

**Registry No.** *fac*-Mo(CO)<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>3</sub>, 24554-64-1; *fac*-Mo(CO)<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>3</sub><sup>+</sup>, 88375-68-2; *mer*-Mo(CO)<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>3</sub>, 24554-82-3; *mer*-Mo(CO)<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>3</sub><sup>+</sup>, 88326-31-2; *fac*-Mo(CO)<sub>3</sub>(P(OPh)<sub>3</sub>)<sub>3</sub>, 41174-20-3; *fac*-Mo(CO)<sub>3</sub>(P(OPh)<sub>3</sub>)<sub>3</sub><sup>+</sup>, 88375-69-3; *mer*-Mo(CO)<sub>3</sub>(P(OPh)<sub>3</sub>)<sub>3</sub>, 88375-67-1; *mer*-Mo(CO)<sub>3</sub>(P(OPh)<sub>3</sub>)<sub>3</sub><sup>+</sup>, 88326-32-3; *fac*-Mo(CO)<sub>3</sub>(P(OMe)<sub>3</sub>)<sub>3</sub>, 15631-24-0; *fac*-Mo(CO)<sub>3</sub>(P(OMe)<sub>3</sub>)<sub>3</sub><sup>+</sup>, 88375-70-6; *mer*-Mo(CO)<sub>3</sub>(P(OMe)<sub>3</sub>)<sub>3</sub>, 15631-23-9; *mer*-Mo(CO)<sub>3</sub>(P(OMe)<sub>3</sub>)<sub>3</sub><sup>+</sup>, 88326-33-4; *fac*-Mo(CO)<sub>3</sub>(P(OMe)<sub>2</sub>Ph)<sub>3</sub>,

88376-11-8; *fac*-Mo(CO)<sub>3</sub>(P(OMe)<sub>2</sub>Ph)<sub>3</sub><sup>+</sup>, 88375-71-7; *mer*-Mo(CO)<sub>3</sub>(P(OMe)<sub>2</sub>Ph)<sub>3</sub>, 26133-41-5; *mer*-Mo(CO)<sub>3</sub>(P(OMe)<sub>2</sub>Ph)<sub>3</sub><sup>+</sup>, 88326-34-5; *fac*-Mo(CO)<sub>3</sub>(P(OMe)Ph<sub>2</sub>)<sub>3</sub>, 88326-29-8; *fac*-Mo(CO)<sub>3</sub>(P(OMe)Ph<sub>2</sub>)<sub>3</sub><sup>+</sup>, 88375-72-8; *mer*-Mo(CO)<sub>3</sub>(P(OMe)Ph<sub>2</sub>)<sub>3</sub>, 88375-74-0; *mer*-Mo(CO)<sub>3</sub>(P(OMe)Ph<sub>2</sub>)<sub>3</sub><sup>+</sup>, 88326-35-6; *fac*-Mo(CO)<sub>3</sub>(PPh<sub>2</sub>(CH<sub>2</sub>Ph))<sub>3</sub>, 88326-30-1; *fac*-Mo(CO)<sub>3</sub>(PPh<sub>2</sub>(CH<sub>2</sub>Ph))<sub>3</sub><sup>+</sup>, 88375-73-9; *mer*-Mo(CO)<sub>3</sub>(PPh<sub>2</sub>(CH<sub>2</sub>Ph))<sub>3</sub>, 88375-75-1; *mer*-Mo(CO)<sub>3</sub>(PPh<sub>2</sub>(CH<sub>2</sub>Ph))<sub>3</sub><sup>+</sup>, 88326-36-7.

## Synthesis of Sulfidoosmium Carbonyl Cluster Compounds by the Photochemical Decomposition of HO<sub>3</sub>(CO)<sub>10</sub>(μ-SPh) and Its Subsequent Reactions with Selected Small Molecules. Synthesis and Crystal and Molecular Structure of Os<sub>3</sub>(CO)<sub>9</sub>(μ<sub>3</sub>-CO)(μ<sub>3</sub>-S)

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Under an atmosphere of carbon monoxide, HO<sub>3</sub>(CO)<sub>10</sub>(μ-SPh) (I) loses benzene when irradiated to form the new cluster compound Os<sub>3</sub>(CO)<sub>9</sub>(μ<sub>3</sub>-CO)(μ<sub>3</sub>-S) (II). II was characterized by a single-crystal X-ray diffraction analysis: space group P $\bar{1}$ , No. 2,  $a = 6.912(2)$  Å,  $b = 9.500(3)$  Å,  $c = 13.235(6)$  Å,  $\alpha = 82.63(3)^\circ$ ,  $\beta = 87.43(3)^\circ$ ,  $\gamma = 72.30(3)^\circ$ ,  $V = 821.1(6)$  Å<sup>3</sup>,  $Z = 2$ ,  $\rho_{\text{calcd}} = 3.57$  g/cm<sup>3</sup>. The structure was solved by the heavy-atom method and refined (2258 reflections,  $F^2 \geq 3.0\sigma(F^2)$ ) by full-matrix least-squares to the final residuals  $R_1 = 0.056$  and  $R_2 = 0.069$ . The molecular structure of II consists of a triangular cluster of three osmium atoms containing a triply bridging sulfido ligand on one threefold face of the cluster and a triply bridging carbonyl ligand on the opposite threefold face. Each osmium atom contains three linear terminal carbonyl ligands. Two Os-Os separations, 2.826 (1) and 2.825 (1) Å, are slightly shorter than the third, 2.840 (1) Å. In the presence of the reagents H<sub>2</sub>, H<sub>2</sub>S, COS, and CS<sub>2</sub>, I loses both benzene and carbon monoxide when irradiated and yields the products H<sub>2</sub>Os<sub>3</sub>(CO)<sub>9</sub>(μ<sub>3</sub>-S) (IV), H<sub>2</sub>Os<sub>3</sub>(CO)<sub>8</sub>(μ<sub>3</sub>-S)<sub>2</sub> (V), Os<sub>3</sub>(CO)<sub>9</sub>(μ<sub>3</sub>-S)<sub>2</sub> (VI), and Os<sub>3</sub>(CO)<sub>8</sub>CS(μ<sub>3</sub>-S)<sub>2</sub> (VII), respectively. In the absence of a reagent the hexaosmium disulfido cluster, Os<sub>6</sub>(CO)<sub>17</sub>(μ<sub>4</sub>-S)<sub>2</sub> (III), is formed. Compounds III, IV, and V were also obtained by the photodecarbonylation of II in the presence of the appropriate reagent. It is proposed that an unsaturated intermediate such as Os<sub>3</sub>(CO)<sub>9</sub>(μ<sub>3</sub>-S) is traversed in the photoreactions of both I and II.

