)-C(6)	95.5 (5)	Os(1)-Os(4)-C(12)	101.5 (5)
Os(3)-Os(2)-S	53.1 (1)	Os(2)-Os(4)-C(10)	102.4 (4)
Os(3)-Os(2)-C(4)	93.7 (4)	Os(2)-Os(4)-C(11)	101.9 (4)
Os(3)-Os(2)-C(5)	122.7 (4)	Os(2)-Os(4)-C(12)	160.2 (5)
Os(3)-Os(2)-C(6)	145.7 (5)	Os(3)-Os(4)-C(10)	101.9 (5)
Os(4)-Os(2)-S	99.7 (1)	Os(3)-Os(4)-C(11)	160.3 (5)
Os(4)-Os(2)-C(4)	129.0 (1)	Os(3)-Os(4)-C(12)	101.7 (4)
Os(4)-Os(2)-C(5)	73.7 (4)		
(C) Involving Metal to Ligands			
Os(1)-S-Os(2)	73.9 (11)	Os(2)-C(6)-O(6)	176.8 (14)
Os(1)-S-Os(3)	73.83 (10)	Os(3)-C(7)-O(7)	176.1 (13)
Os(2)-S-Os(3)	73.65 (11)	Os(3)-C(8)-O(8)	177.9 (14)
Os(1)-C(1)-O(1)	176.3 (13)	Os(3)-C(9)-O(9)	174.5 (12)
Os(1)-C(2)-O(2)	174.5 (14)	Os(4)-C(10)-O(10)	174.2 (14)
Os(1)-C(3)-O(3)	175.0 (14)	Os(4)-C(11)-O(11)	177.3 (13)
Os(2)-C(4)-O(4)	175.2 (14)	Os(4)-C(12)-O(12)	178.7 (14)
Os(2)-C(5)-O(5)	175.9 (15)		

refining again. With this enantiomorph, refinement produced the residuals $R_1 = 0.036$ and $R_2 = 0.039$ upon convergence. This is a significant improvement, and the latter enantiomorph was deemed to be correct. The values of the fractional coordinates listed in Table V correspond to those of the latter enantiomorph. Tables VI and VII list interatomic distances and angles with esds obtained from the inverse matrix obtained on the final cycle of refinement. Tables of structure factor amplitudes are available for both structures.[21]

Results and Discussion

The molecular structure of compound I was determined by a single crystal X-ray diffraction analysis. An ORTEP drawing of the molecular structure of I is shown in Figure 1. Final fractional atomic coordinates and thermal parameters are listed in Table II. Interatomic distances and angles are listed in Tables III and IV, respectively. The molecule consists of a tetrahedral cluster of four osmium atoms with a triply bridging sulfido ligand on one of the triangular faces. The six osmium–osmium distances are separated clearly into two sets. The Os–Os distances bridged by the sulfido ligand range from 2.858 (1) to 2.870 (1) Å ($Os\text{-}Os_{av} = 2.864$ (3) Å) while the unbridged Os–Os distances are significantly shorter and span the range 2.783 (1)–2.788 (1) Å ($Os\text{-}Os_{av} = 2.785$ (1) Å). All the distances are shorter than those found in $Os_3(CO)_{12}$, 2.877 (3) Å[22] but are only slightly shorter for the bridged set. A similar effect was observed by Kaesz in the structure of the related molecule $Os_4(CO)_{12}(\mu_3\text{-}NMe)$.[23] Kaesz attributed the bond shortening to the inherent "electron deficiency" of the capping $Os(CO)_3$ group since to form an "electron precise" cluster one of the metal–metal bonds to the Os(4) capping group must be of a donor–acceptor type.[24]

All the osmium–sulfur distances are similar and range from 2.383 (3) to 2.386 (4) Å. The average distance, 2.385 (1) Å, is similar to that found for triply bridging sulfido ligands in other osmium clusters.[17] The sulfido ligand serves as a four-electron donor, and thus each metal atom in I can achieve an 18-electron configuration.

