Organometallics **1983**, *2*, 1301-1308

value of k_1[CO] (or k_1'[CO]) must be very small compared to k_2 (or k_2') (cf. Scheme I). In other words, 16-electron η^5-$C_5H_5W(CO)_2$(phenethyl) species essentially always transfer β-hydrogen (or -deuterium) to give η^5-$C_5H_5W(CO)_2$(H or D)(styrene) rather than capture CO to yield η^5-$C_5H_5W(CO)_3$(phenethyl). Unfortunately no rate data are available for β-hydrogen transfer[31] and CO capture of η^5-$C_5H_5W(CO)_2R$ to scrutinize this conclusion. However, it was recently shown[32] that α-hydrogen transfer in the complex $(\eta^5\text{-}C_5H_5)_2NbCH_2OZr(H)[\eta^5\text{-}C_5(CH_3)_5]_2$ is roughly 4100 times faster than CO trapping at 1 atm. Thus, our observations seem to be entirely reasonable. Perhaps at higher pressures of CO some hydrogen–deuterium scrambling in the phenethyl group of η^5-$C_5H_5W(CO)_3CD_2CH_2C_6H_5$ or η^5-$C_5H_5W(CO)_3CHDCHDC_6H_5$ would be observable; however, we did not conduct irradiation experiments at pressures above 1 atm.

Acknowledgment. We are grateful to the National Science Foundation for support of this research through Grant CHE-7911882. We also thank Dr. C. E. Cottrell for his help in recording a number of NMR spectra. The Bruker WM-300 spectrometer used in this study was funded in part by the National Science Foundation, Grant CHE-7910019.

Registry No. η^5-$C_5H_5W(CO)_3CHDCHDC_6H_5$-*threo*, 86823-62-3; η^5-$C_5H_5W(CO)_3CHDCHDC_6H_5$-*erythro*, 86852-05-3; η^5-$C_5H_5W(CO)_3S(O)_2CHDCHDC_6H_5$-*erythro*, 86834-42-6; η^5-$C_6H_5W(CO_3S(O)_2CH_2CH_2C_6H_5$, 86834-43-7; η^5-$C_5H_5W(CO)_2(\eta^3\text{-}CH(CH_3)C_6H_5)$, 82615-33-6; η^5-$C_5H_5W(CO)_3CH(CH_3C_6H_5$, 82615-31-4; η^5-$C_5H_5W(CO)_3CD_2CH_2C_6H_5$, 86823-61-2; η^5-$C_5H_5W(CO)_3CH_2CH_2C_6H_5$, 82615-27-8; η^5-$C_5H_5W(CO)_3H$, 12128-26-6; $Na[\eta^5\text{-}C_5H_5W(CO)_3]$, 12107-36-7; $C_6H_5CH_2CH_2OS(O)_2C_6H_4CH_3$-*p*, 4455-09-8; $C_6H_5CH_2CD_2OS(O)_2C_6H_4CH_3$-*p*, 36809-05-9; $C_6H_5CH_2CD_2OH$, 40638-92-4; *p*-$CH_3C_6H_4S(O)_2Cl$, 98-59-9; *erythro*-$C_6H_5CHDCHDOS(O)_2C_6H_4CH_3$-*p*, 26631-76-5; *threo*-$C_6H_5CHDCHDI$, 61012-86-0; *erythro*-$C_6H_5CHDCHDI$, 61012-88-2; $C_6H_5CH(CH_3)Cl$, 672-65-1; SO_2, 7446-09-5; I_2, 7553-56-2; styrene, 100-42-5.

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[31] A recent study[11] showed that, for η^5-$C_5H_5W(CO)_2C_2H_5$, β-hydrogen transfer to form *cis*-η^5-$C_5H_5W(CO)_2(H)(C_2H_4)$ occurs very rapidly compared to cis-to-trans isomerization of the ethylene hydride complex, thus precluding rate constant measurement for the former step.

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Metal-Induced Cleavage of Carbon–Sulfur Bonds in Thiolato Ligands. Thermolysis of $HOs_3(CO)_{10}(\mu\text{-}SC_6H_5)$ under CO Pressure. The Synthesis and Crystal and Molecular Structures of $Os_4(CO)_{13}(\mu_3\text{-}S)$ and $Os_5(CO)_{15}(\mu_4\text{-}S)$

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Received February 2, 1983

The thermolysis of $HOs_3(CO)_{10}(\mu\text{-}SC_6H_5)$, I, has been studied under carbon monoxide pressures of 200 and 1800 psi at 150 °C. At 200 psi, I eliminates C_6H_6 and forms the new compounds $Os_4(CO)_{13}(\mu_3\text{-}S)$, II, and $Os_5(CO)_{15}(\mu_4\text{-}S)$, III, and the known compounds $Os_3(CO)_9(\mu_3\text{-}S)_2$, IV, and $Os_3(CO)_{12}$. Compounds II and III have been characterized by X-ray crystallographic methods. For II: space group $P\bar{1}$, No. 2, a = 9.608 (2) Å, b = 15.402 (2) Å, c = 15.703 (3) Å, α = 113.29 (2)°, β = 99.04 (2)°, γ = 95.52 (2)°, V = 2077 (2) Å^3, Z = 4, ρ_{calcd} = 3.70 g/cm^3. The structure was solved by the heavy-atom method. For 3998 reflections ($F^2 \geq 3.0\sigma(F^2)$) R_F = 0.040 and R_{wF} = 0.046. The structure consists of a butterfly cluster of four osmium atoms with a triply bridging sulfido ligand on one triangular group of three. There are 13 linear terminal carbonyl ligands. When heated in the absence of CO, II loses 1 mol of CO and forms the $Os_4(CO)_{12}(\mu_3\text{-}S)$ which contains a closed tetrahedron of four metal atoms. For III: space group $Pna2_1$, No. 33, a = 19.119 (4) Å, b = 7.724 (6) Å, c = 16.417 (4) Å, V = 2424 (3) Å^3, Z = 4, ρ_{calcd} = 3.84 g/cm^3. The structure was solved by direct methods. For 1520 reflections ($F^2 \geq 3.0\sigma(F^2)$) R_F = 0.037 and R_{wF} = 0.042. The structure consists of a square-pyramidal cluster of five osmium atoms with a quadruply bridging sulfido ligand spanning the square base. Each metal atom contains three linear terminal carbonyl ligands. At 1800 psi of CO pressure thermolysis of I yields C_6H_6, $Os_3(CO)_9(\mu_3\text{-}S)_2$, and $Os(CO)_5$ only. A reaction mechanism involving $Os_3(CO)_9(\mu_3\text{-}S)$ and $Os(CO)_4$ intermediates is proposed and discussed.

Introduction

We have recently shown how the effects of polynuclear coordination promote the cleavage of carbon–sulfur bonds in organosulfur ligands in osmium carbonyl cluster compounds.[1-5] Cleavage of the carbon–sulfur bond of the thiolato ligand in the compound $HOs_3(CO)_{10}(\mu\text{-}SC_6H_5)$, I, is followed by the elimination of benzene and formation of a variety of new sulfido osmium carbonyl cluster compounds.[2] Cleavage of the carbon–sulfur bond in the related compound $HOs_3(CO)_{10}(\mu\text{-}SCH_2C_6H_5)$ occurs in two ways. One process leads to the elimination of toluene and the formation of sulfido osmium carbonyl clusters analogous to those obtained from compound I. However, by a second process, apparently an homolysis of the carbon–sulfur bond, dibenzyl, and several hydride-containing sulfido

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[1] (a) Adams, R. D.; Dawoodi, Z. *J. Am. Chem. Soc.* **1981**, *103*, 6510. (b) Adams, R. D.; Dawoodi, Z.; Foust, D.; Segmüller, B. *Organometallics* **1983**, *2*, 315.