### Introduction

It has been shown recently that the pyrolysis of HO<sub>3</sub>(CO)<sub>10</sub>(μ-SPh) (I) at 150 °C proceeds via the elimination of benzene to produce a variety of new sulfidoosmium carbonyl cluster compounds.<sup>1,2</sup> The distribution of the products is greatly affected by the presence of a carbon monoxide atmosphere and varies according to the carbon monoxide pressure.<sup>2</sup> We have now found that benzene elimination from I is also promoted by irradiation with UV light, and the sulfidoosmium intermediate can be trapped by reaction with selected small molecules. In the absence of such reagents, higher nuclearity sulfidoosmium carbonyl clusters are obtained. The details of these reactions are reported here.

### Experimental Section

Photolysis experiments were performed by using an external high-pressure mercury lamp on reaction solutions contained in Pyrex glassware. The solvents, hexane and nonane, were stored over 4-Å molecular sieves and were degassed with a dispersed

stream of nitrogen gas before use. Infrared spectra were recorded on a Nicolet 5SX FT-IR spectrophotometer. A Bruker HX 270 FT-NMR spectrometer was used to obtain <sup>1</sup>H NMR spectra at 270 MHz. GC analyses were performed on a Perkin-Elmer 990 gas chromatograph using 2% OV101 on Chromosorb WHP, 6 ft × 0.125 in. stainless-steel columns. HO<sub>3</sub>(CO)<sub>10</sub>(μ-SPh) was prepared as described in the literature.<sup>3</sup>

**Synthesis.** In a typical preparation a solution of 0.100 g of HO<sub>3</sub>(CO)<sub>10</sub>(μ-SPh) in 100 mL of hexane was photolyzed under a continuous purge with carbon monoxide for 3 h. After removal of solvent in vacuo, the yellow residue was chromatographed on silica TLC plates. Elution with hexane/CH<sub>2</sub>Cl<sub>2</sub> (85:15) separated the starting material (0.028 g) from the product Os<sub>3</sub>(CO)<sub>9</sub>(μ<sub>3</sub>-CO)(μ<sub>3</sub>-S) (II). Final purification was obtained by crystallization from hexane solvent (yield: 0.036 g, 41%). Reactions with II were performed similarly. Details of the other reactions are summarized in Table I.

**Photolysis of I under CO in Sealed Tube.** In a sealed tube a solution of 96 mg of I in 10 mL of nonane was photolyzed under carbon monoxide (1 atm) for 4 h. The yellow solution was analyzed by GC for benzene (28%). The solvent was removed in vacuo, and the yellow residue was put on silica TLC plates. Elution with benzene/CH<sub>2</sub>Cl<sub>2</sub> (85:15) separated the unreacted

(1) Adams, R. D.; Yang, L. W. *J. Am. Chem. Soc.* **1982**, *104*, 4115.  
(2) Adams, R. D.; Horváth, I. T.; Segmüller, B. E.; Yang, L. W. *Organometallics* **1983**, *2*, 1301.

(3) Crooks, G. R.; Johnson, B. F. G.; Lewis, J.; Williams, I. G. *J. Chem. Soc. A* **1969**, 797.

Table I. Reactions of  $\text{HOs}_3(\text{CO})_{10}(\text{SPh})$  and  $\text{Os}_3(\text{CO})_9(\mu_3\text{-CO})(\mu_3\text{-S})$  under UV Irradiation