According to the skeletal electron pair (SEP) theory, $Os(CO)_3$ groups contribute two electrons for cluster bonding.[25] Assuming the sulfido ligand serves as a four-electron donor, compound I contains 12 electrons for cluster bonding. For this electron count, the SEP theory predicts a trigonal-bipyramidal shape for the cluster. This is the observed structure if one considers the sulfido ligand as a part of the cluster. According to the SEP theory, *each* atom in the cluster contributes only three atomic orbitals

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[21] See supplementary material.

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Table V. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Os_7(CO)_{19}(\mu_4\text{-}S)$, II[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)	−0.8143 (1)	−0.3441 (0)	−0.1476 (1)	2.37 (5)	1.58 (4)	1.48 (5)	−0.09 (5)	−0.00 (5)	0.09 (5)	1.81 (2)
Os(2)	−0.6053 (1)	−0.3142 (1)	−0.2843 (1)	1.93 (5)	1.53 (5)	1.78 (5)	0.12 (4)	−0.08 (4)	−0.17 (4)	1.75 (2)
Os(3)	−0.7611 (1)	−0.5081 (1)	−0.2955 (1)	2.28 (5)	1.51 (4)	2.02 (6)	−0.01 (4)	−0.45 (5)	−0.15 (5)	1.94 (3)
Os(4)	−0.8677 (1)	−0.2817 (1)	−0.3584 (1)	2.06 (5)	1.70 (4)	1.56 (5)	0.08 (4)	−0.19 (4)	−0.08 (5)	1.77 (2)
Os(5)	−0.5879 (1)	−0.4774 (1)	−0.1274 (1)	2.80 (6)	1.84 (5)	2.37 (6)	0.18 (5)	−0.96 (5)	0.13 (5)	2.34 (3)
Os(6)	−0.9024 (1)	−0.1196 (1)	−0.1859 (1)	2.30 (5)	1.63 (5)	1.87 (5)	0.26 (4)	0.31 (5)	−0.07 (5)	1.93 (3)
Os(7)	−0.6889 (1)	−0.0888 (1)	−0.3305 (1)	2.32 (5)	1.49 (4)	1.84 (5)	−0.04 (4)	0.25 (5)	0.22 (5)	1.88 (3)

