

Figure 7. Plot of  $\log Q_f'$  for reaction 9 vs. hydroxamic acid ligand  $pK_a$  ( $\log K_a^{-1}$  for the reverse of reaction 8). Numerical labels for data points are as listed in the legend for Figure 3.

However, in spite of the scatter in Figure 7 some relevant trends are apparent. The relative magnitudes of  $Q_f'$  and  $K_a$  indicate that the hydroxamate ion has a greater affinity for  $Fe^{3+}$  than  $H^+$ , presumably due to the higher positive charge on  $Fe^{3+}$  and the chelate effect. The solid line in Figure 7 was arbitrarily drawn through data points for the simple hydroxamic acids  $CH_3C(O)N(OH)H$  and  $C_6H_5C(O)N(OH)H$  with

a slope of 0.5. Inspection of this plot shows that those data points that fall above the line (i.e., those compounds that form more stable iron(III) complexes than might be expected on the basis of their  $pK_a$  values) correspond to hydroxamic acids either where both the  $R_1$  and  $R_2$  groups are electron donors or when either  $R_1$  or  $R_2$  is one of the "best" functional groups. In other words, when  $R_1$  or  $R_2$  is an electron donor, there is a buildup of negative charge density on the carbonyl oxygen atom, resulting in a greater affinity for  $Fe_{aq}^{3+}$ . This does not correspondingly enhance the hydroxamate ion's affinity for  $H^+$  in aqueous solution, since protonation occurs at the hydroxyl oxygen. Conversely, all of the data points below the line in Figure 7 involve hydroxamic acids with  $R_2$  groups that are capable of electron delocalization away from the carbonyl oxygen. These ligands have a lower affinity for  $Fe^{3+}$  than one would expect on the basis of their  $pK_a$  values because of the decreased electron density at the carbonyl oxygen.

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**Registry No.** I (Y = H), 2446-50-6; I (Y = 4-NO<sub>2</sub>), 1613-77-0; I (Y = 4-CH<sub>3</sub>), 1613-85-0; I (Y = 4-CH<sub>3</sub>O), 2614-48-4; II (Y = H), 1795-83-1; II (Y = 4-CH<sub>3</sub>), 27451-21-4; II (Y = 4-Cl), 1503-91-9; II (Y = 4-I), 67274-49-1; II (Y = 3-I), 80584-64-1; II (Y = 4-CN), 80584-65-2; II (Y = 3-CN), 80584-66-3; II (Y = 4-C(O)CH<sub>3</sub>), 67274-51-5; Fe, 7439-89-6;  $Fe(H_2O)_6^{3+}$ , 15377-81-8;  $Fe(H_2O)_5(OH)^{2+}$ , 15696-19-2.

**Supplementary Material Available:** Tables II–XII, giving rate constant data (30 pages). Ordering information is given on any current masthead page.

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## Selenido Osmium Carbonyl Cluster Compounds. Structure, Bonding, and Reactivity of the Electron-Rich Cluster $Os_4(CO)_{12}(\mu_3-Se)_2$

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The compound  $HOs_3(CO)_{10}(\mu-SePh)$  (**3**) has been prepared (75% yield) by the reaction of  $Os_3(CO)_{10}(NCMe)_2$  with  $PhSeH$ . Under the conditions 160 °C (3000 psi CO), **3** eliminates benzene and is transformed into the compounds  $Os_3(CO)_9(\mu_3-Se)_2$  (**4**) and  $Os(CO)_5$  in 95% yield. When irradiated (UV) under an atmosphere of CO, **3** loses benzene and is converted to  $Os_3(CO)_9(\mu_3-CO)(\mu_3-Se)$  (**5**) in 18% yield. When irradiated in the presence of  $Os(CO)_5$ , **4** adds one  $Os(CO)_4$  moiety to form the compound  $Os_4(CO)_{13}(\mu_3-Se)_2$  (**6**) in 33% yield. At 125 °C, **6** loses 1 mol of CO to form the cluster  $Os_4(CO)_{12}(\mu_3-Se)_2$  (**7**) quantitatively. **7** has been characterized by a single-crystal X-ray diffraction analysis: space group  $P\bar{1}$  (No. 2),  $a = 13.987$  (4) Å,  $b = 16.371$  (6) Å,  $c = 9.491$  (6) Å,  $\alpha = 106.04$  (4)°,  $\beta = 90.31$  (4)°,  $\gamma = 81.63$  (3)°,  $V = 2065$  (3) Å<sup>3</sup>,  $Z = 4$ ,  $\rho_{calcd} = 4.036$  g/cm<sup>3</sup>. The structure was solved by direct methods and refined (4036 reflections,  $F^2 \geq 3.0\sigma(F^2)$ ) to the final residuals  $R_F = 0.047$  and  $R_{wF} = 0.056$ . The molecule consists of a butterfly tetrahedral cluster of four osmium atoms, with triply bridging selenido ligands bridging the two open triangular faces. The metal–metal bonding is irregular, with two of the five metal–metal bonds being greater than 3.00 Å in length. **7** adds 1 mol of CO under mild conditions (25 °C (1 atm CO)) to re-form **6** quantitatively. At 125 °C, **7** oxidatively adds 1 mol of H<sub>2</sub> to yield the compound  $H_2Os_4(CO)_{12}(\mu_3-Se)_2$  (**8**) in 35% yield. **5** reacts with H<sub>2</sub> at 125 °C to form  $H_2Os_3(CO)_9(\mu_3-Se)$  (**9**) in 39% yield.