starting material	reagent	product(s)	color	yield, %	IR, $\text{cm}^{-1}$
$\text{HOs}_3(\text{CO})_{10}(\text{SPh})$	CO	$\text{Os}_3(\text{CO})_9(\mu_3\text{-CO})(\mu_3\text{-S})$ , II	pale yellow	41	2109vw, 2075s, 2028s, 2012w, 1685w <sup>a</sup>
$\text{HOs}_3(\text{CO})_{10}(\text{SPh})$	$\text{N}_2$ purge	$\text{Os}_6(\text{CO})_{17}(\mu_4\text{-S})_2$ , III	green	52	<i>f</i>
$\text{Os}_3(\text{CO})_9(\mu_3\text{-CO})(\mu_3\text{-S})$	$\text{N}_2$ purge	$\text{Os}_6(\text{CO})_{17}(\mu_4\text{-S})_2$ , III	green	44	<i>f</i>
$\text{HOs}_3(\text{CO})_{10}(\text{SPh})$	$\text{H}_2$	$\text{H}_2\text{Os}_3(\text{CO})_9(\mu_3\text{-S})$ , IV	pale yellow	40	<i>g</i>
$\text{Os}_3(\text{CO})_9(\mu_3\text{-CO})(\mu_3\text{-S})$	$\text{H}_2$	$\text{H}_2\text{Os}_3(\text{CO})_9(\mu_3\text{-S})$ , IV	pale yellow	41	<i>g</i>
$\text{HOs}_3(\text{CO})_{10}(\text{SPh})$	$\text{H}_2\text{S}$	$\text{H}_2\text{Os}_3(\text{CO})_8(\mu_3\text{-S})_2$ , <sup>c</sup> V		18	2116 w, 2096 s, 2033 vs, 2026 vs sh, 1964 w <sup>b</sup>
$\text{Os}_3(\text{CO})_9(\mu_3\text{-CO})(\mu_3\text{-S})$	$\text{H}_2\text{S}$	$\text{H}_2\text{Os}_3(\text{CO})_8(\mu_3\text{-S})_2$ , <sup>c</sup> V	pale yellow	26	
$\text{HOs}_3(\text{CO})_{10}(\text{SPh})$	COS	$\text{Os}_3(\text{CO})_9(\mu_3\text{-S})_2$ , VI	yellow	40	<i>g</i>
$\text{HOs}_3(\text{CO})_{10}(\text{SPh})$	$\text{CS}_2$ <sup>d</sup> + $\text{N}_2$ purge	$\text{Os}_3(\text{CO})_8(\text{CS})(\mu_3\text{-S})_2$ , VII	yellow	10	<i>h</i>
$\text{Os}_3(\text{CO})_9(\mu_3\text{-CO})(\mu_3\text{-S})$	$\text{Os}(\text{CO})_5$ <sup>e</sup> + $\text{N}_2$ purge	$\text{Os}_4(\text{CO})_{13}(\mu_3\text{-S})$ , VIII	orange	40	<i>i</i>
		$\text{Os}_5(\text{CO})_{15}(\mu_4\text{-S})$ , IX	red	3	<i>i</i>

<sup>a</sup> Hexane. <sup>b</sup>  $\text{CH}_2\text{Cl}_2$ . <sup>c</sup> <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  -13.65 (s). <sup>d</sup> 10 mL of  $\text{CS}_2$ . <sup>e</sup> Excess  $\text{Os}(\text{CO})_5$ . <sup>f</sup> Reference 9.

<sup>g</sup> Johnson, B. F. G.; Lewis, G.; Lodge, P. G.; Raithby, P. R.; Henrick, K.; McPartlin, M. J. *Chem. Soc., Chem. Commun.* 1979, 719. <sup>h</sup> Reference 12. <sup>i</sup> Reference 2.

starting material (0.055 g, 57%) from the major product  $\text{Os}_9(\text{CO})_9(\mu_3\text{-CO})(\mu_3\text{-S})$  (yield: 0.020 g, 24%).

**Crystallographic Analyses.** Pale yellow crystals of II suitable for diffraction analysis were obtained from solution in hexane solvent by cooling to 0 °C. The data crystal was mounted in a thin-walled glass capillary. Diffraction measurements were made on an Enraf-Nonius CAD-4 fully automated four-circle diffractometer using graphite monochromatized Mo  $K\alpha$  radiation. The unit cell was 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 II. All data processing was performed on a Digital 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.

The triclinic space group  $P\bar{1}$  was selected and confirmed by the successful solution and refinement of the structure. The structure was solved by the heavy-atom method. The coordinates of the three osmium atoms were obtained from a three-dimensional Patterson function. The coordinates of all remaining atoms were obtained from subsequent difference Fourier synthesis. Neutral atom scattering factors were calculated by the standard procedures.<sup>4a</sup> Anomalous dispersion corrections were applied to all atoms.<sup>4b</sup> Full-matrix least-squares refinements minimized the function  $\sum hklw(|F_{\text{obsd}}| - |F_{\text{calcd}}|)^2$ , where  $w = 1/(\sigma(F)^2)$ ,  $\sigma(F) = \sigma(F_{\text{obsd}}^2)/2F_{\text{obsd}}$ , and  $\sigma(F_{\text{obsd}}^2) = [\sigma(I_{\text{raw}})^2 + (PF_{\text{obsd}}^2)^2]^{1/2}/Lp$ .

Atoms heavier than oxygen were refined with anisotropic thermal parameters. All other non-hydrogen atoms were refined isotropically. Refinements with anisotropic thermal parameters for all atoms did not produce a significant improvement in the structure; therefore the previous model was maintained. Estimated standard deviations for the bond distance and angle calculations were obtained by using the inverse matrix obtained on the final cycle of refinement. A table of structure factor amplitudes is available; see supplementary material.