atom	*x*	*y*	*z*	*B*, Å²	atom	*x*	*y*	*z*	*B*, Å²
S	−0.6716 (8)	−0.1742 (7)	−0.1539 (7)	2.1 (2)	C(1)	−0.977 (3)	−0.413 (3)	−0.130 (3)	2.3 (6)
O(1)	−0.909 (3)	−0.949 (2)	−0.883 (2)	3.7 (5)	C(2)	−0.792 (3)	−0.361 (3)	−0.003 (3)	2.5 (7)
O(2)	−0.801 (3)	−0.369 (2)	0.085 (2)	4.5 (6)	C(3)	−0.533 (4)	−0.354 (3)	−0.407 (3)	3.8 (9)
O(3)	−0.484 (3)	−0.371 (2)	−0.491 (2)	4.2 (6)	C(4)	−0.423(5)	−0.307 (4)	−0.248 (4)	5.5 (11)
O(4)	−0.318 (3)	−0.298 (3)	−0.219 (3)	5.6 (7)	C(5)	−0.678 (3)	−0.645 (3)	−0.254 (3)	1.8 (6)
O(5)	−0.635 (3)	−0.742 (3)	−0.246 (3)	5.9 (8)	C(6)	−0.923 (3)	−0.591 (3)	−0.293 (3)	2.4 (6)
O(6)	−1.017 (2)	−0.644 (2)	−0.281 (2)	3.5 (5)	C(7)	−0.716 (3)	−0.564 (3)	−0.431 (3)	2.3 (6)
O(7)	−0.690 (3)	−0.596 (2)	−0.511 (2)	4.7 (6)	C(8)	−0.822 (3)	−0.332 (3)	−0.497 (3)	2.7 (7)
O(8)	−0.798 (3)	−0.355 (2)	−0.579 (2)	4.2 (6)	C(9)	−1.032 (4)	−0.366 (3)	−0.357 (3)	3.1 (8)
O(9)	−1.133 (2)	−0.408 (2)	−0.366 (2)	3.4 (5)	C(10)	−0.955 (3)	−0.161 (3)	−0.424 (3)	2.2 (6)
O(10)	−1.005 (2)	−0.084 (2)	−0.474 (2)	3.2 (5)	C(11)	−0.572 (4)	−0.054 (3)	−0.841 (3)	3.8 (9)
O(11)	−0.665 (3)	−0.104 (3)	−0.814 (3)	6.6 (8)	C(12)	−0.353 (4)	−0.076 (3)	−0.976 (3)	4.0 (9)
O(12)	−0.310 (3)	−0.148 (3)	−0.036 (3)	6.8 (9)	C(13)	−0.503 (4)	−0.403 (3)	−0.022 (3)	2.9 (7)
O(13)	−0.446 (4)	−0.351 (3)	0.045 (3)	7.7 (10)	C(14)	−0.874 (4)	−0.971 (4)	−0.151 (4)	5.2 (10)
O(14)	−0.131 (3)	−0.366 (2)	−0.877 (3)	5.2 (7)	C(15)	−0.065 (5)	−0.079 (4)	−0.243 (4)	6.5 (13)
O(15)	−0.185 (3)	−0.063 (3)	−0.273 (3)	5.7 (7)	C(16)	0.033 (4)	−0.157 (3)	−0.059 (3)	2.9 (7)
O(16)	−0.022 (3)	−0.170 (2)	−0.976 (2)	4.2 (6)	C(17)	−0.638 (4)	−0.114 (3)	−0.472 (3)	3.1 (7)
O(17)	−0.605 (2)	−0.128 (2)	−0.554 (2)	3.6 (5)	C(18)	−0.459 (3)	−0.505 (3)	−0.701 (3)	2.6 (7)
O(18)	−0.443 (3)	−0.955 (2)	−0.263 (2)	4.2 (6)	C(19)	−0.218 (3)	−0.451 (3)	−0.638 (3)	2.1 (6)
O(19)	−0.165 (3)	−0.365 (2)	−0.608 (2)	4.5 (6)					

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}\{h^2a^{*2}B(1,1) + k^2b^{*2}B(2,2) + l^2c^{*2}B(3,3) + 2hka^*b^*B(1,2) + 2hla^*c^*B(1,3) + 2klb^*c^*B(2,3)\}]$.

Table VI. Interatomic Distances (Å) with Esds for $Os_7(CO)_{19}(\mu_4\text{-}S)$, II

Os(1)–Os(2)	2.772 (2)	Os(5)–C(11)	1.89 (3)
Os(1)–Os(3)	2.735 (2)	Os(5)–C(12)	1.85 (3)
Os(1)–Os(4)	2.840 (2)	Os(5)–C(13)	1.81 (3)
Os(1)–Os(5)	2.769 (2)	Os(5)···C(5)	2.68 (3)
Os(1)–Os(6)	2.788 (2)	Os(6)–C(14)	1.79 (4)
Os(2)–Os(3)	2.744 (1)	Os(6)–C(15)	1.85 (5)
Os(2)–Os(4)	2.835 (2)	Os(6)–C(16)	1.81 (3)
Os(2)–Os(5)	2.761 (2)	Os(7)–C(17)	1.91 (3)
Os(2)–Os(7)	2.802 (1)	Os(7)–C(18)	1.83 (3)
Os(3)–Os(4)	2.943 (1)	Os(7)–C(19)	1.89 (2)
Os(3)–Os(5)	2.786 (2)	C(1)–O(1)	1.24 (4)
Os(4)–Os(6)	2.919 (2)	C(2)–O(2)	1.14 (3)
Os(4)–Os(7)	2.893 (2)	C(3)–O(3)	1.21 (4)
Os(6)–Os(7)	2.874 (2)	C(4)–O(4)	1.13 (4)
S–Os(1)	2.439 (7)	C(5)–O(5)	1.21 (3)
S–Os(2)	2.423 (7)	C(6)–O(6)	1.14 (3)
S–Os(6)	2.449 (7)	C(7)–O(7)	1.12 (3)
S–Os(7)	2.471 (7)	C(8)–O(8)	1.10 (3)
S···Os(4)	3.501 (7)	C(9)–O(9)	1.14 (3)
Os(1)–C(1)	1.85 (3)	C(10)–O(10)	1.20 (3)
Os(1)–C(2)	1.88 (3)	C(11)–O(11)	1.16 (4)
Os(2)–C(3)	1.79 (4)	C(12)–O(12)	1.21 (5)
Os(2)–C(4)	1.90 (4)	C(13)–O(13)	1.20 (4)
Os(3)–C(5)	1.87 (2)	C(14)–O(14)	1.27 (4)
Os(3)–C(6)	1.90 (3)	C(15)–O(15)	1.28 (5)
Os(3)–C(7)	1.91 (3)	C(16)–O(16)	1.20 (3)
Os(4)–C(8)	1.93 (3)	C(17)–O(17)	1.11 (3)
Os(4)–C(9)	1.93 (3)	C(18)–O(18)	1.23 (4)
Os(4)–C(10)	1.85 (3)	C(19)–O(19)	1.20 (3)