### Introduction

The thermally and photochemically induced eliminations of benzene from the benzenethiolato osmium carbonyl cluster compound  $HOs_3(CO)_{10}(\mu-SPh)$  (**1**) have proved to be important routes for the synthesis of a variety of interesting new sulfido osmium carbonyl cluster compounds.<sup>1–4</sup> Perhaps the most intriguing of these compounds is the electron-rich cluster

$Os_4(CO)_{12}(\mu_3-S)_2$  (**2**), which readily and reversibly adds 1 mol of CO under mild conditions to form the open planar cluster  $Os_4(CO)_{13}(\mu_3-S)_2$ . Recently, a mixed-metal analogue of **2**,  $Os_3W(CO)_{12}(PMe_2Ph)(\mu_3-S)_2$ , has been made, and it exhibits bonding and reactivity properties similar to those of **2**.<sup>5</sup>

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In this report is described the nature of elimination of benzene from the benzeneselenolato homologue of **1**,  $\text{HO}_3\text{-(CO)}_{10}(\mu\text{-SePh})$  (**3**). A number of selenido osmium carbonyl cluster homologues of the sulfido series have been made in good yield. These include the cluster  $\text{Os}_4(\text{CO})_{12}(\mu_3\text{-Se})_2$ , which has been characterized by X-ray crystallographic methods.

### Experimental Section

All the products are air stable. Solvents were stored over 4-Å molecular sieves before use.  $\text{PhSeH}$  was purchased from Alfa Inorganics, Danvers, MA.  $\text{Os}_3(\text{CO})_{12}$ <sup>6</sup> and  $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ <sup>7</sup> were prepared by established procedures. Infrared spectra were recorded on a Nicolet 5SX FTIR instrument. Mass spectra were recorded on a Hewlett-Packard Model 5895 GC/mass spectrometer by the direct-inlet method. A Bruker WM500 FT-NMR spectrometer was used to obtain <sup>1</sup>H NMR spectra at 500 MHz. High-pressure reactions were performed in an Autoclave Engineers Model APB-300 magnedrive high-pressure apparatus.

**Preparations.**  $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-SePh})$  (**3**). Under an  $\text{N}_2$  atmosphere 0.190 g (0.19 mmol) of  $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$  was dissolved in 30 mL of  $\text{CH}_2\text{Cl}_2$  in a round-bottom flask at room temperature. A 30- $\mu\text{L}$  sample of benzeneselenol was added via syringe. The mixture was stirred 4 h at room temperature, and the solvent was then removed in vacuo. The yellow residue was dissolved in hexane and chromatographed on a silica column with hexane. The yellow product was recrystallized from hexane: yield 0.130 g (75%); IR ( $\nu(\text{CO})$ , hexane) 2108 m, 2068 vs, 2058 s, 2025 vs, 2015 s, 2002 s, 1988 m  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  7.3 (m, 5 H), -17.6 (s, 1 H).

$\text{Os}_3(\text{CO})_9(\mu_3\text{-Se})_2$  (**4**). A 0.190-g (0.19 mmol) sample of **3** was dissolved in 80 mL of octane. The solution was placed in a high-pressure apparatus and heated to 160 °C under a pressure of 3000 psi CO for 6 h. The solution was shown by IR spectroscopy to consist of two products only:  $\text{Os}_3(\text{CO})_9(\mu_3\text{-Se})_2$  and  $\text{Os}(\text{CO})_5$ . The solvent that was shown to contain benzene by GC and  $\text{Os}(\text{CO})_5$  were collected by distillation at 25 °C (0.1 mmHg) and photolyzed for 2 h at room temperature to give 0.081 g (0.093 mmol) of  $\text{Os}_3(\text{CO})_{12}$ . On the basis of  $\text{Os}_3(\text{CO})_{12}$  formed, the yield of  $\text{Os}(\text{CO})_5$  was calculated to be 0.086 g (0.268 mmol, 92%). The yellow residue of the reaction was chromatographed on silica TLC plates with hexane/ $\text{CH}_2\text{Cl}_2$  (95/5) solvent. The yellow product **4** was recrystallized from hexane: yield 0.088 g (0.09 mmol, 95% on the basis of selenium); IR ( $\nu(\text{CO})$ , hexane) 2075 s, 2055 s, 2015 s, 2009 sh  $\text{cm}^{-1}$ .

$\text{Os}_3(\text{CO})_9(\mu_3\text{-CO})(\mu_3\text{-Se})$  (**5**). In a sealed tube a solution of 0.100 g of  $\text{HO}_3(\text{CO})_{10}(\mu\text{-SePh})$  in 150 mL of cyclohexane was photolyzed under carbon monoxide (1 atm) for 2 h. After removal of solvent in vacuo, the yellow residue was chromatographed on silica TLC plates. Elution with hexane/ $\text{CH}_2\text{Cl}_2$  (90/10) separated the starting material (0.038 g) from the product  $\text{Os}_3(\text{CO})_9(\mu_3\text{-CO})(\mu_3\text{-Se})$  (**5**). Final purification was obtained by crystallization from hexane solvent: yield 0.016 g (0.017 mmol, 18%); IR ( $\nu(\text{CO})$ , hexane) 2075 vs, 2066 w, 2028 s, 2012 w, 1680 w  $\text{cm}^{-1}$ ; mass spectrum (70 eV)  $\text{M}^+$  936 plus ions corresponding to the loss of each of 10 carbonyl ligands. Anal. Calcd: C, 12.92; H, 0.00. Found: C, 13.07; H, 0.03.

$\text{Os}_4(\text{CO})_{13}(\mu_3\text{-Se})_2$  (**6**). A solution of **4** (0.039 g, 0.04 mmol) and an excess of  $\text{Os}(\text{CO})_5$  in 50 mL of octane in a 100-mL Pyrex flask was photolyzed (UV) for 90 min under an  $\text{N}_2$  atmosphere. The solvent was removed in vacuo, and the reddish brown residue was chromatographed on silica TLC plates. Elution with hexane/ $\text{CH}_2\text{Cl}_2$  (90/10) separated the starting material (0.021 g) from the major product  $\text{Os}_4(\text{CO})_{13}(\mu_3\text{-Se})_2$  (**6**): yield 0.017 g (0.013 mmol, 33%); IR ( $\nu(\text{CO})$ , hexane) 2089 s, 2063 s, 2047 w, 2026 s, 2020 sh, 1998 w, 1989 w, 1984 w, 1935 w  $\text{cm}^{-1}$ .