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0276-7333/83/2302-1301$01.50/0

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Os_4(CO)_{13}(\mu_3\text{-}S)$, 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)	0.09371 (9)	0.28433 (6)	0.15139 (5)	2.04 (3)	2.04 (3)	1.86 (3)	0.12 (3)	0.27 (2)	0.65 (2)	2.07 (2)
Os(2)	0.17214 (9)	0.12095 (6)	0.17028 (5)	2.40 (4)	2.27 (3)	1.94 (3)	0.65 (3)	0.26 (3)	0.61 (2)	2.30 (2)
Os(3)	−0.06205 (9)	0.19749 (5)	0.23798 (5)	2.21 (4)	2.04 (3)	2.07 (3)	0.28 (3)	0.50 (3)	0.83 (2)	2.12 (2)
Os(4)	−0.17418 (9)	0.34430 (6)	0.19267 (4)	2.20 (4)	2.32 (3)	2.58 (3)	0.54 (3)	0.30 (3)	0.93 (2)	2.41 (2)
Os(5)	0.56909 (9)	0.68444 (5)	0.33706 (5)	2.19 (4)	2.01 (3)	0.32 (3)	0.31 (3)	0.36 (3)	0.96 (2)	2.17 (2)
Os(6)	0.32848 (9)	0.72832 (6)	0.41414 (5)	2.29 (4)	2.21 (3)	2.14 (3)	0.16 (3)	0.44 (3)	0.82 (2)	2.26 (2)
Os(7)	0.42497 (9)	0.82125 (6)	0.30877 (5)	2.61 (4)	2.21 (3)	2.35 (3)	0.51 (3)	0.53 (3)	1.14 (2)	2.32 (2)
Os(8)	0.68264 (10)	0.78610 (6)	0.23690 (5)	2.71 (4)	2.53 (3)	2.30 (3)	−0.01 (3)	0.64 (3)	0.87 (2)	2.58 (2)
S(1)	−0.0440 (10)	0.1229 (4)	0.0736 (3)	2.7 (2)	2.1 (2)	1.8 (2)	−0.0 (2)	−0.01 (2)	0.1 (1)	2.5 (1)
S(2)	0.5519 (6)	0.8357 (4)	0.4608 (3)	2.9 (2)	2.3 (2)	2.0 (2)	−0.1 (2)	0.4 (2)	0.5 (1)	2.5 (1)

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
O(1)	0.360 (2)	0.260 (1)	0.571 (12)	6.3 (5)	C(1)	0.250 (3)	0.266 (2)	0.100 (1)	3.7 (5)
O(2)	0.282 (2)	0.445 (1)	0.3309 (9)	3.8 (3)	C(2)	0.209 (2)	0.387 (1)	0.261 (1)	2.8 (4)
O(3)	0.033 (2)	0.298 (1)	0.0302 (11)	5.3 (4)	C(3)	0.041 (3)	0.357 (2)	0.077 (1)	3.6 (5)
O(4)	0.392 (2)	0.266 (1)	0.3586 (10)	4.9 (4)	C(4)	0.311 (2)	0.178 (1)	0.283 (1)	3.4 (5)
O(5)	0.381 (2)	0.053 (1)	0.0391 (11)	5.7 (5)	C(5)	0.303 (2)	0.080 (1)	0.090 (1)	3.0 (5)
O(6)	0.141 (2)	−0.079 (1)	0.1635 (11)	5.0 (4)	C(6)	0.153 (2)	0.000 (1)	0.169 (1)	3.0 (5)
O(7)	0.061 (2)	0.333 (1)	0.4496 (11)	5.3 (4)	C(7)	0.004 (3)	0.279 (2)	0.365 (2)	4.9 (6)
O(8)	−0.381 (2)	0.152 (1)	0.2335 (12)	6.3 (5)	C(8)	−0.255 (3)	0.172 (2)	0.233 (1)	3.5 (5)
O(9)	−0.039 (2)	0.035 (1)	0.3014 (10)	4.5 (4)	C(9)	−0.040 (2)	0.094 (1)	0.272 (1)	3.0 (5)
O(10)	−0.006 (2)	0.494 (1)	0.3890 (10)	4.2 (4)	C(10)	−0.065 (3)	0.437 (2)	0.315 (1)	3.6 (5)
O(11)	−0.339 (2)	0.183 (1)	0.0028 (9)	3.8 (3)	C(11)	−0.276 (2)	0.241 (1)	0.070 (1)	3.2 (5)
O(12)	−0.449 (2)	0.361 (1)	0.2660 (12)	6.1 (5)	C(12)	−0.345 (2)	0.351 (1)	0.235 (1)	3.3 (5)
O(13)	−0.216 (2)	0.499 (1)	0.1186 (10)	4.7 (4)	C(13)	−0.194 (3)	0.442 (2)	0.149 (1)	3.7 (5)
O(14)	0.883 (2)	0.665 (1)	0.3523 (10)	4.9 (4)	C(14)	0.767 (2)	0.677 (1)	0.344 (1)	2.9 (5)
O(15)	0.578 (2)	0.567 (1)	0.4564 (10)	4.5 (4)	C(15)	0.567 (3)	0.614 (2)	0.413 (1)	3.8 (5)
O(16)	0.432 (2)	0.503 (1)	0.1615 (11)	5.5 (4)	C(16)	0.484 (2)	0.572 (1)	0.228 (1)	3.2 (5)
O(17)	0.311 (2)	0.625 (1)	0.5432 (10)	4.7 (4)	C(17)	0.316 (3)	0.665 (2)	0.493 (2)	4.4 (6)
O(18)	0.111 (2)	0.575 (1)	0.2462 (10)	4.0 (4)	C(18)	0.189 (2)	0.636 (1)	0.315 (1)	2.7 (4)
O(19)	0.124 (2)	0.845 (1)	0.5195 (12)	6.5 (5)	C(19)	0.202 (2)	0.800 (2)	0.478 (1)	3.4 (5)
O(20)	0.521 (2)	1.018 (1)	0.3126 (13)	7.3 (6)	C(20)	0.489 (3)	0.943 (2)	0.311 (2)	5.0 (6)
O(21)	0.152 (2)	0.906 (1)	0.3563 (12)	6.5 (5)	C(21)	0.262 (3)	0.870 (2)	0.342 (2)	3.9 (5)
O(22)	0.243 (2)	0.704 (1)	0.1072 (11)	5.4 (4)	C(22)	0.318 (2)	0.755 (1)	0.184 (1)	3.1 (5)
O(23)	0.689 (2)	0.925 (1)	0.1407 (12)	6.1 (5)	C(23)	0.686 (3)	0.876 (2)	0.182 (2)	4.8 (6)
O(24)	0.510 (2)	0.618 (1)	0.0492 (11)	5.6 (4)	C(24)	0.572 (2)	0.681 (1)	0.122 (1)	2.9 (4)
O(25)	0.966 (2)	0.725 (1)	0.1905 (12)	6.7 (5)	C(25)	0.857 (3)	0.747 (2)	0.205 (1)	3.8 (5)
O(26)	0.849 (2)	0.940 (1)	0.4331 (10)	4.6 (4)	C(26)	0.786 (2)	0.885 (1)	0.363 (1)	3.2 (5)

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

osmium carbonyl cluster compounds are formed.[5]

We have now discovered that when the thermolysis of I is carried out under a low pressure (200 psi) of carbon monoxide, two new compounds $Os_4(CO)_{13}(\mu_3\text{-}S)$, II, and $Os_5(CO)_{15}(\mu_4\text{-}S)$, III, are obtained,[6] in addition to the known compounds $Os_3(CO)_{12}$, $Os_3(CO)_9(\mu_3\text{-}S)_2$, IV, and a trace of $Os(CO)_5$. At a moderate carbon monoxide pressure (1800 psi) only $Os_3(CO)_9(\mu_3\text{-}S)_2$ and $Os(CO)_5$ are formed.

Results and Discussion

Thermolysis of Compound I at 200 psi of CO Pressure. When thermolyzed at 150 °C for 5 h under 200 psi pressure of CO, compound I loses C_6H_6 and yields the products $Os_3(CO)_{12}$ (17%), $Os_4(CO)_{13}(\mu_3\text{-}S)$, II (27%), $Os_5(CO)_{15}(\mu_4\text{-}S)$, III (7%), and $Os_3(CO)_9(\mu_3\text{-}S)_2$ IV (38%) which have been isolated and purified by using the methods of TLC and fractional crystallization. Evidence for trace amounts of $Os(CO)_5$ was obtained by IR spectroscopy of the reaction solutions. Compounds II and III are new and have thus been investigated by X-ray crystallographic methods.