toward cluster bonding. In I atom Os(4) uses three orbitals and has a connectivity of three, while the sulfur-bridged metal atoms use three orbitals and have connectivities of four. Thus, an alternative explanation of the long and short bonds in I is simply the long bonds are between metal atoms in which both have connectivities of four while the short bonds are between metal atoms in which one has a connectivity of three and the other has a connectivity of four.

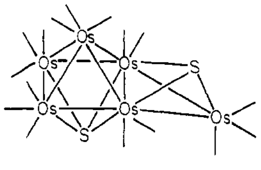
Each metal atom contains three linear terminal carbonyl ligands, but on each of the sulfur bridged metal atoms, there is one carbonyl ligand positioned trans to the sulfido ligand that makes a close approach to the unique metal atom (Os(4)···C(3) = 2.860 (16) Å, Os(4)···C(5) = 2.891 (15) Å, and Os(4)···C(9) = 2.872 (14) Å. These could be regarded as weakly semibridging ligands. Overall the molecule has C_{3v} symmetry, but this is not crystallographically imposed. The shortest intermolecular contract is between carbonyl oxygen atoms, O(4)···O(4) = 2.96 (2) Å.

The compound $Os_7(CO)_{19}(\mu_4\text{-}S)$, II, is obtained in 23% yield when a solution of $Os_4(CO)_{12}(\mu_3\text{-}S)$, I, and $Os_3(CO)_{10}(NCMe)_2$, III, is refluxed 3 h in octane solvent. Compound II can also be made, albeit in lower yield (4%), when the compounds $H_2Os_3(CO)_9(\mu_3\text{-}S)$ and $HOs_3(CO)_{10}(OMe)$ are refluxed 22 h in nonane solvent. The molecular structure of II was established by a single-crystal X-ray diffraction analysis, and an ORTEP diagram of its structure is shown in Figure 2. Final positional and thermal parameters are listed in Table V. Interatomic distances and angles are listed in Tables VI and VII, respectively. The molecule consists of a cluster of seven osmium atoms with one quadruply bridging sulfido ligand. These eight atoms are arranged in the form of two polyhedra (an octahedron and a trigonal bipyramid) which have one triangular group Os(1), Os(2), and Os(4) in common. The group Os(1), Os(2), Os(4), Os(6), Os(7), and S has an octahedral shape while the group Os(1), Os(2), Os(3), Os(4), and Os(5) has the shape of a trigonal bipyramid. The Os–Os internuclear separations range from 2.735 (2) to 2.943 (1) Å. The Os–Os separations in $Os_3(CO)_{12}$ average 2.877 (3) Å.[22] Compound II is most similar to the compound $Os_6(CO)_{16}(\mu_4\text{-}S)(\mu_3\text{-}S)$, IV, which we have prepared by coupling the clusters $Os_3(CO)_9(\mu_3\text{-}S)_2$ and III.[13,17] Compound IV also contains an octahedral group consisting of five osmium atoms and a quadruply bridging sulfido ligand. Electron counting shows that all the metal atoms in II achieve an 18-electron