$\text{Os}_4(\text{CO})_{12}(\mu_3\text{-Se})_2$  (**7**). A 0.013-g (0.01 mmol) sample of  $\text{Os}_4(\text{CO})_{13}(\mu_3\text{-Se})_2$  was refluxed for 2 h in 30 mL of octane solvent under an  $\text{N}_2$  atmosphere. The solvent was removed in vacuo, and the green residue was crystallized from hexane/ $\text{CH}_2\text{Cl}_2$  (80/20) by slow evaporation at 4 °C to give 0.012 g (0.0096 mmol, 94%) of  $\text{Os}_4(\text{CO})_{12}(\mu_3\text{-Se})_2$  (**7**): IR ( $\nu(\text{CO})$ , hexane) 2072 vs, 2064 s, 2058 s, 2022 w, 2017 w, 1998 w  $\text{cm}^{-1}$ .

Table I. Crystallographic Data for X-ray Diffraction Study

(A) Cell Parameters	
compd	7
formula	$\text{Os}_4\text{Se}_2\text{O}_{12}\text{C}_{12}$
temp ( $\pm 3$ °C)	24
space group	$P\bar{1}$ , No. 2
a, Å	13.987 (4)
b, Å	16.371 (6)
c, Å	9.491 (6)
$\alpha$ , deg	106.04 (4)
$\beta$ , deg	90.31 (4)
$\gamma$ , deg	81.63 (3)
V, Å <sup>3</sup>	2065 (3)
$M_r$	1254.85
Z	4
$\rho_{\text{calcd}}$ , g/cm <sup>3</sup>	4.036
(B) Measurement of Intensity Data	
radiation ( $\lambda$ , Å)	$\text{Mo K}\alpha$ (0.71073)
monochromator	graphite
detector aperture, mm	
horizn ( $A + B \tan \theta$ ): A, B	3.0, 1.0
vert	4.0
cryst faces	100, $\bar{1}00$ , $\bar{1}\bar{1}0$ , 010, $\bar{1}\bar{1}0$ , 110, $\bar{1}\bar{1}1$ , $\bar{1}\bar{1}\bar{1}$ , 001, $11\bar{2}$ , 010
cryst size, mm	0.09 × 0.14 × 0.40
cryst orientation direction, deg	normal to 012, 4.8
from $\phi$ axis	
reflcs measd	$h, \pm k, \pm l$
max $2\theta$ , deg	46
scan type	moving-cryst stationary-counter
$\omega$ -scan width ( $A + 0.347 \tan \theta$ ), deg	1.00
bkgd	addnl scan at each end of scan
$\omega$ -scan rate (variable), deg/min:	10.0, 1.5
max, min	
no. of reflcs measd	5704
no. of data used ( $F^2 \geq 3.0\sigma(F^2)$ )	4036
(C) Treatment of Data	
abs cor coeff, $\text{cm}^{-1}$	281.2
grid	6 × 8 × 20
transmissn coeff: max, min	0.191, 0.093
P factor	0.03
final residuals: $R_F, R_{wF}$	0.047, 0.056
esd of unit weight observn	2.26
largest shift/error value of final cycle	0.14
largest peak in final diff Fourier, e/Å <sup>3</sup>	3.0

**Reaction of  $\text{Os}_4(\text{CO})_{12}(\mu_3\text{-Se})_2$  (**7**) with CO.** A solution of **7** (0.020 g, 0.016 mmol) in 15 mL of methylene chloride solvent was stirred under an atmosphere of carbon monoxide at room temperature. After 24 h, the solution had changed color from greenish red to red-orange. The only product observed by infrared spectroscopy was **6**. **6** can be purified by TLC and crystallized from hexane solutions at -20 °C; yield 0.020 g (0.0159 mmol, 98%).

**Preparations.**  $\text{H}_2\text{Os}_4(\text{CO})_{12}(\mu_3\text{-Se})_2$  (**8**). A solution of **7** (0.010 g, 0.008 mmol) was refluxed 8 h in 25 mL of octane solvent under a  $\text{H}_2$  atmosphere. The solvent was removed in vacuo, and the yellow residue was chromatographed on silica TLC plates. Elution with hexane/ $\text{CH}_2\text{Cl}_2$  (95/5) separated the product  $\text{H}_2\text{Os}_4(\text{CO})_{12}(\mu_3\text{-Se})_2$  (**8**). Final purification was obtained by crystallization from hexane solvent: yield 0.0035 g (0.003 mmol, 35%); IR ( $\nu(\text{CO})$ , hexane) 2113 w, 2092 s, 2077 vs, 2051 s, 2034 w, 2022 s, 2018 sh, 2006 m, 1986 w, 1980 w  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  -14.9 (s, 2 H).

$\text{H}_2\text{Os}_3(\text{CO})_9(\mu_3\text{-Se})$  (**9**). A solution of **5** (0.012 g, 0.013 mmol) was refluxed 2 h in 20 mL of octane solvent under a  $\text{H}_2$  atmosphere. The solvent was removed in vacuo, and the yellow residue was chromatographed on silica TLC plates. Elution with hexane/ $\text{CH}_2\text{Cl}_2$  (98/2) separated the yellow  $\text{H}_2\text{Os}_3(\text{CO})_9(\mu_3\text{-Se})$  (**9**): yield 0.0045 g (0.005 mmol, 39%); IR ( $\nu(\text{CO})$ , hexane) 2117 w, 2085 s, 2058 vs, 2035 m, 2012 s, 1998 m, 1991 w, 1983 w  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  -21.2 (s, 2 H); mass spectrum (70 eV)  $\text{M}^+$  910 plus ions corresponding to the loss of each of nine CO ligands.