## Results

Under an atmosphere of carbon monoxide,  $\text{HOs}_3(\text{CO})_{10}(\mu\text{-SPh})$  (I) loses benzene when irradiated and forms the new carbonyl cluster compound  $\text{Os}_3(\text{CO})_9(\mu_3\text{-CO})(\mu_3\text{-S})$  (II) in 41% yield. As expected, the yield of benzene appears to be correlated one to one with the yield of II. The molecular structure of II was determined by a single-crystal X-ray diffraction analysis, and an ORTEP diagram of the molecule is shown in Figure 1. Final fractional atomic coordinates and thermal parameters are listed in Table III. Interatomic distances and angles are listed in Tables IV and V. The molecule consists of a triangular cluster of three osmium atoms joined by three osmium-osmium

Table II. Crystallographic Data for the X-ray Diffraction Study

(A) Crystal Parameters			
compound	II	$\alpha$ , deg	82.63 (3)
formula	$\text{Os}_3\text{SO}_{10}\text{C}_{10}$	$\beta$ , deg	87.43 (3)
temp, $\pm 3$ °C	24	$\gamma$ , deg	72.30 (3)
space group	$P\bar{1}$ , No. 2	$V$ , $\text{Å}^3$	821.1 (6)
a, Å	6.912 (2)	$M_r$	882.77
b, Å	9.500 (3)	$Z$	2
c, Å	13.235 (6)	$\rho_{\text{calcd}}$ , $\text{g}/\text{cm}^3$	3.57
(B) Measurement of Intensity Data			
radiation	Mo $K\alpha$ (0.71073 Å)		
monochromator	graphite		
detector aperture, mm	horiz ( $A + B \tan \theta$ )		
	A	3.0	
	B	1.0	
	Vert	4.0	
cryst faces:	$101, \bar{1}0\bar{1}, 0\bar{1}0, 010$ $\bar{1}02, 10\bar{2}, \bar{1}2\bar{2}, 11\bar{1}$		
cryst size, mm	0.12 × 0.30 × 0.33		
cryst orientation			
direction; deg from $\phi$ axis	$c^*$ ; 23.3		
reflens measd	$h, \pm k, \pm l$		
max $2\theta$	50°		
scan type	moving crystal-stationary counter		
$\omega$ scan width			
( $A + 0.347$ $\tan \theta$ ) deg	0.95		
bkgd	$1/4$ additional scan at each end of scan		
$\omega$ scan rate (variable)			
max, deg/min	10.0		
min, deg/min	1.5		
no. of reflens measd	2866		
data used ( $F^2 \geq 3.0\sigma(F^2)$ )	2258		
(C) Treatment of Data			
abs corr	$P$ factor		
coeff, $\text{cm}^{-1}$	233.6	final residuals, $R_F$	0.03
grid	$8 \times 10 \times 12$	$R_{wF}$	0.056
trans coeff	esd of unit wt		
max	0.17	observation	
min	0.01		
decay corr	largest shift/error		
max	1.00	value of final cycle	
min	0.92	largest peak in final	
		diff Fourier, $e^{\circ}/\text{Å}^3$	
		3.22	

bonds. Two of the metal-metal bonds,  $\text{Os}(1)\text{-Os}(2) = 2.826$  (1) Å and  $\text{Os}(1)\text{-Os}(3) = 2.825$  (1) Å, are of equal length and on the basis of statistics ( $15\sigma$ ) are significantly shorter than the third bond,  $\text{Os}(2)\text{-Os}(3) = 2.840$  (1) Å. All three bonds are shorter than those found in  $\text{Os}_3(\text{CO})_{12}$ ,

(4) "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 III. Positional and Thermal Parameters and Their Estimated Standard Deviations for Os<sub>3</sub>(CO)<sub>10</sub>(μ<sub>3</sub>-S) (II)

atom	x	y	z	B <sub>1,1</sub> <sup>a</sup>	B <sub>2,2</sub>	B <sub>3,3</sub>	B <sub>1,2</sub>	B <sub>1,3</sub>	B <sub>2,3</sub>	B <sub>eqv</sub>
Os1	0.2382 (1)	0.47391 (8)	0.22446 (6)	2.65 (3)	2.17 (2)	2.65 (3)	-0.80 (2)	-0.57 (3)	0.14 (2)	2.50 (2)
Os2	0.3557 (1)	0.18378 (8)	0.16596 (7)	2.47 (3)	2.48 (3)	3.13 (3)	-0.44 (2)	0.01 (3)	-0.44 (2)	2.75 (2)
Os3	0.1715 (1)	0.23716 (8)	0.35917 (6)	2.50 (3)	2.16 (2)	2.45 (3)	-0.62 (2)	-0.47 (2)	0.09 (2)	2.41 (2)
S	0.0187 (8)	0.3311 (5)	0.1975 (4)	2.7 (2)	2.6 (2)	3.0 (2)	-0.7 (1)	-0.6 (2)	-0.4 (1)	2.8 (1)

atom	x	y	z	B	atom	x	y	z	B
O1	0.245 (3)	0.633 (2)	0.010 (2)	6.4 (5)	C1	0.238 (4)	0.572 (2)	0.092 (2)	3.9 (5)
O2	0.554 (3)	0.601 (2)	0.293 (1)	5.5 (4)	C2	0.444 (4)	0.551 (2)	0.265 (2)	3.7 (4)
O3	-0.094 (3)	0.722 (2)	0.307 (1)	5.6 (4)	C3	0.032 (3)	0.624 (2)	0.278 (2)	3.6 (4)
O4	0.318 (3)	0.287 (2)	-0.062 (2)	7.1 (5)	C4	0.337 (4)	0.243 (3)	0.029 (2)	5.2 (6)
O5	0.812 (4)	0.034 (2)	0.151 (2)	7.4 (6)	C5	0.634 (4)	0.090 (3)	0.155 (2)	4.9 (6)
O6	0.267 (3)	-0.109 (2)	0.163 (2)	5.7 (4)	C6	0.296 (4)	0.003 (2)	0.163 (2)	3.9 (5)
O7	0.439 (3)	0.151 (2)	0.548 (2)	5.8 (4)	C7	0.336 (3)	0.179 (2)	0.479 (2)	3.5 (4)
O8	-0.182 (3)	0.421 (2)	0.477 (1)	5.4 (4)	C8	-0.052 (3)	0.354 (2)	0.433 (2)	3.4 (4)
O9	0.048 (3)	-0.047 (2)	0.387 (1)	5.4 (4)	C9	0.084 (3)	0.064 (2)	0.379 (2)	3.3 (4)
O10	0.613 (2)	0.244 (2)	0.331 (1)	3.8 (3)	C10	0.450 (3)	0.269 (2)	0.295 (2)	3.0 (4)