Structure of $Os_4(CO)_{13}(\mu_3\text{-}S)$, II. Compound II crystallizes with two independent molecules in the asymmetric crystal unit. An ORTEP drawing of one of these molecules is shown in Figure 1. Final positional and thermal parameters are listed in Table I. Interatomic distances for molecule 1 with the corresponding values for molecule 2 are listed in Table II. Interatomic angles for molecule 1 and for molecule 2 are listed in Table III. Both independent molecules of II are essentially identical structurally. The structure consists of a butterfly cluster of four osmium atoms containing five osmium–osmium bonds, as would be expected for a 62-electron cluster. Interestingly, the dihedral angle between the planes Os(1)–Os(2)–Os(3) and Os(1)–Os(3)–Os(4) is rather large, 170.0° [176.5°]. The value in brackets here and hereafter will be the corresponding value for molecule 2. Carty et al. have recently compared values of dihedral angles for a series of 62-electron and 64-electron Ru_4 clusters and

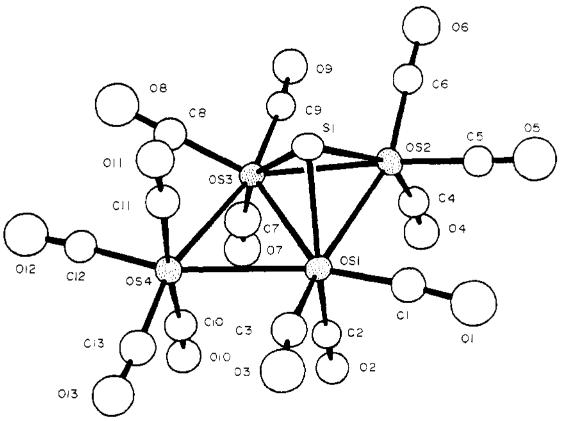

Figure 1. An ORTEP diagram of $Os_4(CO)_{13}(\mu_3\text{-}S)$, II, showing 50% probability thermal-motion ellipsoids.

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(6) In a reinvestigation of the thermolysis of compound I under a nitrogen atmosphere, we have detected small quantities of compound III.[2]

Table II. Interatomic Distances (Å) with Esds for $Os_4(CO)_{13}(\mu_3\text{-}S)$, II

molecule 1		molecule 2	
Os(1)-Os(2)	2.807 (1)	Os(5)-Os(6)	2.793 (1)
Os(1)-Os(3)	2.752 (1)	Os(5)-Os(7)	2.769 (1)
Os(1)-Os(4)	2.899 (1)	Os(5)-Os(8)	2.877 (1)
Os(2)-Os(3)	2.803 (1)	Os(6)-Os(7)	2.783 (1)
Os(3)-Os(4)	2.878 (1)	Os(7)-Os(8)	2.889 (1)
Os(1)-S(1)	2.427 (4)	Os(5)-S(2)	2.414 (4)
Os(2)-S(1)	2.382 (4)	Os(6)-S(2)	2.398 (4)
Os(3)-S(1)	2.418 (4)	Os(7)-S(2)	2.418 (4)
Os(1)-C(1)	1.81 (2)	Os(5)-C(14)	1.90 (2)
Os(1)-C(2)	1.90 (2)	Os(5)-C(15)	1.92 (2)
Os(1)-C(3)	1.96 (2)	Os(5)-C(16)	1.89 (2)
Os(2)-C(4)	1.87 (2)	Os(6)-C(17)	1.86 (2)
Os(2)-C(5)	1.89 (2)	Os(6)-C(18)	1.86 (2)
Os(2)-C(6)	1.84 (2)	Os(6)-C(19)	1.86 (2)
Os(3)-C(7)	1.85 (2)	Os(7)-C(20)	1.90 (2)
Os(3)-C(8)	1.84 (2)	Os(7)-C(21)	1.86 (2)
Os(3)-C(9)	1.89 (2)	Os(7)-C(22)	1.88 (2)
Os(4)-C(10)	1.93 (2)	Os(8)-C(23)	1.90 (2)
Os(4)-C(11)	1.97 (2)	Os(8)-C(24)	1.94 (2)
Os(4)-C(12)	1.86 (2)	Os(8)-C(25)	1.91 (2)
Os(4)-C(13)	1.89 (2)	Os(8)-C(26)	1.99 (2)
C(1)-O(1)	1.33 (2)	C(14)-O(14)	1.15 (2)
C(2)-O(2)	1.17 (2)	C(15)-O(15)	1.17 (2)
C(3)-O(3)	1.14 (2)	C(16)-O(16)	1.15 (2)
C(4)-O(4)	1.21 (2)	C(17)-O(17)	1.19 (2)
C(5)-O(5)	1.17 (2)	C(18)-O(18)	1.19 (2)
C(6)-O(6)	1.18 (2)	C(19)-O(19)	1.18 (2)
C(7)-O(7)	1.26 (2)	C(20)-O(20)	1.16 (2)
C(8)-O(8)	1.22 (2)	C(21)-O(21)	1.25 (2)
C(9)-O(9)	1.17 (2)	C(22)-O(23)	1.21 (2)
C(10)-O(10)	1.16 (2)	C(23)-O(23)	1.18 (2)
C(11)-O(11)	1.11 (2)	C(24)-O(24)	1.18 (2)
C(12)-O(12)	1.18 (2)	C(25)-O(25)	1.17 (2)
C(13)-O(13)	1.18 (2)	C(26)-O(26)	1.11 (2)
Os-S(av)	2.410 (7)		

pointed out that the 62-electron clusters had comparatively small dihedral angles while the 64-electron complexes had fairly large ones.[7] Unfortunately, all the 62-electron complexes he cited contained bridging ligands which were bonded to both the wing-tip atoms of the butterfly tetrahedron. The present results show that in the absence of such a bridging ligand the dihedral angle in the 62-electron cluster can be very large. Conversely, 64-electron clusters which contain bridging ligands that link the wing tips may have fairly small dihedral angles. A case in point is $Os_4(CO)_{12}(\mu_3\text{-}S)_2$ which is a 64-electron cluster that has two sulfido ligands bridging the wing tips of the butterfly tetrahedron. For this molecule the dihedral angle is 86.9°.[8] The point, very simply, is the size of the dihedral angle in butterfly clusters will be much more sensitive to the influences of bridging ligands than the electronic configurations although it may be influenced by both factors.

The triangular group Os(1)–Os(2)–Os(3) contains a triply briding sulfido ligand, S(1). The longest Os–Os bonds are the two which are not spanned by the bridging sulfido ligand, Os(1)–Os(4) and Os(3)–Os(4) [Os(5)–Os(8) and Os(7)–Os(8)], and which are of similar lengths, 2.899 (1) and 2.878 (1) Å [2.877 (1) and 2.889 (1) Å], respectively. These values are very similar to those found in $Os_3(CO)_{12}$, average 2.877 (3) Å.[9] Bonds Os(1)–Os(2) and Os(2)–Os(3) [Os(5)–Os(6) and Os(6)–Os(7)] bridged by the sulfido ligand are significantly shorter, 2.807 (1) and 2.803 (1) Å [2.793 (1) and 2.783 (1) Å], respectively, while the shortest bond is Os(1)–Os(3) [Os(5)–Os(7)] which is bridged by both the sulfido ligand and Os(4) [Os(8)], 2.752 (1) Å [2.769 (1) Å]. The osmium–sulfur distances range from 2.382 (4) to 2.427 (4) Å. The average distance Os–S (average) = 2.410 (7) Å is slightly longer than that found for triply bridging sulfido ligands in the similar clusters $Os_4(CO)_{12}(\mu_3\text{-}S)$, V, 2.381 (3) Å,[10] and $Os_6(CO)_{16}(\mu_4\text{-}S)(\mu_3\text{-}S)$, 2.34 (2) Å.[2]

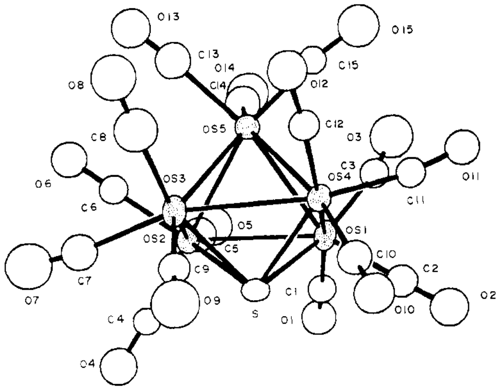

Figure 2. An ORTEP diagram of $Os_5(CO)_{15}(\mu_4\text{-}S)$, III, showing 50% probability thermal-motion ellipsoids.

The molecule contains 13 linear terminal carbonyl ligands arranged such that each of the sulfido-bridged metal atoms contains three while the remaining metal atom Os(4) [Os(8)] contains four. Except for slight inequalities in some of the bonds the molecule has overall C_s symmetry with atoms Os(4), S(1), and Os(2) lying in the reflection plane. The shortest intermolecular contacts were between oxygen atoms of the carbonyl ligands. There were four such contacts less than 3.0 Å: O(3)···O(26) = 2.98 (2) Å, O(5)···O(23) = 2.95 (2) Å, O(8)···O(17) = 2.99 (2) Å, and O(12)···O(24) = 2.96 (2) Å.