**Crystallographic Analysis.** Dark red crystals of **7** suitable for X-ray diffraction measurements were grown from hexane/methylene chloride solutions by slow evaporation of the solvent at 0 °C. The data crystal was mounted in thin-walled glass capillary. Diffraction measurements were made on an Enraf-Nonius CAD-4 automated diffractometer

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Table II. Final Fractional Atomic Coordinates with Esds for Os<sub>4</sub>(CO)<sub>12</sub>(μ<sub>3</sub>-Se)<sub>2</sub> (7)

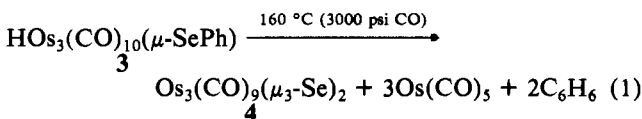
atom	x	y	z	atom	x	y	z
Os(1)	0.35387 (8)	0.34917 (6)	0.8975 (1)	O(19)	-0.005 (2)	-0.016 (1)	1.345 (2)
Os(2)	0.50901 (8)	0.19516 (6)	0.8467 (1)	O(20)	-0.092 (2)	0.061 (1)	0.967 (2)
Os(3)	0.43879 (8)	0.29348 (6)	1.1453 (1)	O(21)	-0.284 (2)	0.132 (1)	1.340 (2)
Os(4)	0.34157 (8)	0.14505 (6)	0.9676 (1)	O(22)	0.265 (2)	0.304 (1)	1.488 (2)
Os(5)	-0.07973 (8)	0.33139 (6)	1.2582 (1)	O(23)	0.054 (2)	0.262 (1)	1.823 (2)
Os(6)	-0.13258 (8)	0.29934 (6)	1.5425 (1)	O(24)	0.172 (2)	0.054 (1)	1.466 (2)
Os(7)	-0.07624 (8)	0.15454 (6)	1.2841 (1)	C(1)	0.233 (2)	0.398 (2)	0.850 (3)
Os(8)	0.07452 (8)	0.23492 (6)	1.4938 (1)	C(2)	0.421 (2)	0.370 (2)	0.737 (3)
Se(1)	0.3456 (2)	0.1971 (2)	0.7381 (3)	C(3)	0.382 (2)	0.453 (2)	1.022 (3)
Se(2)	0.2645 (2)	0.2991 (2)	1.0868 (3)	C(4)	0.546 (3)	0.108 (2)	0.669 (4)
Se(3)	0.0666 (2)	0.2133 (2)	1.2185 (3)	C(5)	0.592 (2)	0.261 (1)	0.797 (3)
Se(4)	-0.0072 (2)	0.3875 (2)	1.5067 (3)	C(6)	0.600 (2)	0.149 (2)	0.960 (3)
O(1)	0.157 (2)	0.426 (1)	0.831 (2)	C(7)	0.398 (2)	0.393 (2)	1.287 (3)
O(2)	0.459 (2)	0.386 (1)	0.651 (2)	C(8)	0.567 (2)	0.318 (2)	1.142 (3)
O(3)	0.402 (2)	0.518 (1)	1.098 (2)	C(9)	0.471 (2)	0.239 (2)	1.290 (3)
O(4)	0.579 (2)	0.056 (1)	0.565 (3)	C(10)	0.229 (2)	0.104 (2)	0.912 (3)
O(5)	0.649 (2)	0.302 (1)	0.777 (2)	C(11)	0.334 (2)	0.118 (2)	1.141 (3)
O(6)	0.661 (2)	0.114 (1)	1.015 (3)	C(12)	0.422 (2)	0.039 (2)	0.874 (3)
O(7)	0.375 (2)	0.458 (1)	1.383 (3)	C(13)	-0.010 (2)	0.395 (2)	1.175 (3)
O(8)	0.638 (2)	0.342 (1)	1.141 (3)	C(14)	-0.140 (2)	0.280 (2)	1.089 (3)
O(9)	0.490 (2)	0.205 (1)	1.385 (2)	C(15)	-0.185 (3)	0.417 (2)	1.308 (4)
O(10)	0.154 (2)	0.078 (1)	0.864 (2)	C(16)	-0.151 (2)	0.376 (2)	1.730 (3)
O(11)	0.326 (2)	0.100 (1)	1.254 (2)	C(17)	-0.159 (2)	0.209 (1)	1.608 (3)
O(12)	0.463 (2)	-0.027 (1)	0.823 (2)	C(18)	-0.264 (2)	0.325 (2)	1.498 (3)
O(13)	0.031 (2)	0.435 (1)	1.114 (2)	C(19)	-0.032 (2)	0.048 (2)	1.319 (3)
O(14)	-0.171 (2)	0.254 (1)	0.973 (2)	C(20)	-0.087 (2)	0.100 (2)	1.086 (3)
O(15)	-0.255 (2)	0.472 (1)	1.339 (2)	C(21)	-0.202 (3)	0.142 (2)	1.319 (3)
O(16)	-0.161 (2)	0.423 (1)	1.844 (3)	C(22)	0.191 (2)	0.276 (2)	1.493 (3)
O(17)	-0.175 (2)	0.153 (1)	1.655 (2)	C(23)	0.063 (2)	0.251 (2)	1.696 (3)
O(18)	-0.341 (2)	0.341 (1)	1.473 (2)	C(24)	0.130 (2)	0.121 (2)	1.481 (3)

and refined from 25 randomly selected reflections obtained by using the CAD-4 automatic search, center, index, and least-squares routines. The triclinic space group  $P\bar{1}$  was selected and confirmed by the successful solution and refinement of the structure. 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.<sup>8a</sup> Anomalous dispersion corrections were applied to all non-hydrogen atoms.<sup>8b</sup> Full-matrix least-squares refinements minimized the function  $\sum w(|F_o| - |F_c|)^2$ , where  $w = 1/\sigma(F)^2$ ,  $\sigma(F) = \sigma(F_o^2)/2F_o$ , and  $\sigma(F_c^2) = [\sigma(I_{raw})^2 + (PF_o^2)^2]^{1/2}/Lp$ .