<sup>a</sup> All B units are Å<sup>2</sup>. <sup>b</sup> 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 IV. Interatomic Distances (Å) with Esd's for Os<sub>3</sub>(CO)<sub>9</sub>(μ<sub>3</sub>-CO)(μ<sub>3</sub>-S) (II)

Atoms	Distance	Atoms	Distance
Os(1)-Os(2)	2.826 (1)	Os(3)-C(9)	1.903 (12)
Os(1)-Os(3)	2.825 (1)	Os(1)-C(10)	2.179 (13)
Os(2)-Os(3)	2.840 (1)	Os(2)-C(10)	2.188 (12)
Os(1)-S	2.386 (3)	Os(3)-C(10)	2.157 (12)
Os(2)-S	2.375 (3)	C(1)-O(1)	1.164 (18)
Os(3)-S	2.372 (3)	C(2)-O(2)	1.106 (15)
Os(1)-C(1)	1.876 (15)	C(3)-O(3)	1.153 (16)
Os(1)-C(2)	1.915 (14)	C(4)-O(4)	1.215 (12)
Os(1)-C(3)	1.872 (14)	C(5)-O(5)	1.187 (20)
Os(2)-C(4)	1.828 (18)	C(6)-O(6)	1.146 (15)
Os(2)-C(5)	1.866 (18)	C(7)-O(7)	1.148 (17)
Os(2)-C(6)	1.890 (13)	C(8)-O(8)	1.118 (15)
Os(3)-C(7)	1.910 (15)	C(9)-O(9)	1.146 (15)
Os(3)-C(8)	1.921 (14)	C(10)-O(10)	1.183 (15)

2.877 (3) Å.<sup>5</sup> On one triangular face is a triply bridging sulfido ligand. Two osmium-sulfur bonds, Os(2)-S and Os(3)-S, are essentially equal in length, 2.375 (3) and 2.372 (3) Å, respectively, and are shorter than the third, Os(1)-S = 2.386 (3) Å. However, all three distances are similar to those found for the triply bridging ligand in other sulfidoosmium carbonyl clusters.<sup>2,6</sup> On the other side of the triosmium plane is a triply bridging carbonyl ligand. The three Os-C distances range from 2.157 (12) to 2.188 (12) Å and are not significantly different. The only previously reported example of an osmium cluster containing a triply bridging carbonyl ligand was for the compound Os<sub>6</sub>(CO)<sub>18</sub>(μ<sub>3</sub>-CO)(μ<sub>3</sub>-O), and the osmium-carbon distances were 2.15 (4) Å.<sup>7</sup> Each osmium atom also contains three linear terminal carbonyl ligands. The Os-C distances range from 1.828 to 1.921 Å. There does not appear to be any systematic pattern in their variation. The shortest intermolecular contacts are between oxygen atoms of the carbonyl ligands, O(3)⋯O(9) = 2.986 (15) and O(2)⋯O(3) = 3.010 (16) Å. Overall, the molecular structure of II is very similar to that of its iron homologue Fe<sub>3</sub>(CO)<sub>9</sub>(μ<sub>3</sub>-CO)(μ<sub>3</sub>-S).<sup>8</sup>

When photolyzed under a nitrogen atmosphere, I loses C<sub>6</sub>H<sub>6</sub> and CO and agglomerizes to form the hexaosmium

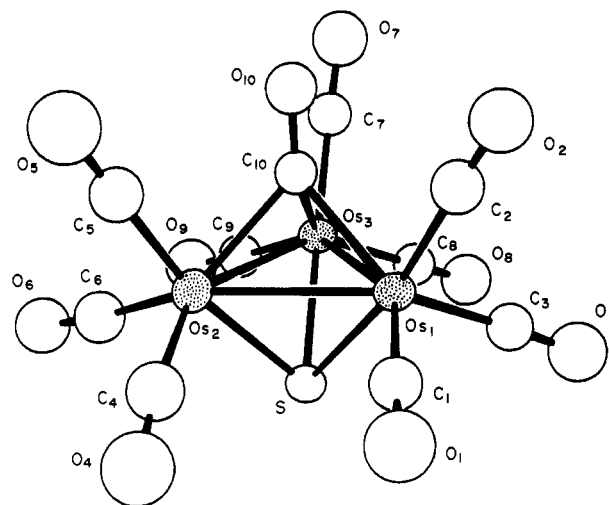


Figure 1. An ORTEP diagram of Os<sub>3</sub>(CO)<sub>9</sub>(μ<sub>3</sub>-CO)(μ<sub>3</sub>-S) (II) showing 50% probability thermal ellipsoids.