Table VII. Selected Interatomic Angles with Esds for $Os_7(CO)_{19}(\mu_4\text{-}S)$, II

		(A) Involving Metal Atoms Only			
Os(2)-Os(1)-Os(3)	59.77 (4)	Os(3)-Os(2)-Os(5)	60.80 (4)	Os(2)-Os(4)-Os(3)	56.67 (3)
Os(2)-Os(1)-Os(4)	60.59 (4)	Os(3)-Os(2)-Os(7)	125.30 (5)	Os(2)-Os(4)-Os(6)	87.08 (5)
Os(2)-Os(1)-Os(5)	59.76 (4)	Os(4)-Os(2)-Os(5)	112.86 (5)	Os(2)-Os(4)-Os(7)	58.56 (4)
Os(2)-Os(1)-Os(6)	90.96 (4)	Os(4)-Os(2)-Os(7)	61.74 (4)	Os(3)-Os(4)-Os(6)	114.25 (5)
Os(3)-Os(1)-Os(4)	63.69 (4)	Os(5)-Os(2)-Os(7)	143.84 (6)	Os(3)-Os(4)-Os(7)	115.18 (5)
Os(3)-Os(1)-Os(5)	60.80 (4)	Os(1)-Os(3)-Os(2)	60.78 (4)	Os(6)-Os(4)-Os(7)	59.26 (4)
Os(3)-Os(1)-Os(6)	126.08 (5)	Os(1)-Os(3)-Os(4)	59.88 (4)	Os(1)-Os(5)-Os(2)	60.17 (4)
Os(4)-Os(1)-Os(5)	112.46 (5)	Os(1)-Os(3)-Os(5)	60.21 (4)	Os(1)-Os(5)-Os(3)	58.99 (4)
Os(4)-Os(1)-Os(6)	62.48 (4)	Os(2)-Os(3)-Os(4)	59.69 (4)	Os(2)-Os(5)-Os(3)	59.31 (4)
Os(5)-Os(1)-Os(6)	142.93 (6)	Os(2)-Os(3)-Os(5)	59.89 (4)	Os(1)-Os(6)-Os(4)	59.62 (4)
Os(1)-Os(2)-Os(3)	59.44 (4)	Os(4)-Os(3)-Os(5)	108.94 (5)	Os(1)-Os(6)-Os(7)	89.31 (4)
Os(1)-Os(2)-Os(4)	60.83 (4)	Os(1)-Os(4)-Os(2)	58.48 (4)	Os(4)-Os(6)-Os(7)	59.91 (4)
Os(1)-Os(2)-Os(5)	60.07 (4)	Os(1)-Os(4)-Os(3)	56.43 (4)	Os(2)-Os(7)-Os(4)	59.70 (4)
Os(1)-Os(2)-Os(7)	91.11 (5)	Os(1)-Os(4)-Os(6)	57.90 (4)	Os(2)-Os(7)-Os(6)	88.60 (4)
Os(3)-Os(2)-Os(4)	63.63 (4)	Os(1)-Os(4)-Os(7)	87.93 (4)	Os(4)-Os(7)-Os(6)	60.82 (4)
		(B) Involving Metal-Metal-Ligand			
Os(2)-Os(1)-S	55.0 (2)	Os(4)-Os(2)-C(4)	168.7 (12)	Os(7)-Os(4)-C(10)	76.7 (8)
Os(3)-Os(1)-S	114.7 (2)	Os(5)-Os(2)-C(4)	78.0 (12)	Os(1)-Os(5)-C(11)	161.6 (11)
Os(4)-Os(1)-S	82.7 (2)	Os(7)-Os(2)-C(4)	107.7 (11)	Os(2)-Os(5)-C(11)	102.6 (11)
Os(5)-Os(1)-S	87.9 (2)	Os(1)-Os(3)-C(5)	118.7 (8)	Os(3)-Os(5)-C(11)	107.9 (11)
Os(6)-Os(1)-S	55.4 (2)	Os(2)-Os(3)-C(5)	114.8 (8)	Os(1)-Os(5)-C(12)	98.1 (10)
Os(1)-Os(2)-S	55.5 (2)	Os(4)-Os(3)-C(5)	174.5 (8)	Os(2)-Os(5)-C(12)	157.4 (11)
Os(3)-Os(2)-S	114.9 (2)	Os(5)-Os(3)-C(5)	66.9 (8)	Os(3)-Os(5)-C(12)	105.6 (11)
Os(4)-Os(2)-S	83.1 (2)	Os(1)-Os(3)-C(6)	99.6 (8)	Os(1)-Os(5)-C(13)	101.1 (9)
Os(5)-Os(2)-S	88.5 (2)	Os(2)-Os(3)-C(6)	155.1 (8)	Os(2)-Os(5)-C(13)	104.2 (9)
Os(7)-Os(2)-S	55.9 (2)	Os(4)-Os(3)-C(6)	98.0 (8)	Os(3)-Os(5)-C(13)	158.1 (9)