Structure of $Os_5(CO)_{15}(\mu_4\text{-}S)$, III. The molecular structure of compound III is shown in Figure 2. The molecule consists of a square-pyramidal cluster of five osmium atoms with a quadruply bridging sulfido ligand spanning the square base. Final positional and thermal parameters are given in Table IV. Interatomic bond distances and angles are listed in Tables V and VI, respectively. The square base is very slightly folded. The dihedral angle between Os(1)–Os(2)–Os(3) and Os(2)–Os(3)–Os(4) is 3.6°. The osmium–osmium bond distances span the range 2.803 (2)- to 2.902 (2) Å. While the variation of these lengths is significant, this is not yet fully understandable. The molecule is electron precise, namely, each metal atom achieves an 18-electron configuration. However the structure also obeys the skeletal electron pair theory since the Os_5S group contains 14 skeletal electron pairs (assuming the sulfido ligand serves as a four-electron donor) and contains the predicted shape of an octahedron. The Os–S bond distances range from 2.418 (9) to 2.502 (10) Å and average 2.46 (2) Å. The latter is similar to that observed for quadruply bridging sulfido ligands in the related clusters $Os_6(CO)_{16}(\mu_4\text{-}S)(\mu_3\text{-}S)$, 2.44 (1) Å,[2] and $Os_7(CO)_{19}(\mu_4\text{-}S)$, 2.45 (1) Å.[10] These distances are all significantly larger than the average Os–S distances found for triply bridging sulfido ligands (vide supra). The Os(5)···S distance at 3.44 (1) Å is probably too long to involve a significant bonding interaction. Each metal atom contains three linear terminal carbonyl ligands. The $Os(CO)_3$ groups seem to be twisted slightly in order to minimize the

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Table III. Interatomic Angles (deg) with Esds for $Os_4(CO)_{13}(\mu_3\text{-}S)$, II

molecule 1		molecule 2	
Os(2)-Os(1)-Os(3)	60.55 (2)	Os(6)-Os(5)-Os(7)	60.06 (2)
Os(2)-Os(1)-Os(4)	120.93 (3)	Os(6)-Os(5)-Os(8)	121.49 (3)
Os(3)-Os(1)-Os(4)	61.17 (2)	Os(7)-Os(5)-Os(8)	61.53 (2)
Os(1)-Os(2)-Os(3)	58.75 (2)	Os(5)-Os(6)-Os(7)	59.55 (2)
Os(1)-Os(3)-Os(2)	60.70 (2)	Os(5)-Os(7)-Os(6)	60.39 (2)
Os(1)-Os(3)-Os(4)	61.95 (2)	Os(5)-Os(7)-Os(8)	61.08 (2)
Os(2)-Os(3)-Os(4)	121.85 (3)	Os(6)-Os(7)-Os(8)	121.37 (3)
Os(1)-Os(4)-Os(3)	56.88 (2)	Os(5)-Os(8)-Os(7)	57.40 (2)
Os(1)-S(1)-Os(2)	71.4 (1)	Os(5)-S(2)-Os(6)	70.9 (1)
Os(1)-S(1)-Os(3)	69.2 (1)	Os(5)-S(2)-Os(7)	69.9 (1)
Os(2)-S(1)-Os(3)	71.4 (1)	Os(6)-S(2)-Os(7)	70.6 (1)
Os(2)-Os(1)-S(1)	53.55 (9)	Os(6)-Os(5)-S(2)	54.25 (9)
Os(2)-Os(1)-C(1)	75.8 (5)	Os(6)-Os(5)-C(14)	154.2 (5)
Os(2)-Os(1)-C(2)	103.4 (4)	Os(6)-Os(5)-C(15)	77.4 (5)
Os(2)-Os(1)-C(3)	152.5 (5)	Os(6)-Os(5)-C(16)	99.5 (5)
Os(3)-Os(1)-S(1)	55.25 (9)	Os(7)-Os(5)-S(2)	55.10 (9)
Os(3)-Os(1)-C(1)	136.4 (5)	Os(7)-Os(5)-C(14)	128.5 (4)
Os(3)-Os(1)-C(2)	99.5 (4)	Os(7)-Os(5)-C(15)	137.0 (5)
Os(3)-Os(1)-C(3)	132.3 (5)	Os(7)-Os(5)-C(16)	102.5 (5)
Os(4)-Os(1)-S(1)	85.60 (9)	Os(8)-Os(5)-S(2)	89.4 (9)
Os(4)-Os(1)-C(1)	161.3 (5)	Os(8)-Os(5)-C(14)	71.3 (4)
Os(4)-Os(1)-C(2)	94.6 (5)	Os(8)-Os(5)-C(15)	158.7 (5)
Os(4)-Os(1)-C(3)	73.5 (5)	Os(8)-Os(5)-C(16)	95.6 (5)
S(1)-Os(1)-C(1)	100.3 (6)	S(2)-Os(5)-C(14)	107.6 (5)
S(1)-Os(1)-C(2)	150.8 (4)	S(2)-Os(5)-C(15)	95.6 (5)
S(1)-Os(1)-C(3)	109.8 (5)	S(2)-Os(5)-C(16)	150.6 (5)
C(1)-Os(1)-C(2)	88.9 (7)	C(14)-Os(5)-C(15)	87.4 (7)
C(1)-Os(1)-C(3)	87.8 (7)	C(14)-Os(5)-C(16)	101.4 (7)
C(2)-Os(1)-C(3)	98.1 (7)	C(15)-Os(5)-C(16)	90.2 (7)
Os(1)-Os(2)-S(1)	55.03 (9)	Os(5)-Os(6)-S(2)	54.81 (10)
Os(1)-Os(2)-C(4)	100.6 (5)	Os(5)-Os(6)-C(17)	107.0 (6)
Os(1)-Os(2)-C(5)	105.4 (4)	Os(5)-Os(6)-C(18)	98.8 (5)
Os(1)-Os(2)-C(6)	159.1 (5)	Os(5)-Os(6)-C(19)	160.4 (5)
Os(3)-Os(2)-S(1)	54.89 (9)	Os(7)-Os(6)-S(2)	55.03 (3)
Os(3)-Os(2)-C(4)	99.1 (5)	Os(7)-Os(6)-C(17)	164.6 (5)
Os(3)-Os(2)-C(5)	160.1 (4)	Os(7)-Os(6)-C(18)	96.0 (4)
Os(3)-Os(2)-C(6)	105.2 (5)	Os(7)-Os(6)-C(19)	106.3 (5)
S(1)-Os(2)-C(4)	150.1 (5)	S(2)-Os(6)-C(17)	112.0 (6)
S(1)-Os(2)-C(5)	107.0 (5)	S(2)-Os(6)-C(18)	147.0 (5)
S(1)-Os(2)-C(6)	105.5 (5)	S(2)-Os(6)-C(19)	106.4 (5)
C(4)-Os(2)-C(5)	95.6 (7)	C(17)-Os(6)-C(18)	93.5 (7)
C(4)-Os(2)-C(6)	94.9 (7)	C(17)-Os(6)-C(19)	84.7 (7)
C(5)-Os(2)-C(6)	86.8 (7)	C(18)-Os(6)-C(19)	96.2 (7)
Os(1)-Os(3)-S(1)	55.54 (9)	Os(5)-Os(7)-S(2)	54.98 (10)
Os(1)-Os(3)-C(7)	101.9 (6)	Os(5)-Os(7)-C(20)	132.7 (6)
Os(1)-Os(3)-C(8)	133.1 (5)	Os(5)-Os(7)-C(21)	134.7 (5)
Os(1)-Os(3)-C(9)	133.1 (5)	Os(5)-Os(7)-C(22)	103.1 (5)
Os(2)-Os(3)-S(1)	53.68 (9)	Os(6)-Os(7)-S(2)	54.36 (9)
Os(2)-Os(3)-C(7)	107.1 (6)	Os(6)-Os(7)-C(20)	144.5 (6)
Os(2)-Os(3)-C(8)	145.2 (5)	Os(6)-Os(7)-C(21)	74.4 (5)
Os(2)-Os(3)-C(9)	72.5 (5)	Os(6)-Os(7)-C(22)	107.0 (5)
Os(4)-Os(3)-S(1)	86.22 (9)	Os(8)-Os(7)-S(2)	89.06 (9)
Os(4)-Os(3)-C(7)	92.9 (6)	Os(8)-Os(7)-C(20)	79.7 (6)
Os(4)-Os(3)-C(8)	76.3 (5)	Os(8)-Os(7)-C(21)	164.2 (5)
Os(4)-Os(3)-C(9)	164.4 (5)	Os(8)-Os(7)-C(22)	88.8 (5)
S(1)-Os(3)-C(7)	154.5 (6)	S(2)-Os(7)-C(20)	102.5 (6)
S(1)-Os(3)-C(8)	103.9 (5)	S(2)-Os(7)-C(21)	100.3 (5)
S(1)-Os(3)-C(9)	99.6 (5)	S(2)-Os(7)-C(22)	155.3 (5)
C(7)-Os(3)-C(8)	100.6 (8)	C(20)-Os(7)-C(21)	85.8 (8)
C(7)-Os(3)-C(9)	88.0 (7)	C(20)-Os(7)-C(22)	101.3 (7)
C(8)-Os(3)-C(9)	88.2 (7)	C(21)-Os(7)-C(22)	87.9 (7)
Os(1)-Os(4)-C(10)	87.0 (5)	Os(5)-Os(8)-C(23)	155.2 (6)
Os(1)-Os(4)-C(11)	89.1 (5)	Os(5)-Os(8)-C(24)	86.4 (4)
Os(1)-Os(4)-C(12)	160.7 (5)	Os(5)-Os(8)-C(25)	110.5 (5)
Os(1)-Os(4)-C(13)	105.2 (5)	Os(5)-Os(8)-C(26)	86.6 (4)
Os(3)-Os(4)-C(10)	87.7 (5)	Os(7)-Os(8)-C(23)	97.8 (6)
Os(3)-Os(4)-C(11)	86.9 (4)	Os(7)-Os(8)-C(24)	90.3 (5)
Os(3)-Os(4)-C(12)	103.8 (5)	Os(7)-Os(8)-C(25)	167.8 (5)
Os(3)-Os(4)-C(13)	162.1 (5)	Os(7)-Os(8)-C(26)	85.9 (5)
C(10)-Os(4)-C(11)	174.5 (7)	C(23)-Os(8)-C(24)	93.9 (7)
C(10)-Os(4)-C(12)	92.5 (7)	C(23)-Os(8)-C(25)	94.3 (7)
C(10)-Os(4)-C(13)	91.1 (7)	C(23)-Os(8)-C(26)	92.4 (7)
C(11)-Os(4)-C(12)	89.9 (7)	C(24)-Os(8)-C(25)	90.8 (7)
C(11)-Os(4)-C(13)	93.7 (7)	C(24)-Os(8)-C(26)	92.0 (5)
C(12)-Os(4)-C(13)	94.1 (7)	C(25)-Os(8)-C(26)	91.8 (7)
Os(1)-C(1)-O(1)	173 (1)	Os(5)-C(14)-O(14)	172 (1)