disulfido cluster Os<sub>6</sub>(CO)<sub>17</sub>(μ<sub>4</sub>-S)<sub>2</sub> (III). This compound was recently prepared through the reaction of Os<sub>3</sub>(CO)<sub>9</sub>(μ<sub>3</sub>-S)<sub>2</sub> and Os<sub>3</sub>(CO)<sub>10</sub>(NCMe)<sub>2</sub>.<sup>9</sup> When photolyzed under a hydrogen atmosphere, I loses 1 mol of C<sub>6</sub>H<sub>6</sub> and 1 mol of CO, adds 1 mol of H<sub>2</sub>, and forms the known compound H<sub>2</sub>Os<sub>3</sub>(CO)<sub>9</sub>(μ<sub>3</sub>-S) (IV).<sup>6c</sup> When photolyzed under an atmosphere of H<sub>2</sub>S, I loses C<sub>6</sub>H<sub>6</sub> and 2 mol of CO and adds 1 mol of H<sub>2</sub>S to yield the new compound H<sub>2</sub>Os<sub>3</sub>(CO)<sub>8</sub>(μ<sub>3</sub>-S)<sub>2</sub> (V). V has been characterized by X-ray crystallographic methods<sup>10</sup> and has been found to contain a structure analogous to the known compound H<sub>2</sub>Os<sub>3</sub>(CO)<sub>7</sub>(CS)(μ<sub>3</sub>-S)<sub>2</sub>.<sup>11</sup> When photolyzed under an atmosphere of COS or in CS<sub>2</sub> solvent, I loses C<sub>6</sub>H<sub>6</sub> and 2 mol of CO and adds 1 mol of COS or CS<sub>2</sub> to form the known compounds Os<sub>3</sub>(CO)<sub>9</sub>(μ<sub>3</sub>-S)<sub>2</sub> (VI)<sup>6b</sup> and Os<sub>3</sub>(CO)<sub>8</sub>(CS)(μ<sub>3</sub>-S)<sub>2</sub> (VII),<sup>12</sup> respectively.

Compounds III-VII can also be prepared by the photodecarbonylation of compound II in the presence of the appropriate reagents. In addition, it has been found that II will add mononuclear metal carbonyl fragments when

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Table V. Interatomic Angles (deg) with Esd's for Os<sub>3</sub>(CO)<sub>9</sub>(μ<sub>3</sub>-CO)(μ<sub>3</sub>-S) (II)

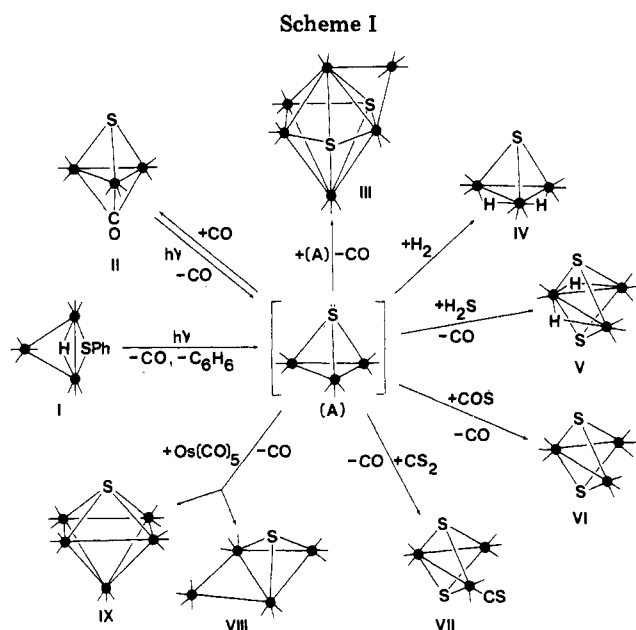
Atoms	Angle	Atoms	Angle
Os(1)-Os(2)-Os(3)	59.80 (2)	S-Os(2)-C(10)	87.6 (3)
Os(1)-Os(3)-Os(2)	59.85 (2)	C(4)-Os(2)-C(5)	91.3 (8)
Os(2)-Os(1)-Os(3)	60.35 (2)	C(4)-Os(2)-C(6)	96.9 (7)
Os(1)-S-Os(2)	72.82 (9)	C(4)-Os(2)-C(10)	134.1 (6)
Os(1)-S-Os(3)	72.83 (9)	C(5)-Os(2)-C(6)	92.0 (6)
Os(2)-S-Os(3)	73.49 (9)	C(5)-Os(2)-C(10)	82.8 (6)
Os(2)-Os(1)-S	53.41 (8)	C(6)-Os(2)-C(10)	128.7 (5)
Os(2)-Os(1)-C(1)	95.5 (4)	Os(1)-Os(3)-S	53.81 (7)
Os(2)-Os(1)-C(2)	118.6 (4)	Os(1)-Os(3)-C(7)	115.5 (4)
Os(2)-Os(1)-C(3)	146.4 (4)	Os(1)-Os(3)-C(8)	97.3 (4)
Os(2)-Os(1)-C(10)	49.8 (3)	Os(1)-Os(3)-C(9)	148.7 (4)
Os(3)-Os(1)-S	53.37 (8)	Os(1)-Os(3)-C(10)	49.7 (3)
Os(3)-Os(1)-C(1)	150.1 (4)	Os(2)-Os(3)-S	53.30 (8)
Os(3)-Os(1)-C(2)	115.2 (4)	Os(2)-Os(3)-C(7)	119.4 (4)
Os(3)-Os(1)-C(3)	95.5 (4)	Os(2)-Os(3)-C(8)	146.9 (4)
Os(3)-Os(1)-C(10)	49.0 (3)	Os(2)-Os(3)-C(19)	95.9 (4)
S-Os(1)-C(1)	98.8 (4)	Os(2)-Os(3)-C(10)	49.6 (3)
S-Os(1)-C(2)	167.6 (4)	S-Os(3)-C(7)	168.5 (4)
S-Os(1)-C(3)	93.9 (4)	S-Os(3)-C(8)	94.3 (4)
S-Os(1)-C(10)	87.6 (3)	S-Os(3)-C(9)	96.5 (4)
C(1)-Os(1)-C(2)	91.2 (6)	S-Os(3)-C(10)	88.4 (4)
C(1)-Os(1)-C(3)	97.4 (6)	C(7)-Os(3)-C(8)	91.2 (6)
C(1)-Os(1)-C(10)	129.6 (6)	C(7)-Os(3)-C(9)	93.1 (6)
C(2)-Os(1)-C(3)	92.0 (6)	C(7)-Os(3)-C(10)	80.5 (5)
C(2)-Os(1)-C(10)	80.4 (5)	C(8)-Os(3)-C(9)	94.5 (5)
C(3)-Os(1)-C(10)	132.2 (5)	C(8)-Os(3)-C(10)	134.4 (5)
Os(1)-Os(2)-S	53.77 (7)	C(9)-Os(3)-C(10)	130.5 (5)
Os(1)-Os(2)-C(4)	95.6 (5)	Os(1)-C(1)-O(1)	177.6 (14)
Os(1)-Os(2)-C(5)	116.7 (5)	Os(1)-C(2)-O(2)	175.6 (13)
Os(1)-Os(2)-C(6)	148.4 (4)	Os(1)-C(3)-O(3)	175.9 (13)
Os(1)-Os(2)-C(10)	49.5 (3)	Os(2)-C(4)-O(4)	177.7 (16)
Os(3)-Os(2)-S	53.21 (8)	Os(2)-C(5)-O(5)	177.0 (14)
Os(3)-Os(2)-C(4)	145.3 (6)	Os(2)-C(6)-O(6)	177.0 (13)
Os(3)-Os(2)-C(5)	120.8 (5)	Os(3)-C(7)-O(7)	175.9 (12)
Os(3)-Os(2)-C(6)	95.0 (4)	Os(3)-C(8)-O(8)	179.0 (11)
Os(3)-Os(2)-C(10)	48.7 (3)	Os(3)-C(9)-O(9)	173.7 (12)
S-Os(2)-C(4)	93.0 (6)	Os(1)-C(10)-O(10)	131.4 (9)
S-Os(2)-C(5)	169.9 (5)	Os(2)-C(10)-O(10)	130.2 (10)
S-Os(2)-C(6)	96.6 (5)	Os(3)-C(10)-O(10)	132.2 (10)