The structure was solved by combination of direct methods and difference Fourier techniques. The eight independent metal atoms were located in an electron density map based on the phases (MULTAN) of 340 reflections ( $E_{min} = 1.79$ ). Only the osmium and selenium atoms were refined anisotropically. The values of the final fractional atomic coordinates are listed in Table II. Tables III and IV list interatomic distances and angles with esds obtained from the inverse matrix obtained on the final cycle of refinement. Tables of structure factor amplitudes and thermal parameters are available as supplementary material.

## Results

When heated to 160 °C under a pressure of 3000 psi CO, 3 loses benzene and is converted to the products Os<sub>3</sub>(CO)<sub>9</sub>(μ<sub>3</sub>-Se)<sub>2</sub> (4) and Os(CO)<sub>5</sub> according to eq 1. Os<sub>3</sub>(CO)<sub>9</sub>(μ<sub>3</sub>-Se)<sub>2</sub> has been reported previously as a product of the reaction of Os<sub>3</sub>(CO)<sub>12</sub> with elemental selenium at 125 °C.<sup>9</sup> It is spectroscopically similar to the analogous sulfido com-



ound Os<sub>3</sub>(CO)<sub>9</sub>(μ<sub>3</sub>-S)<sub>2</sub>. In contrast, under the influence of UV irradiation and under an atmosphere of CO, 3 loses

Table III. Interatomic Distances (Å) with Esds for Os<sub>4</sub>(CO)<sub>12</sub>(μ<sub>3</sub>-Se)<sub>2</sub> (7)

Molecule 1			
Os(1)-Os(2)	3.008 (1)	Os(3)-C(7)	1.824 (21)
Os(1)-Os(3)	2.935 (1)	Os(3)-C(8)	1.903 (23)
Os(2)-Os(3)	2.938 (1)	Os(3)-C(9)	1.855 (19)
Os(2)-Os(4)	2.930 (1)	Os(4)-C(10)	1.815 (20)
Os(3)-Os(4)	3.045 (1)	Os(4)-C(11)	1.827 (10)
Os(1)-Se(1)	2.549 (2)	Os(4)-C(12)	1.914 (20)
Os(1)-Se(2)	2.569 (2)	C(1)-O(1)	1.127 (23)
Os(2)-Se(1)	2.502 (2)	C(2)-O(2)	1.092 (21)
Os(3)-Se(2)	2.492 (2)	C(3)-O(3)	1.181 (20)
Os(4)-Se(1)	2.553 (2)	C(4)-O(4)	1.156 (33)
Os(4)-Se(2)	2.539 (2)	C(5)-O(5)	1.159 (21)
Se(1)···Se(2)	3.386 (3)	C(6)-O(6)	1.156 (24)
Os(1)-C(1)	1.872 (21)	C(7)-O(7)	1.196 (23)
Os(1)-C(2)	1.922 (20)	C(8)-O(8)	1.119 (25)
Os(1)-C(3)	1.876 (17)	C(9)-O(9)	1.190 (21)
Os(2)-C(4)	1.903 (23)	C(10)-O(10)	1.225 (23)
Os(2)-C(5)	1.841 (18)	C(11)-O(11)	1.193 (22)
Os(2)-C(6)	1.875 (22)	C(12)-O(12)	1.129 (26)
		Os(1)···Os(4)	3.611 (1)
Molecule 2			
Os(5)-Os(6)	3.003 (1)	Os(7)-C(19)	1.883 (18)
Os(5)-Os(7)	2.966 (1)	Os(7)-C(20)	1.861 (19)
Os(6)-Os(7)	2.919 (1)	Os(7)-C(21)	1.841 (25)
Os(6)-Os(8)	2.928 (1)	Os(8)-C(22)	1.855 (20)
Os(7)-Os(8)	3.075 (1)	Os(8)-C(23)	1.869 (20)
Os(5)-Se(3)	2.546 (2)	Os(8)-C(24)	1.885 (20)
Os(5)-Se(4)	2.555 (2)	C(13)-O(13)	1.179 (22)
Os(6)-Se(3)	2.508 (2)	C(14)-O(14)	1.184 (22)
Os(7)-Se(4)	2.491 (2)	C(15)-O(15)	1.200 (27)
Os(8)-Se(3)	2.561 (3)	C(16)-O(16)	1.137 (21)
Os(8)-Se(4)	2.541 (2)	C(17)-O(17)	1.163 (20)
Se(3)···Se(4)	3.397 (3)	C(18)-O(18)	1.101 (23)
Os(5)-C(13)	1.854 (20)	C(19)-O(19)	1.150 (20)
Os(5)-C(14)	1.847 (21)	C(20)-O(20)	1.137 (21)
Os(5)-C(15)	1.843 (26)	C(21)-O(21)	1.212 (27)
Os(6)-C(16)	1.870 (19)	C(22)-O(22)	1.192 (23)
Os(6)-C(17)	1.841 (17)	C(23)-O(23)	1.173 (22)
Os(6)-C(18)	1.900 (21)	C(24)-O(24)	1.146 (22)
		Os(5)···Os(8)	3.613 (1)

(8) "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.

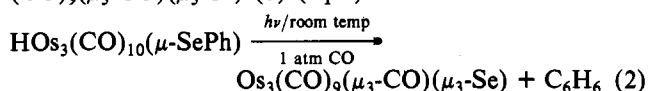
(9) Johnson, B. F. G.; Lewis, J.; Lodge, P. G.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* 1979, 719.

ound Os<sub>3</sub>(CO)<sub>9</sub>(μ<sub>3</sub>-S)<sub>2</sub>. In contrast, under the influence of UV irradiation and under an atmosphere of CO, 3 loses

Table IV. Selected Interatomic Angles (deg) with Esds for  $\text{Os}_4(\text{CO})_{12}(\mu_3\text{-Se})_2$  (7)