Table III (*Continued*)

molecule 1		molecule 2	
Os(1)-C(2)-O(2)	174 (1)	Os(5)-C(15)-O(15)	173 (1)
Os(1)-C(3)-O(3)	169 (1)	Os(5)-C(16)-O(16)	179 (2)
Os(2)-C(4)-O(4)	171 (1)	Os(6)-C(17)-O(17)	179 (2)
Os(2)-C(5)-O(5)	178 (2)	Os(6)-C(18)-O(18)	173 (1)
Os(2)-C(6)-O(6)	176 (1)	Os(6)-C(19)-O(19)	179 (1)
Os(3)-C(7)-O(7)	174 (2)	Os(7)-C(20)-O(20)	177 (2)
Os(3)-C(8)-O(8)	176 (1)	Os(7)-C(21)-O(21)	172 (1)
Os(3)-C(9)-O(9)	170 (1)	Os(7)-C(22)-O(22)	172 (1)
Os(4)-C(10)-O(10)	176 (1)	Os(8)-C(23)-O(23)	175 (2)
Os(4)-C(11)-O(11)	177 (1)	Os(8)-C(24)-O(24)	177 (1)
Os(4)-C(12)-O(12)	176 (1)	Os(8)-C(25)-O(25)	176 (1)
Os(4)-C(13)-O(13)	175 (2)	Os(8)-C(26)-O(26)	177 (2)

Table IV. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Os_5(CO)_{15}(\mu_4\text{-}S)$, III[a]

atom	x	y	z	$B(1,1)$	$B(2,2)$	$B(3,3)$	$B(1,2)$	$B(1,3)$	$B(2,3)$
Os(1)	0.23265 (8)	0.4398 (3)	0.2500 (1)	1.75 (6)	3.64 (9)	1.64 (6)	0.36 (8)	−0.03 (6)	−0.19 (8)
Os(2)	0.10258 (8)	0.4316 (3)	0.1614 (1)	2.15 (6)	2.91 (8)	1.35 (6)	0.12 (8)	−0.23 (6)	−0.11 (8)
Os(3)	0.03065 (8)	0.4321 (3)	0.3136 (1)	1.74 (6)	3.19 (8)	1.71 (6)	−0.09 (8)	0.07 (6)	0.15 (9)
Os(4)	0.15803 (8)	0.4634 (2)	0.3992 (1)	2.04 (6)	2.64 (7)	1.25 (5)	0.25 (7)	−0.14 (6)	−0.02 (8)
Os(5)	0.12919 (10)	0.7027 (2)	0.2705 (1)	2.34 (6)	2.06 (7)	1.94 (6)	−0.06 (8)	−0.26 (6)	0.05 (8)
S	0.1340 (6)	0.259 (1)	0.2849 (7)	2.7 (4)	1.5 (4)	2.6 (4)	−0.2 (5)	0.1 (4)	0.3 (5)

atom	x	y	z	B_{iso}, Å^2	atom	x	y	z	B_{iso}, Å^2
O(1)	0.294 (2)	0.267 (5)	0.097 (2)	4.8 (8)	C(1)	0.273 (2)	0.330 (6)	0.151 (3)	3.0 (10)
O(2)	0.334 (2)	0.228 (5)	0.357 (2)	5.1 (9)	C(2)	0.298 (2)	0.305 (6)	0.314 (3)	3.6 (10)
O(3)	0.330 (2)	0.756 (5)	0.229 (2)	7.4 (11)	C(3)	0.303 (2)	0.639 (6)	0.236 (3)	3.2 (11)
O(4)	0.052 (2)	0.097 (5)	0.077 (2)	5.1 (9)	C(4)	0.075 (2)	0.217 (6)	0.105 (3)	2.7 (9)
O(5)	0.190 (2)	0.547 (5)	0.013 (2)	6.2 (9)	C(5)	0.154 (3)	0.496 (7)	0.060 (3)	4.7 (13)
O(6)	−0.016 (2)	0.656 (4)	0.092 (2)	4.7 (8)	C(6)	0.029 (2)	0.571 (6)	0.119 (3)	3.0 (9)
O(7)	−0.088 (2)	0.307 (5)	0.196 (2)	6.9 (11)	C(7)	−0.045 (2)	0.340 (6)	0.232 (3)	4.2 (12)
O(8)	−0.066 (2)	0.699 (5)	0.400 (2)	5.7 (9)	C(8)	−0.032 (3)	0.595 (7)	0.370 (3)	5.5 (14)
O(9)	−0.014 (2)	0.149 (5)	0.442 (2)	6.3 (10)	C(9)	0.001 (2)	0.251 (6)	0.398 (3)	2.8 (9)
O(10)	0.157 (2)	0.178 (4)	0.531 (2)	4.4 (8)	C(10)	0.160 (2)	0.282 (6)	0.481 (3)	3.4 (10)
O(11)	0.296 (2)	0.603 (4)	0.463 (2)	3.8 (7)	C(11)	0.247 (2)	0.535 (6)	0.438 (2)	2.8 (9)
O(12)	0.073 (2)	0.701 (5)	0.511 (2)	4.4 (8)	C(12)	0.108 (2)	0.599 (6)	0.473 (2)	2.7 (9)
O(13)	−0.002 (2)	0.932 (4)	0.259 (2)	5.1 (8)	C(13)	0.045 (2)	0.859 (6)	0.263 (3)	4.3 (11)
O(14)	0.192 (2)	0.898 (5)	0.117 (2)	6.9 (10)	C(14)	0.164 (2)	0.832 (7)	0.170 (3)	4.6 (12)
O(15)	0.210 (2)	0.938 (5)	0.390 (2)	5.8 (9)	C(15)	0.175 (2)	0.859 (6)	0.345 (2)	2.5 (9)

[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 V. Interatomic Distances (Å) with Esds for $Os_5(CO)_{15}(\mu_4\text{-}S)$, III