irradiated. For example, in the presence of Os(CO)<sub>5</sub> the known compounds Os<sub>4</sub>(CO)<sub>13</sub>(μ<sub>3</sub>-S) (VIII)<sup>2</sup> and Os<sub>5</sub>(CO)<sub>15</sub>(μ<sub>4</sub>-S) (IX)<sup>2</sup> are formed.

### Discussion

The reactions reported in this study are summarized in Scheme I. It is proposed that all take place via an unsaturated intermediate such as Os<sub>3</sub>(CO)<sub>9</sub>(μ<sub>3</sub>-S)(A), which contains only 46 electrons. The formation of A by the photodecarbonylation of compound II would seem to be fairly straightforward. The addition of selected small molecules to A and its condensation to yield III would seem to be a natural consequence of a tendency to remove its inherent unsaturation.

The formation of A from I is more speculative, but an initial photodecarbonylation step does not seem to be unreasonable. Indeed, it could be argued that such a step could facilitate the cleavage of the carbon-sulfur bond in the phenylthiolato ligand. It has been shown that decarbonylation and formation of a triply bridged ligand are important steps in carbon-sulfur bond cleavage in the desulfurization of bridging thioformamido ligands in triosmium clusters,<sup>13</sup> and Carty has shown that the compound H<sub>2</sub>Ru<sub>3</sub>(CO)<sub>9</sub>(μ-PPH<sub>2</sub>), which also eliminates benzene when heated, contains a significant interaction between the phosphorus-carbon bond of one of the phenyl groups and the third ruthenium atom.<sup>14</sup>



While photochemical techniques have been very effective in promoting ligand substitution reactions in mononuclear metal complexes, metal-metal bond cleavage and declusterification reactions have dominated the photochemistry of polynuclear metal complexes.<sup>15</sup> The present

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studies, particularly those of compound II, strongly suggest that photochemical fragmentation processes can be effectively inhibited by the presence of certain bridging ligands, and ligand substitution reactions become important.

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**Registry No.** I, 23733-19-9; II, 88746-45-6; III, 84647-91-6; IV, 38979-82-7; V, 88825-32-5; VI, 72282-40-7; VII, 76000-21-0; VIII, 86437-18-5; IX, 86437-19-6.

**Supplementary Material Available:** A table of structure factor amplitudes is available for the crystal structure analysis (10 pages). Ordering information is given on any current masthead page.