Molecule 1			
Os(1)-Os(2)-Os(3)	59.14 (2)	Os(2)-Os(3)-Se(2)	94.65 (5)
Os(1)-Os(3)-Os(2)	61.61 (2)	Os(3)-Os(1)-Se(1)	94.55 (5)
Os(2)-Os(1)-Os(3)	59.25 (2)	Os(4)-Os(3)-Se(2)	53.47 (4)
Os(1)-Os(2)-Os(4)	74.90 (3)	Os(2)-Os(4)-Se(1)	53.77 (5)
Os(1)-Os(3)-Os(4)	74.26 (3)	Os(3)-Os(4)-Se(2)	52.05 (5)
Os(3)-Os(2)-Os(4)	62.52 (2)	Os(2)-Os(1)-Se(1)	52.74 (5)
Os(2)-Os(3)-Os(4)	58.60 (2)	Os(3)-Os(1)-Se(2)	53.34 (5)
Os(2)-Os(4)-Os(3)	58.88 (2)	Se(1)-Os(1)-Se(2)	82.83 (6)
Os(1)-Se(1)-Os(2)	73.08 (5)	Se(1)-Os(4)-Se(2)	88.34 (6)
Os(1)-Se(2)-Os(3)	70.87 (5)	Os(1)-C(1)-O(1)	174 (2)
Os(1)-Se(1)-Os(4)	90.09 (6)	Os(1)-C(2)-O(2)	176 (2)
Os(1)-Se(2)-Os(4)	89.96 (6)	Os(1)-C(3)-O(3)	178 (2)
Os(2)-Se(1)-Os(4)	70.83 (6)	Os(2)-C(4)-O(4)	172 (2)
Os(3)-Se(2)-Os(4)	74.48 (6)	Os(2)-C(5)-O(5)	174 (2)
Os(2)-Os(1)-Se(1)	52.74 (5)	Os(2)-C(6)-O(6)	172 (2)
Os(3)-Os(1)-Se(2)	53.34 (5)	Os(3)-C(7)-O(7)	177 (2)
Os(1)-Os(2)-Se(1)	54.18 (4)	Os(3)-C(8)-O(8)	172 (2)
Os(1)-Os(3)-Se(2)	55.78 (5)	Os(3)-C(9)-O(9)	178 (2)
Os(4)-Os(2)-Se(1)	55.40 (5)	Os(4)-C(10)-O(10)	175 (2)
Os(4)-Os(3)-Se(2)	53.47 (4)	Os(4)-C(11)-O(11)	178 (2)
Os(3)-Os(2)-Se(1)	95.48 (5)	Os(4)-C(12)-O(12)	174 (2)
Molecule 2			
Os(5)-Os(6)-Os(7)	60.09 (2)	Os(6)-Os(7)-Se(4)	94.07 (5)
Os(5)-Os(7)-Os(6)	61.37 (2)	Os(7)-Os(5)-Se(3)	94.77 (5)
Os(6)-Os(5)-Os(7)	58.54 (2)	Os(8)-Os(7)-Se(4)	53.08 (5)
Os(5)-Os(6)-Os(8)	75.05 (3)	Os(6)-Os(8)-Se(3)	53.87 (5)
Os(5)-Os(7)-Os(8)	73.45 (3)	Os(7)-Os(8)-Se(4)	51.60 (5)
Os(7)-Os(6)-Os(8)	63.46 (3)	Os(6)-Os(5)-Se(3)	52.95 (5)
Os(6)-Os(7)-Os(8)	58.41 (2)	Os(7)-Os(5)-Se(4)	53.02 (5)
Os(6)-Os(8)-Os(7)	58.13 (2)	Se(3)-Os(5)-Se(4)	83.52 (6)
Os(5)-Se(4)-Os(7)	71.99 (6)	Se(3)-Os(8)-Se(4)	83.49 (6)
Os(5)-Se(3)-Os(6)	72.91 (5)	Os(5)-C(13)-O(13)	176 (2)
Os(5)-Se(4)-Os(8)	90.32 (6)	Os(5)-C(14)-O(14)	171 (2)
Os(5)-Se(3)-Os(8)	90.05 (6)	Os(5)-C(15)-O(15)	178 (2)
Os(7)-Se(4)-Os(8)	75.31 (8)	Os(6)-C(16)-O(16)	179 (2)
Os(6)-Se(3)-Os(8)	70.56 (5)	Os(6)-C(17)-O(17)	177 (2)
Os(6)-Os(5)-Se(3)	52.95 (5)	Os(6)-C(18)-O(18)	180 (1)
Os(7)-Os(5)-Se(4)	53.02 (5)	Os(7)-C(19)-O(19)	178 (2)
Os(5)-Os(6)-Se(3)	54.14 (5)	Os(7)-C(20)-O(20)	176 (2)
Os(5)-Os(7)-Se(4)	54.99 (5)	Os(7)-C(21)-O(21)	179 (2)
Os(8)-Os(6)-Se(3)	55.57 (5)	Os(8)-C(22)-O(22)	177 (2)
Os(8)-Os(7)-Se(4)	53.08 (5)	Os(8)-C(23)-O(23)	178 (2)
Os(7)-Os(6)-Se(3)	96.78 (5)	Os(8)-C(24)-O(24)	172 (2)

benzene to yield the monoselenido triosmium cluster  $\text{Os}_3(\text{CO})_9(\mu_3\text{-CO})(\mu_3\text{-Se})$  (5) (eq 2). The formula for 5 was



established by a mass spectral analysis that shows a parent ion at  $m/e$  936 for  $^{192}\text{Os}$  and  $^{80}\text{Se}$  plus ions corresponding to the loss of each of 10 CO ligands. The IR spectrum of 5 shows an absorption at  $1680\text{ cm}^{-1}$  that can be attributed to the CO stretching vibration of a triply bridging carbonyl ligand. 5 is thus believed to be structurally analogous to its sulfido homologue  $\text{Os}_3(\text{CO})_9(\mu_3\text{-CO})(\mu_3\text{-S})$ , which contains a triply bridging carbonyl ligand that absorbs in the IR spectrum at  $1685\text{ cm}^{-1}$ .<sup>4</sup>

When photolyzed (UV) in the presence of  $\text{Os}(\text{CO})_5$ , 4 captures an  $\text{Os}(\text{CO})_4$  fragment and forms the compound  $\text{Os}_4(\text{CO})_{13}(\mu_3\text{-Se})_2$  (6) in 33% yield. From the similarities of their IR spectra it can be concluded that 6 is structurally analogous to its sulfido homologue  $\text{Os}_4(\text{CO})_{13}(\mu_3\text{-S})_2$ . When heated to  $125^\circ\text{C}$ , 6 loses 1 mol of CO to form  $\text{Os}_4(\text{CO})_{12}(\mu_3\text{-Se})_2$  (7) quantitatively. This decarbonylation is reversible, and under an atmosphere of CO at  $25^\circ\text{C}$ , 7 adds 1 mol of CO to re-form 6 quantitatively within 24 h.