Os(1)-Os(2)	2.882 (2)	Os(3)-C(9)	2.05 (4)
Os(1)-Os(4)	2.840 (2)	Os(4)-C(10)	1.94 (4)
Os(1)-Os(5)	2.855 (2)	Os(4)-C(11)	1.90 (3)
Os(2)-Os(3)	2.853 (2)	Os(4)-C(12)	1.86 (3)
Os(2)-Os(5)	2.803 (2)	Os(5)-C(13)	2.02 (4)
Os(3)-Os(4)	2.822 (2)	Os(5)-C(14)	2.04 (4)
Os(3)-Os(5)	2.902 (2)	Os(5)-C(15)	1.93 (3)
Os(4)-Os(5)	2.861 (2)	C(1)-O(1)	1.09 (4)
Os(1)···Os(3)	4.001 (2)	C(2)-O(2)	1.16 (4)
Os(2)···Os(4)	4.053 (2)	C(3)-O(3)	1.05 (4)
Os(1)-S	2.418 (9)	C(4)-O(4)	1.13 (4)
Os(2)-S	2.502 (10)	C(5)-O(5)	1.10 (4)
Os(3)-S	2.432 (10)	C(6)-O(6)	1.16 (4)
Os(4)-S	2.496 (9)	C(7)-O(7)	1.05 (4)
Os(5)···S	3.44 (1)	C(8)-O(8)	1.15 (4)
Os(1)-C(1)	1.98 (4)	C(9)-O(9)	1.10 (4)
Os(1)-C(2)	1.93 (4)	C(10)-O(10)	1.15 (4)
Os(1)-C(3)	2.06 (4)	C(11)-O(11)	1.16 (3)
Os(2)-C(4)	1.97 (4)	C(12)-O(12)	1.22 (4)
Os(2)-C(5)	2.00 (4)	C(13)-O(13)	1.06 (4)
Os(2)-C(6)	1.91 (4)	C(14)-O(14)	1.14 (4)
Os(3)-C(7)	2.09 (4)	C(15)-O(15)	1.16 (3)
Os(3)-C(8)	1.97 (4)	Os-S(av)	2.46 (2)

steric interactions between neighboring groups. The shortest intermolecular contacts were between atoms of the carbonyl ligands. Those less than 2.95 Å were as follows C(1)···O(7) = 2.94 (5) Å, O(1)···O(7) = 2.84 (4) Å, O(5)···O(15) = 2.92 (4) Å, and O(6)···O(9) = 2.95 (4) Å. Compound III has a close structural resemblance to $Os_5(CO)_{15}[\mu_4\text{-}P(OCH_3)]$ obtained from the pyrolysis of $Os_3(CO)_{11}[P(OCH_3)_3]$ at 210 °C.[12]

Thermolysis of Compound I at 1800 psi of CO Pressure. When thermolyzed at 150 °C for 5 h under a pressure of carbon monoxide at 1800 psi, only two metal-containing products, $Os_3(CO)_9(\mu_3\text{-}S)_2$ and $Os(CO)_5$, were obtained in yields quantitative according to eq 1

$$2HOs_3(CO)_{10}(\mu\text{-}SC_6H_5) \xrightarrow[-2C_6H_6]{150\ ^\circ C/1800\ psi\ CO} Os_3(CO)_9(\mu_3\text{-}S)_2 + 3Os(CO)_5 \quad (1)$$

Mechanism. The first important step in the thermolytic degradation of compound I is the elimination of the molecule C_6H_6. This was observed in these studies and also in our studies performed under a ntirogen atmosphere.[2] Cleavage of the phenyl carbon–sulfur bond by either an intramolecular metal-activated process or a C–S homolysis would seem to be the most logical, but the intramolecular process is strongly favored for the following reasons: (1) a facile intramolecular C–S cleavage was observed for the related molecules $HOs_3(CO)_9(\mu_3\text{-}SC(H)NR)$, R = C_6H_5, $p\text{-}C_6H_4F$, $p\text{-}C_6H_4CH_3$, and CH_3;[1] (2) $HOs_3(CO)_{10}(\mu\text{-}SCH_2C_6H_5)$ decomposes by two mechanisms of which one is believed to be a C–S homolysis process and this yields dibenzyl- and hydride-containing sulfido osmium carbonyl clusters;[5] (3) Carty et al. have shown that

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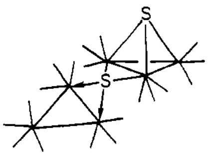
Table VI. Selected Interatomic Angles (deg) with Esds for $Os_5(CO)_{15}(\mu_4\text{-}S)$, III

Os(2)-Os(1)-Os(4)	90.19 (5)	Os(1)-Os(2)-C(6)	144 (1)	Os(1)-Os(5)-C(13)	167 (1)
Os(2)-Os(1)-Os(5)	58.50 (5)	Os(3)-Os(2)-S	53.6 (2)	Os(1)-Os(5)-C(14)	91 (1)
Os(4)-Os(1)-Os(5)	60.30 (5)	Os(3)-Os(2)-C(4)	107 (1)	Os(1)-Os(5)-C(15)	102 (1)
Os(1)-Os(2)-Os(3)	88.49 (5)	Os(3)-Os(2)-C(5)	165 (1)	Os(2)-Os(5)-C(13)	105 (1)
Os(1)-Os(2)-Os(5)	60.27 (5)	Os(3)-Os(2)-C(6)	88 (1)	Os(2)-Os(5)-C(14)	85 (1)
Os(3)-Os(2)-Os(5)	61.73 (5)	Os(5)-Os(2)-S	80.6 (2)	Os(2)-Os(5)-C(15)	163 (1)
Os(2)-Os(3)-Os(4)	91.16 (5)	Os(5)-Os(2)-C(4)	168 (1)	Os(3)-Os(5)-C(13)	86 (1)
Os(2)-Os(3)-Os(5)	58.29 (5)	Os(5)-Os(2)-C(5)	105 (1)	Os(3)-Os(5)-C(14)	140 (1)
Os(4)-Os(3)-Os(5)	59.95 (5)	Os(5)-Os(2)-C(6)	87 (1)	Os(3)-Os(5)-C(15)	126 (1)
Os(1)-Os(4)-Os(3)	89.92 (5)	Os(2)-Os(3)-S	55.8 (2)	Os(4)-Os(5)-C(13)	126 (1)
Os(1)-Os(4)-Os(5)	60.09 (5)	Os(2)-Os(3)-C(7)	77 (1)	Os(4)-Os(5)-C(14)	148 (1)
Os(3)-Os(4)-Os(5)	61.40 (5)	Os(2)-Os(3)-C(8)	135 (1)	Os(4)-Os(5)-C(15)	81 (1)
Os(1)-Os(5)-Os(2)	61.24 (4)	Os(2)-Os(3)-C(9)	137 (1)	Os(1)-S-Os(2)	71.7 (2)
Os(1)-Os(5)-Os(3)	88.07 (5)	Os(4)-Os(3)-S	56.1 (2)	Os(1)-S-Os(3)	111.2 (3)
Os(1)-Os(5)-Os(4)	59.60 (5)	Os(4)-Os(3)-C(7)	160 (1)	Os(1)-S-Os(4)	70.6 (2)
Os(2)-Os(5)-Os(3)	59.98 (4)	Os(4)-Os(3)-C(8)	104 (1)	Os(2)-S-Os(3)	70.6 (3)
Os(2)-Os(5)-Os(4)	91.39 (5)	Os(4)-Os(3)-C(9)	88 (1)	Os(2)-S-Os(4)	108.4 (3)
Os(3)-Os(5)-Os(4)	58.64 (5)	Os(5)-Os(3)-S	79.8 (2)	Os(3)-S-Os(4)	69.9 (3)
Os(2)-Os(1)-S	55.5 (2)	Os(5)-Os(3)-C(7)	123 (1)	Os(1)-C(1)-O(1)	178 (4)
Os(2)-Os(1)-C(1)	85 (1)	Os(5)-Os(3)-C(8)	93 (1)	Os(1)-C(2)-O(2)	175 (3)
Os(2)-Os(1)-C(2)	145 (1)	Os(5)-Os(3)-C(9)	147 (1)	Os(1)-C(3)-O(3)	168 (4)
Os(2)-Os(1)-C(3)	122 (1)	Os(1)-Os(4)-S	53.4 (2)	Os(2)-C(4)-O(4)	172 (3)
Os(4)-Os(1)-S	56.0 (2)	Os(1)-Os(4)-C(10)	123 (1)	Os(2)-C(5)-O(5)	168 (4)
Os(4)-Os(1)-C(1)	158 (1)	Os(1)-Os(4)-C(11)	82 (1)	Os(2)-C(6)-O(6)	179 (3)
Os(4)-Os(1)-C(2)	84 (1)	Os(1)-Os(4)-C(12)	149 (1)	Os(3)-C(7)-O(7)	171 (4)
Os(4)-Os(1)-C(3)	112 (1)	Os(3)-Os(4)-S	54.0 (2)	Os(3)-C(8)-O(8)	175 (4)
Os(5)-Os(1)-S	81.0 (2)	Os(3)-Os(4)-C(10)	107 (1)	Os(3)-C(9)-O(9)	177 (3)
Os(5)-Os(1)-C(1)	132 (1)	Os(3)-Os(4)-C(11)	165 (1)	Os(4)-C(10)-O(10)	176 (3)
Os(5)-Os(1)-C(2)	140 (1)	Os(3)-Os(4)-C(12)	86 (1)	Os(4)-C(11)-O(11)	170 (3)
Os(5)-Os(1)-C(3)	86 (1)	Os(5)-Os(4)-S	79.6 (2)	Os(4)-C(12)-O(12)	171 (3)
Os(1)-Os(2)-S	52.8 (2)	Os(5)-Os(4)-C(10)	169 (1)	Os(5)-C(13)-O(13)	175 (4)
Os(1)-Os(2)-C(4)	119 (1)	Os(5)-Os(4)-C(11)	103 (1)	Os(5)-C(14)-O(14)	171 (4)
Os(1)-Os(2)-C(5)	90 (1)	Os(5)-Os(4)-C(12)	91 (1)	Os(5)-C(15)-O(15)	171 (3)