Os(1)-Os(6)-S	55.1 (2)	Os(5)-Os(3)-C(6)	126.2 (9)	Os(1)-Os(6)-C(14)	143.0 (13)
Os(4)-Os(6)-S	80.9 (2)	Os(1)-Os(3)-C(7)	155.7 (8)	Os(4)-Os(6)-C(14)	141.4 (13)
Os(7)-Os(6)-S	54.6 (2)	Os(2)-Os(3)-C(7)	100.6 (8)	Os(7)-Os(6)-C(14)	85.5 (12)
Os(2)-Os(7)-S	54.3 (2)	Os(4)-Os(3)-C(7)	98.0 (8)	Os(1)-Os(6)-C(15)	125.9 (14)
Os(4)-Os(7)-S	81.1 (2)	Os(5)-Os(3)-C(7)	126.5 (8)	Os(4)-Os(6)-C(15)	88.6 (14)
Os(6)-Os(7)-S	53.9 (2)	Os(1)-Os(4)-C(8)	138.9 (8)	Os(7)-Os(6)-C(15)	112.4 (14)
Os(3)-Os(1)-C(1)	88.0 (8)	Os(2)-Os(4)-C(8)	92.3 (9)	Os(1)-Os(6)-C(16)	74.6 (9)
Os(4)-Os(1)-C(1)	93.6 (9)	Os(3)-Os(4)-C(8)	84.0 (8)	Os(4)-Os(6)-C(16)	124.8 (9)
Os(5)-Os(1)-C(1)	119.0 (8)	Os(6)-Os(4)-C(8)	157.0 (8)	Os(7)-Os(6)-C(16)	152.3 (10)
Os(6)-Os(1)-C(1)	98.1 (8)	Os(7)-Os(4)-C(8)	101.2 (8)	Os(2)-Os(7)-C(17)	88.6 (9)
Os(3)-Os(1)-C(2)	126.0 (8)	Os(1)-Os(4)-C(9)	91.3 (10)	Os(4)-Os(7)-C(17)	86.4 (9)
Os(4)-Os(1)-C(2)	170.3 (8)	Os(2)-Os(4)-C(9)	137.3 (9)	Os(6)-Os(7)-C(17)	143.2 (9)
Os(5)-Os(1)-C(2)	75.8 (8)	Os(3)-Os(4)-C(9)	82.1 (9)	Os(2)-Os(7)-C(18)	101.8 (9)
Os(6)-Os(1)-C(2)	107.9 (8)	Os(6)-Os(4)-C(9)	102.2 (9)	Os(4)-Os(7)-C(18)	161.4 (9)
Os(3)-Os(2)-C(3)	88.9 (10)	Os(7)-Os(4)-C(9)	158.1 (9)	Os(6)-Os(7)-C(18)	122.6 (9)
Os(4)-Os(2)-C(3)	97.4 (11)	Os(1)-Os(4)-C(10)	135.3 (9)	Os(2)-Os(7)-C(19)	167.7 (8)
Os(5)-Os(2)-C(3)	115.7 (11)	Os(2)-Os(4)-C(10)	133.9 (8)	Os(4)-Os(7)-C(19)	108.4 (8)
Os(7)-Os(2)-C(3)	100.4 (10)	Os(3)-Os(4)-C(10)	165.6 (9)	Os(6)-Os(7)-C(19)	82.3 (8)
Os(3)-Os(2)-C(4)	127.0 (11)	Os(6)-Os(4)-C(10)	78.4 (9)		
		(C) Involving Metal to Ligands			
Os(1)-S-Os(2)	69.52 (19)	Os(2)-C(4)-O(4)	174 (3)	Os(5)-C(12)-O(12)	174 (3)
Os(1)-S-Os(6)	69.56 (19)	Os(3)-C(5)-O(5)	166 (3)	Os(5)-C(13)-O(13)	177 (3)
Os(1)-S-Os(7)	108.28 (28)	Os(3)-C(6)-O(6)	173 (3)	Os(6)-C(14)-O(14)	173 (3)
Os(2)-S-Os(6)	108.93 (29)	Os(3)-C(7)-O(7)	180 (3)	Os(6)-C(15)-O(15)	171 (4)
Os(2)-S-Os(7)	69.84 (20)	Os(4)-C(8)-O(8)	177 (3)	Os(6)-C(16)-O(16)	171 (3)
Os(6)-S-Os(7)	71.47 (21)	Os(4)-C(9)-O(9)	172 (3)	Os(7)-C(17)-O(17)	178 (2)
Os(1)-C(1)-O(1)	174 (2)	Os(4)-C(10)-O(10)	175 (2)	Os(7)-C(18)-O(18)	171 (3)
Os(1)-C(2)-O(2)	168 (3)	Os(5)-C(11)-O(11)	174 (3)	Os(7)-C(19)-O(19)	173 (2)
Os(2)-C(3)-O(3)	174 (3)				