Compound 7 was further characterized by a single-crystal X-ray structural analysis. The compound crystallizes in the triclinic space group  $P\bar{1}$  with 2 crystallographically independent molecules in the asymmetric crystal unit. The shortest in-

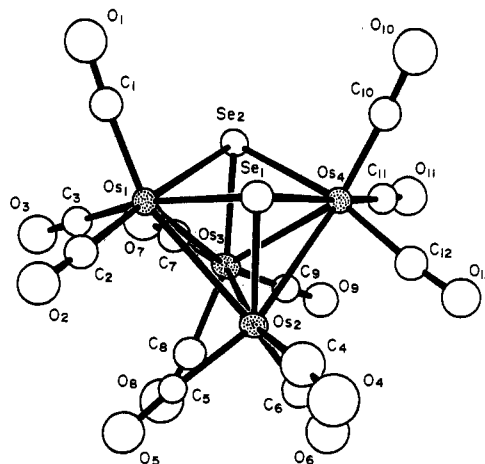


Figure 1. ORTEP diagram of one of the two crystallographically independent molecules of  $\text{Os}_4(\text{CO})_{12}(\mu_3\text{-Se})_2$  (7) showing 50% probability thermal ellipsoids.

termolecular contact was between carbonyl oxygen atoms,  $\text{O}(8)\cdots\text{O}(15) = 3.00(2)\text{ \AA}$ . An ORTEP diagram of one of the two independent molecules is shown in Figure 1. Final fractional atomic coordinates are listed in Table II. Interatomic distances and angles are listed in Tables III and IV. Both independent molecules are essentially identical structurally. The molecule consists of a butterfly tetrahedron of four osmium atoms. The five metal-metal bonds show significant variations in their lengths. Each molecule contains two osmium-osmium bonds in excess of  $3.00\text{ \AA}$  in length,  $\text{Os}(1)\text{-Os}(2) = 3.008(1)\text{ \AA}$  [ $3.003(1)\text{ \AA}$ ] and  $\text{Os}(3)\text{-Os}(4) = 3.045(1)\text{ \AA}$  [ $3.075(1)\text{ \AA}$ ],<sup>10</sup> which are significantly different from each other. The osmium-osmium bond distance in  $\text{Os}_3(\text{CO})_{12}$  is  $2.877(3)\text{ \AA}$ .<sup>11</sup> The remaining metal-metal bonds in 7 are considerably shorter and range from  $2.919(1)$  to  $2.966(1)\text{ \AA}$  but are still significantly longer than those in  $\text{Os}_3(\text{CO})_{12}$ . The homologous sulfido cluster  $\text{Os}_4(\text{CO})_{12}(\mu_3\text{-S})_2$  showed a similar variation in the metal-metal bond lengths.<sup>2</sup> The  $\text{Os}(1)\cdots\text{Os}(4)$  distance at  $3.611(1)\text{ \AA}$  [ $3.613(1)\text{ \AA}$ ] is a nonbonding distance. The dihedral angle between the  $\text{Os}(1)\text{-Os}(2)\text{-Os}(3)$  and  $\text{Os}(2)\text{-Os}(3)\text{-Os}(4)$  planes is  $88.2^\circ$  [ $87.4^\circ$ ]. Triply bridging selenido ligands bridge the two open triangular faces of the butterfly tetrahedron. The  $\text{Os-Se}$  distances to the wing-tip osmium atoms,  $2.539(2)\text{-}2.569(2)\text{ \AA}$ , are significantly longer than those to the hinge atoms,  $2.491(2)\text{-}2.508(2)\text{ \AA}$ . The osmium-selenium distances in the related compound  $\text{H}_2\text{Os}_4(\text{CO})_{12}(\mu_3\text{-Se})_2$  (8) range from  $2.537(1)$  to  $2.576(1)\text{ \AA}$ .<sup>9</sup> The intramolecular  $\text{Se}\cdots\text{Se}$  distance at  $3.386(3)\text{ \AA}$  [ $3.397(3)\text{ \AA}$ ] is a nonbonding distance. Each metal atom in 7 contains three linear terminal carbonyl ligands.

Compound 8 was originally prepared by the reaction of  $\text{Os}_3(\text{CO})_{12}$  with elemental selenium under a pressure of  $\text{CO}/\text{H}_2$  (1/1, 35 atm).<sup>9</sup> However, it can also be made in moderate yield (35%) by the reaction of 7 with  $\text{H}_2$  (1 atm) at  $125^\circ\text{C}$  over a period of 8 h.