the molecule $HRu_3(CO)_9(\mu\text{-}P(C_6H_5)_2)$ which contains a metal-activated P–C bond loses C_6H_6 when heated.[13]

CO loss in I may precede the C–S cleavage as suggested by the nature of this related ruthenium compound. An unobserved intermediate such as $Os_3(CO)_9(\mu_3\text{-}S)$, A, would seem to be a likely product upon elimination of C_6H_6. Intermediate A having a 46-electron configuration would probably be very reactive toward electron pair donors and could dimerize by donation of a lone pair of electrons on the sulfido ligand of one molecule to the second. This coupling could be the first step in the transfer of a sulfido ligand from one cluster to the second. An intermediate such as B could be formed by the coupling of 2 mol of A and addition of 1 mol of CO. B is very similar in the known compound $H_2Os_6(CO)_{17}(\mu\text{-}HC{=}NR)_2(\mu_3\text{-}S)(\mu_4\text{-}S)$ formed in the decarbonylation and coupling of two clusters of $HOs_3(CO)_9(\mu\text{-}HC{=}NR)(\mu_3\text{-}S)$.[14] Alternatively, intermediate A might also add one mole of CO to form $Os_3(CO)_{10}(\mu_3\text{-}S)$ which would contain a closed-shell 48-electron configuration. However, $Os_3(CO)_{10}(\mu_3\text{-}S)$ has not been reported previously and no direct evidence for its existence was obtained in this work, but if $Os_3(CO)_{10}(\mu_3\text{-}S)$ were formed, B could be formed simply by ligand displacement.



B

Completion of the shift of the sulfido ligand would give compound IV directly. The remaining triosmium group could then add CO to give one of the other products, $Os_3(CO)_{12}$, or, we believe, fragment to give mononuclear osmium species. The importance of mononuclear fragments is suggested by the formations of compounds II and III. For example, the combination of A with a mononuclear species such as $Os(CO)_4$ would lead to compound II while addition of 2 mol of $Os(CO)_4$ to A might be the means of formation of compound III; see Scheme I. Mononuclear fragments could be obtained from any of a number of the species present in the reaction solutions. This includes $Os_3(CO)_{12}$ which we have shown yields significant quantities of $Os(CO)_5$ under CO (1800 psi/150 °C); see Experimental Section.

In the absence of CO pressure, ligand loss should be more important and intermediate B might yield hexanuclear species. In accord with this, it was observed that $Os_6(CO)_{16}(\mu_3\text{-}S)(\mu_4\text{-}S)$ was a major product of the thermolysis of compound I under a nitrogen atmosphere.[2]

Loss of CO from compound II yields $Os_4(CO)_{12}(\mu_3\text{-}S)$, V, quantitatively which contains a closed tetrahedron for four osmium atoms.[10] Compound V is also a major product of the thermolysis of I under a nitrogen atmosphere.[2] Under 1600 psi of CO pressure, V adds 1 mol of CO and reforms II although significant amounts of IV and $Os_3(CO)_{12}$ are also formed.

Experimental Section

All the products are air stable. Solvents were stored over 4 Å molecular sieves before use. $HOs_3(CO)_{10}(\mu\text{-}SC_6H_5)$ was prepared by established procedure.[16] Infrared spectra were recorded on a Nicolet 7199 FT-IR. Melting points were obtained on a Thomas-Hoover apparatus and are uncorrected. High-pressure reactions were performed in an Autoclave Engineers Model APB-300 magnedrive high-pressure apparatus.

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Table VII. Crystallographic Data for X-ray Diffraction Studies

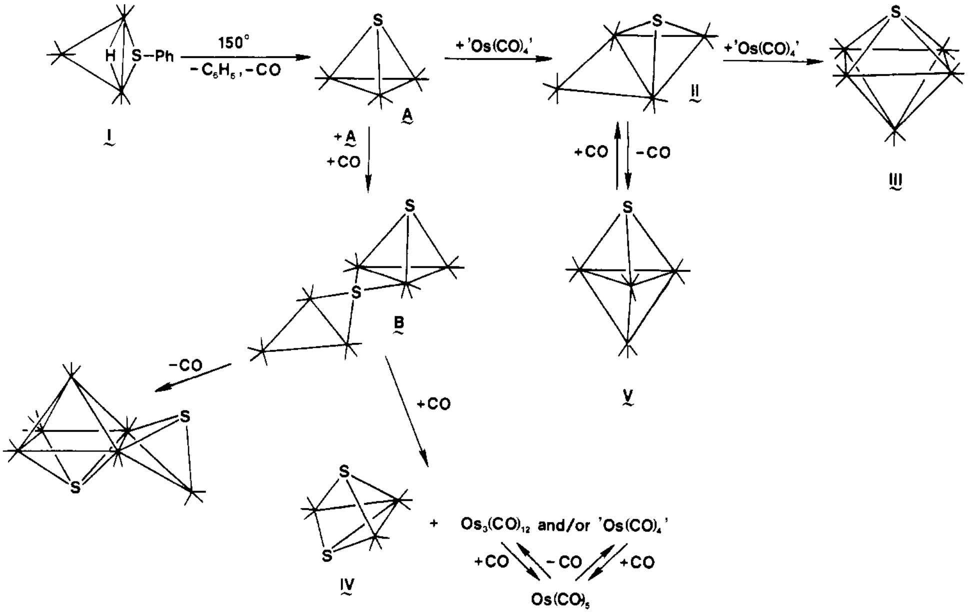
	II	III
	(A) Crystal Data	
formula	$Os_4SO_{13}C_{13}$	$Os_5SO_{15}C_{15}$
temp, ±3 °C	25	23
space group	$P\bar{1}$, No. 2	$Pna2_1$, No. 33
a, Å	9.608 (2)	19.119 (4)
b, Å	15.408 (2)	7.724 (6)
c, Å	15.703 (3)	16.417 (4)
α, deg	113.29 (2)	90.0
β, deg	99.04 (2)	90.0
γ, deg	95.52 (2)	90.0
V, Å^3	2077 (2)	2424 (3)
M_r	1157.0	1403.2
Z	4	4
ρ_{calcd}, g/cm^3	3.70	3.84
	(B) Measurement of Intensity Data	
radiatn	Mo K$\bar{\alpha}$ (0.710 73 Å)	Mo Kα (0.710 73 Å)
monochromator	graphite	graphite
detector aperture, mm		
horizontal ($A + B \tan\theta$)		
A	3.0	3.0
B	1.0	1.0
vertical	4.0	4.0
cryst faces	010, $0\bar{1}0$, 001, $0\bar{1}\bar{1}$, $00\bar{1}$, $1\bar{1}0$, $\bar{1}1\bar{1}$, $\bar{1}\bar{1}2$	201, 001, $\bar{1}00$, $00\bar{1}$, $\bar{1}\bar{1}1$, $\bar{1}20$
cryst size (mm):	0.45 × 0.10 × 0.14	0.098 × 0.17 × 0.12
cryst orientation direction; deg from ϕ axis	normal to 201; 8.9	b; 9.06
reflctns measd	$h,\pm k,\pm l$	$-h,k,l$
max 2θ	46	50
scan type	moving crystal–stationary counter	moving crystal–stationary counter
ω scan width $(A + 0.347 \tan\theta)^\circ$, A =	0.95	0.90
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	10.0	6.7
min, deg/min	1.5	1.2
no. of reflctns measd	5716	2448
data used ($F^2 \geqslant 3.0\sigma(F^2)$)	3998	1520
	(C) Treatment of Data	
abs correctn		
coeff, cm^{-1}	245.97	279.2
grid	14 × 6 × 10	8 × 8 × 14
transmissn coeff		
max	0.173	0.24
min	0.053	0.17
decay correctn		
max	1.016	
min	0.875	
P factor	0.020	0.01
final residuals		
R_F	0.040	0.037
R_{wF}	0.046	0.042
esd of unit weight observn	2.307	2.050
largest shift/error value of final cycle	0.11	0.16
largest peak in final diff Fourier, e/Å^3	1.75	0.70