configuration if the two metal–metal bonds Os(4)–Os(3) and Os(3)–Os(5) are viewed as donor–acceptor bonds from Os(4) to Os(3) and from Os(3) to Os(5), respectively. Interestingly, the Os(3)–Os(4) bond at 2.943 (1) Å is the longest metal–metal bond in the molecule.



IV

The Os–S distances to the quadruply bridging sulfido ligand in II ($Os–S_{av}$ = 2.45 (1) Å) are essentially identical with those in IV ($Os–S_{av}$ = 2.44 (1) Å) and are significantly longer than the Os–S distances of triply bridging sulfido ligands (e.g., 2.385 (1) Å in I, see above).[17] This could be due to the fact that quadruply bridging sulfido ligand serving as a four-electron donor has only three atomic orbitals for use in bonding to four metal atoms. The Os(4)···S distance at 3.501 (7) Å is nonbonding. All the carbonyl ligands are of a linear terminal type except C(5)–O(5) which is a semibridging ligand to Os(5) (Os(5)···C(5) = 2.68 (3) Å, Os(5)–Os(3)–C(5) = 66.9 (8)°, Os(3)–C(5)–O(5) = 166 (3)°). This is probably a consequence of the donor–acceptor character of the Os(3)–Os(5) bond.[26]

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[26] (a) Cotton, F. A. *Prog. Inorg. Chem.* **1976**, *21*, 1. (b) Colton, R.; McCormick, M. G. *Coord. Chem. Rev.* **1980**, *31*, 1.

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, $Z = 8$, $\rho_{\text{calcd}} = 3.79$ 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, $Z = 4$, $\rho_{\text{calcd}} = 3.82$ 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, $Z = 2$, $\rho_{\text{calcd}} = 3.76$ 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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