At  $125^\circ\text{C}$  5 reacts with  $\text{H}_2$  to form the compound  $\text{H}_2\text{Os}_3(\text{CO})_9(\mu_3\text{-Se})$  (9) in 39% yield. 9 is spectroscopically similar to the analogous sulfido compound  $\text{H}_2\text{Os}_3(\text{CO})_9(\mu_3\text{-S})$ .<sup>12</sup>

## Discussion

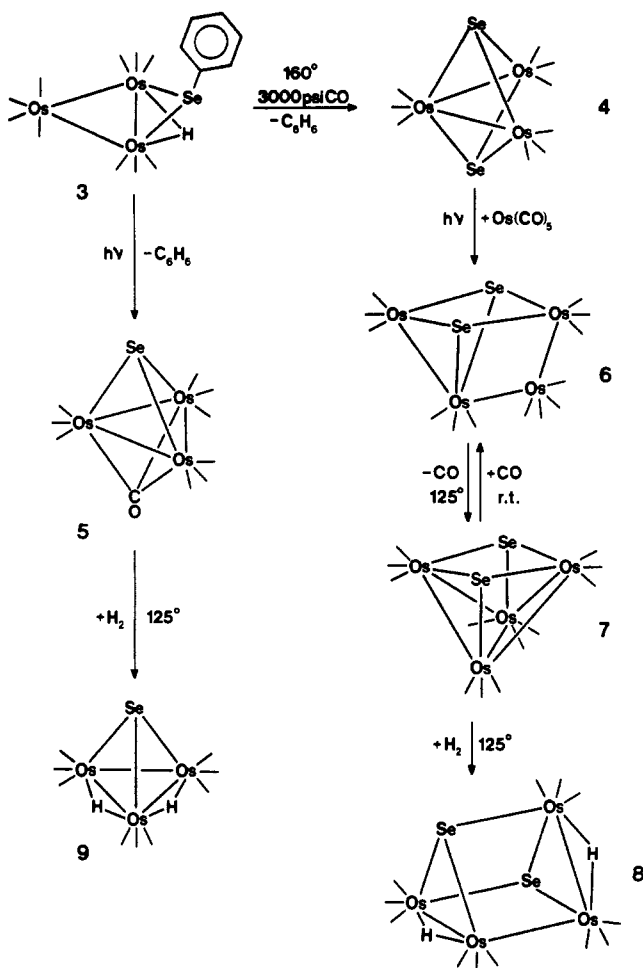
Compound 3 loses benzene both thermally and photochemically to yield the selenido triosmium carbonyl clusters 4 and

(10) The value given in brackets is the corresponding value from the second crystallographically independent molecule.

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(12) Johnson, B. F. G.; Lewis, J.; Pippard, D.; Raithby, P. R.; Sheldrick, G. M.; Rause, K. D. *J. Chem. Soc., Dalton Trans.* 1979, 616.

Scheme I



**5**, respectively (Scheme I). The analogous sulfido triosmium carbonyl clusters were obtained by decomposition of compound **1** under similar conditions.<sup>4</sup> These reactions are believed to occur via an intramolecular elimination of benzene and the formation of monochalcogenide triosmium carbonyl intermediates. The transfer of a chalcogenide ligand from one cluster to a second permits the formation of the dichalcogenide species **4**. This is accompanied by the formation of 3 equiv of Os(CO)<sub>5</sub> (eq 1), when performed under CO pressure.

When photolyzed, compound **4** reacts with Os(CO)<sub>5</sub> to yield the electron-precise, open cluster **6**. Compound **6** loses 1 mol of CO when heated to yield **7**. Assuming that the selenido ligands serve as four-electron donors, **7** contains 64 electrons. Electron-precise clusters with 64 electrons should contain only four metal-metal bonds.<sup>13</sup> However, the structural analysis

shows clearly the existence of five significant metal-metal bonding interactions that, according to the application of the effective atomic number rule, would imply that **7** contains two too many electrons. There is, however, an alternative explanation of the bonding in metal clusters. This uses a delocalized scheme and is known as the polyhedral skeletal electron pair (PSEP) theory.<sup>14</sup> According to this theory, the Os<sub>4</sub>Se<sub>2</sub> cluster of **7** would be regarded as a *nido* pentagonal bipyramid. Such a cluster would contain eight bonding orbitals that would be filled with 16 electrons. Indeed, **7** contains 16 cluster-bonding electrons. Two electrons are provided by each osmium tricarbonyl group and four electrons from each selenido ligand. The reasons for the large distortions in the metal-metal bonding are not clear but are probably a consequence of a nonuniform delocalization. Other examples of 64-electron tetranuclear clusters that contain five metal-metal bonds and significant distortions in the metal-metal bonding are Ru<sub>4</sub>(CO)<sub>13</sub>(μ-η<sup>2</sup>-C=C-*t*-Bu)(μ-PPh<sub>2</sub>),<sup>13</sup> FeRu<sub>3</sub>(CO)<sub>13</sub>(μ-PPh<sub>2</sub>)<sub>2</sub>,<sup>15</sup> and Ru<sub>4</sub>(CO)<sub>8</sub>[glyoxal bis(isopropylimine)].<sup>16</sup>

The unusual electronic configuration in **7** could be responsible for its high reactivity. For example, **7** readily adds 1 mol of CO (25 °C (1 atm CO)) to re-form **6**. The mechanism of this addition is unclear, but recent evidence suggests that the site of addition may be one of the wing-tip metal atoms.<sup>5</sup> Even more intriguing is the ability of **7** to activate H<sub>2</sub>. Under an atmosphere of H<sub>2</sub> (1 atm) at 125 °C, **7** oxidatively adds 1 mol of H<sub>2</sub> to yield **8**. It is well-known that both nucleophilic and oxidative addition reactions are key steps in catalytic cycles.<sup>17</sup> It is possible that the unusual reactivity exhibited by **7** may play a role in the development of cluster compounds as catalysts.<sup>18</sup> When heated, **5** loses 1 mol of CO and adds 1 mol of H<sub>2</sub> to form H<sub>2</sub>Os<sub>3</sub>(CO)<sub>9</sub>(μ<sub>3</sub>-Se). Mechanistically, the H<sub>2</sub> addition is probably preceded by the loss of the CO ligand.

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**Registry No.** **3**, 93503-79-8; **4**, 72282-41-8; **5**, 93529-99-8; **6**, 93503-80-1; **7**, 93503-81-2; **8**, 72268-06-5; **9**, 93503-82-3; Os<sub>3</sub>(CO)<sub>10</sub>(NCMe<sub>2</sub>)<sub>2</sub>, 61817-93-4; Os(CO)<sub>5</sub>, 16406-49-8.

**Supplementary Material Available:** Listings of temperature factors and observed and calculated structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

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