Thermolysis of $HOs_3(CO)_{10}(\mu\text{-}SC_6H_5)$ under CO. (a) At a CO Pressure of 200 psi. A 0.25-g (0.26-mmol) sample of I was dissolved in 50 mL of nonane and the solution placed in a high-pressure apparatus and treated with CO at 200 psi/150 °C for 5 h. After removal from the high-pressure apparatus, the solvent that was shown to contain C_6H_6 by GC analysis was removed in vacuo, and the orange-yellow residue was extracted with hexane, leaving insoluble $Os_3(CO)_{12}$, 0.040 g (0.044 mmol, 17%). The orange hexane solution was chromatographed on a silica column. The first yellow band eluted with hexane yielded 0.087 g (0.10 mmol, 38%) of $Os_3(CO)_9(\mu_3\text{-}S)_2$. The second orange band eluted with hexane/benzene (90/10, v/v) was shown by IR to consist of two products that were subsequently separated by fractional crystallization. From hexane/CH_2Cl_2 (85/15, v/v) at −20 °C red crystals of the major product $Os_4(CO)_{13}(\mu_3\text{-}S)$ 0.068 g (0.060 mmol, 27%), were obtained: IR (ν(CO) in hexane) 2123 (w), 2082 (s), 2061 (w), 2048 (vs), 2043 (vs), 2008 (m), 2001 (w), 1985 (vw) cm^{-1}; mp 157 °C. The mother liquid was concentrated and yielded the second product $Os_5(CO)_{15}(\mu_4\text{-}S)$, 0.024 g (0.017 mmol, 7%), when cooled to 0 °C: IR (ν(CO) in hexane) 2065 (vs), 2062 (vs, sh), 2049 (w), 2041 (s), 2022 (w), 2016 (w), 2003 (w), 1998 (w) cm^{-1}; mp 212 °C dec.

(b) At a CO Pressure of 1800 psi. A 0.250-g (0.26-mmol) sample of I was dissolved in 50 mL of nonane and the solution placed in a high-pressure apparatus and heated with CO at 1800 psi to 150 °C for 5 h. The reaction mixture was shown by IR to consist of two products only: $Os_3(CO)_9(\mu_3\text{-}S)_2$ and $Os(CO)_5$ (IR 2043 (s), 1191 cm^{-1} (vs)). The solvent and $Os(CO)_5$ were collected by distillation at 0.1 mmHg/25 °C and photolyzed for 2 h at room temperature to give 0.117 g (0.13 mmol) $Os_3(CO)_{12}$. On the basis of $Os_3(CO)_{12}$ formed, the yield of $Os(CO)_5$ was calculated to be 0.129 g (0.39 mmol, 99%). The yellow residue was crystallized from hexane to give 0.108 g (0.13 mmol, 99%) of $Os_3(CO)_9(\mu_3\text{-}S)_2$.

Thermolysis of $Os_4(CO)_{13}(\mu_3\text{-}S)$. A 0.020 g (0.018-mmol) sample of $Os_4(CO)_{13}(\mu_3\text{-}S)$ was refluxed 1 h in 30 mL of octane solvent under a N_2 atmosphere. The solvent was removed in

Scheme I



vacuo, and the red residue was crystallized from hexane/CH_2Cl_2 (90/10, v/v) to give 0.019 g (0.01 mmol, 97%) of $Os_4(CO)_{12}(\mu_3\text{-}S)$.

Carbonylation of $Os_4(CO)_{12}(\mu_3\text{-}S)$, V. A 0.030-g (0.026-mmol) sample of $Os_4(CO)_{12}(\mu_3\text{-}S)$ was dissolved in 60 mL of octane and the solution placed in a high-pressure apparatus and heated under CO at 1600 psi/125 °C for 5 h. The solvent was removed in vacuo, and the orange-yellow residue was extracted with hexane, leaving insoluble $Os_3(CO)_{12}$, 0.008 g (0.006 mmol, 23%). The orange hexane solution was chromatographed on silica TLC plates by using a hexane/CH_2Cl_2 (90/10, v/v) solvent mixture. The first fraction was crystallized from hexane to give 0.006 g (0.007 mmol, 27%) of $Os_3(CO)_9(\mu_3\text{-}S)_2$. The second fraction was crystallized from hexane/benzene (90/10, v/v) to give 0.012 g (0.01 mmol, 38%) of $Os_4(CO)_{13}(\mu_3\text{-}S)$.

Carbonylation of $Os_3(CO)_{12}$. A 0.5-g (0.55-mmol) sample of $Os_3(CO)_{12}$ and 50 mL of nonane was placed in a high-pressure apparatus and heated with CO at 1800 psi to 150 °C for 16 h. The reaction mixture was shown by IR to consist of two products only: $Os(CO)_5$ and $Fe(CO)_5$, the latter apparently formed from the walls of the reactor. The solvent and $Os(CO)_5$ were collected by distillation at 0.1 mmHg/25 °C and photolyzed for 3 h at room temperature to give 0.204 g (0.23 mmol) of $Os_3(CO)_{12}$. On the basis of $Os_3(CO)_{12}$ formed, the yield of $Os(CO)_5$ was calculated to be 0.228 g (0.69 mmol, 42%). The yellow reaction residue was crystallized from hot octane to give 0.290 g (0.32 mmol), 58% unreacted $Os_3(CO)_{12}$.

Crystallographic Analyses. Crystals of II suitable for X-ray diffraction measurements were grown from hexane/benzene (9/1) solutions by slow evaporation at room temperature. Crystals of III suitable for diffraction measurements were grown from methylene chloride/hexane (9/1) solutions by slow evaporation at room temperature. The crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on an Enraf-Nonius CAD-4 fully automated diffractometer 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 VII. All data processing was performed on a Digital Equipment Corp. PDP 11/45 computer using the Enraf-Nonius SDP program library (version 16). Absorption corrections of a Gaussian integration type were applied to the data of both structures. Neutral atom scattering factors were calculated by the standard procedures.[17a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[17b] 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 $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (PF_o^2)^2]^{1/2}/Lp$.

For II the space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. The structure was solved by a combination of Patterson and difference Fourier techniques. The coordinates of three of the eight independent osmium atoms were obtained from a three-dimensional Patterson function. The coordinates of all remaining atoms were obtained from a series of difference Fourier syntheses. The osmium and sulfur atoms were refined with anisotropic thermal parameters. The carbon and oxygen atoms were refined with isotropic thermal parameters.

For III the observed systematic absences were consistent with either of the space groups *Pnma* or *Pna*2₁. Attempts to solve the structure in the space group *Pnma* were unsuccessful. The structure solution was subsequently obtained by using the space group *Pna*2₁. The coordinates of the five metal atoms were obtained from an *E* map based on the phasing (MULTAN) of 136 reflections ($E \geq 1.63$). All remaining atoms were obtained from difference Fourier syntheses. The thermal parameters of the osmium and sulfur atoms were refined anisotropically. The thermal parameters of carbon and oxygen atoms were refined isotropically.

Estimated standard deviations for the bond distance and angle calculations were calculated by using the inverse matrix obtained on the final cycle of refinement. Tables of structure factor amplitudes are available for both structures; see supplementary material.

Acknowledgment. This work was supported by the National Science Foundation and the Alfred P. Sloan Foundation through a fellowship to R.D.A. We wish to thank Engelhard Industries for a loan of osmium tetroxide.

Registry No. I, 23733-19-9; II, 86437-18-5; III, 86437-19-6; IV, 72282-40-7; V, 82080-90-8; $Os_3(CO)_{12}$, 15696-40-9; $Os(CO)_5$, 16406-49-8.

Supplementary Material Available: Tables of structure factor amplitudes for both structures (25 pages). Ordering information is given on any current masthead page.

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(17) "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.