## Synthesis, Structure, and Reactivity of a Polynuclear Chromium Tetraanion, Tetrakis( $(\mu_3$ -methoxy)tricarbonylchromate(0))

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Reaction of  $\text{Cr}(\text{CO})_6$  with excess hydroxide ion in refluxing methanol yields a polynuclear chromium tetraanion,  $[\text{Cr}_4(\text{CO})_{12}(\mu_3\text{-OCH}_3)_4]^{4-}$ , isolated as its  $\text{R}_4\text{N}^+$  ( $\text{R} = \text{Me, Et}$ ) salt. The X-ray structure of  $[\text{Et}_4\text{N}]_4[\text{Cr}_4(\text{CO})_{12}(\mu_3\text{-OCH}_3)_4]$  has been determined; the crystals are orthorhombic, space group  $Fddd (D_{2h}^{24})$ ,  $Z = 8$ , with unit cell dimensions  $a = 12.766$  (4),  $b = 23.694$  (7), and  $c = 38.601$  (12) Å. The anion consists of a distorted cubic  $\text{A}_4\text{B}_4$  ( $\text{A} = \text{chromium, B} = \text{oxygen}$ ) arrangement with triply bridging  $\mu_3$ -methoxy groups and  $\text{Cr}(\text{CO})_3$  units. A nonbonding Cr-Cr distance of 3.31 (6) Å (average) is consistent with a closed-shell metal configuration.  $\text{Cr}(\text{CO})_3(\text{CH}_3\text{CN})_3$  is formed as the exclusive product when  $[\text{Cr}_4(\text{CO})_{12}(\mu_3\text{-OCH}_3)_4]^{4-}$  is treated with HCl in acetonitrile. Addition of the tetraanion to concentrated ammonium hydroxide quantitatively yields  $\text{Cr}(\text{CO})_3(\text{NH}_3)_3$ .

### Introduction

Reactions of the group 6B metal hexacarbonyls with hydroxide ion have received considerable attention owing to the ability of these solutions to catalyze the water gas shift reaction.<sup>2</sup> Depending upon reaction conditions, it has been noted that reaction of  $\text{Cr}(\text{CO})_6$  with base yields  $\text{HCr}(\text{CO})_5^-$  and  $(\mu\text{-H})\text{Cr}_2(\text{CO})_{10}^{2-}$ ,<sup>3</sup> as well as other, structurally uncharacterized, polynuclear carbonyl metalates.<sup>4</sup> These metalates, isolated from  $\text{KOH}/\text{Cr}(\text{CO})_6$  reaction mixtures in protic solvents, such as methanol, were believed to be binuclear anions with bridging hydroxo and methoxy groups and containing CO,  $\text{OH}^-$ , and  $\text{CH}_3\text{OH}$  as ligands.

In comparison, a few related polynuclear carbonyl complexes of molybdenum and tungsten have been characterized. In these complexes rather long M-M distances are consistent with the absence of direct metal-metal bonding. The structure of  $[\text{W}_2(\mu\text{-OH})_3(\text{CO})_6]^{3-}$ ,<sup>5</sup> a product of the alkaline hydrolysis of  $\text{W}(\text{CO})_6$ , consists of two  $\text{W}(\text{CO})_3$  fragments bridged by three hydroxo groups. Hieber's acid,  $[\text{HM}(\text{CO})_3(\mu_3\text{-OH})]_4$  ( $\text{M} = \text{Mo, W}$ ),<sup>6</sup> is a tetrahedral array of  $\text{M}(\text{CO})_3$  units (structurally characterized for the W derivative) with triply bridging OH groups. The neutral adduct,  $[\text{Mo}(\text{CO})_2(\text{NO})(\mu_3\text{-OH})]_4$ ,<sup>7</sup> prepared from the molybdenum derivative of Hieber's acid by replace-

ment of one CO at each metal atom by a nitrosyl group, also contains  $\mu_3\text{-OH}$  bridges. Unusual trimeric species with both doubly and triply bridging ligands are known,  $[\text{Mo}_3(\text{CO})_6(\text{NO})_3(\mu\text{-OCH}_3)_3(\mu_3\text{-OCH}_3)]^{-8}$  and  $[\text{W}_3(\text{CO})_9(\mu\text{-OC}_2\text{H}_5)(\mu_3\text{-OC}_2\text{H}_5)_2]^{3-}$ ,<sup>9</sup> the tungsten anion is noteworthy in that it is believed to contain a W-W bond on the basis of bond length and the 18-electron requirement.

We now wish to report the synthesis, spectral, and X-ray structural characterization of a polynuclear chromium tetraanion,  $[\text{Cr}_4(\text{CO})_{12}(\mu_3\text{-OCH}_3)_4]^{4-}$ , a species isolated as its  $\text{R}_4\text{N}^+$  ( $\text{R} = \text{Me, Et}$ ) salt from the reaction of  $\text{Cr}(\text{CO})_6$  and excess hydroxide ion in methanol. Procedures for the efficient syntheses of  $\text{Cr}(\text{CO})_3(\text{CH}_3\text{CN})_3$  and  $\text{Cr}(\text{CO})_3(\text{N-H}_3)_3$  from this polynuclear tetraanion are also presented.

### Experimental Section

**General Methods.** All manipulations involving air-sensitive compounds were performed with Schlenk techniques under an argon atmosphere or in a Vacuum Atmospheres inert atmosphere chamber under prepurified argon. All solvents were purified by distillation under nitrogen prior to use. Acetonitrile and methanol were distilled from calcium hydride, tetrahydrofuran from lithium aluminum hydride. IR spectra were obtained on a Perkin-Elmer 283 spectrometer. <sup>1</sup>H NMR spectra were recorded on a Varian EM-360 spectrometer or Varian HFT-80 spectrometer. <sup>13</sup>C NMR spectra were obtained with a Bruker HFX-90 spectrometer. All NMR data are listed in ppm relative to internal  $\text{Me}_4\text{Si}$ . GC analyses were performed with a Gow-Mac 69-100 gas chromatograph using a 4 ft  $\times$  1/4 in. stainless-steel column packed with Carbowax 20M. Chromium hexacarbonyl was purchased from Pressure Chemical Co., tetramethylammonium hydroxide (20% (w/w) in MeOH) from Alfa Products. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories.

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