

the CO IX is not significantly higher in energy than other intermediate configurations. Comparing IV and IX, it is clear that the major difference is that in IX each metal center is formally saturated (18 e), whereas in IV the third, equatorial metal center is formally unsaturated (only 16 e). Thus, the extra CO in IX serves to stabilize the metal center not involved in bonding to the edge-coordinated alkyne.

Recently, Vollhardt and co-workers²² reported evidence for an intramolecular "deck shift" reaction (eq 3). This

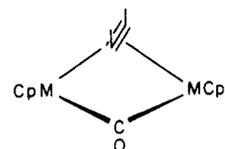
$$\text{R}_3\text{SiC}\equiv\text{C}-\text{C}[\text{Co}_3\text{Cp}_3]\text{C}-\text{C}[\text{Co}_3\text{Cp}_3]\text{CSiR}_3 \rightarrow \text{R}_3\text{SiC}[\text{Co}_3\text{Cp}_3]\text{C}-\text{C}\equiv\text{C}-\text{C}[\text{Co}_3\text{Cp}_3]\text{CSiR}_3 \quad (3)$$

was interpreted in terms of an alkyldiyne coupling/de-coupling sequence involving structures related to I \rightarrow IV \rightarrow III \rightarrow IV \rightarrow I. The reconstituted alkyne ligand, however, is necessarily a conjugated diyne, and the second alkyne center can provide the two electrons needed for a saturated intermediate analogous to IX. The accessibility of an unsaturated structure such as IV remains to be determined experimentally.

In other work we have shown that alkyne scission in an "allowed" process on a d^9-d^9 M_2L_6 template.¹ In the case

(22) Allison, N. T.; Fritch, J. R.; Vollhardt, K. P. C.; Walborsky, E. C. *J. Am. Chem. Soc.* 1983, 105, 1384-1386.

of IX the $\text{CpM}(\text{CO})$ fragment is a $d^8 \text{ML}_4$ isolobal with CH_2 isolobal with CO. Therefore, IX is isolobal with XI, a



XI

complex very similar to those we have discussed in the binuclear case.

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Registry No. I (M = Rh, R = Ph), 88801-72-3; I (M = Ir, R = Ph), 88801-74-5; $\text{Cp}_3\text{Rh}_3(\text{CO})(\text{C}_2\text{Ph}_2)$, 39346-10-6; $\text{Cp}_3\text{Ir}_3(\text{CO})(\text{C}_2\text{Ph}_2)$, 88801-70-1; $\text{Cp}_3\text{Rh}_3(\text{CO})_3$, 12148-54-8; $\text{Cp}_3\text{Ir}_3(\text{CO})_3$, 80630-37-1; $\text{Cp}_3\text{Rh}_3(\text{CO})(\text{C}_2\text{PhTol})$, 88801-71-2; $\text{Cp}_3\text{Rh}_3(\text{CPh})(\text{CTol})$, 88801-73-4; C_2Ph_2 , 501-65-5; C_2PhTol , 3287-02-3; Rh, 7440-16-6; Ir, 7439-88-5.

Cluster Synthesis. 5. Synthesis and Crystal and Molecular Structures of $\text{Os}_6(\text{CO})_{19}(\mu_3\text{-S})$ and $\text{Os}_6(\text{CO})_{17}(\mu_4\text{-S})$

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The cluster compounds $\text{Os}_3(\text{CO})_{10}(\mu_3\text{-S})$ (I) and $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ (II) combine when refluxed in benzene solvent to yield the new cluster compound $\text{Os}_6(\text{CO})_{19}(\mu_3\text{-S})$ (III) in 31% yield and the known cluster $\text{Os}_5(\text{CO})_{15}(\mu_4\text{-S})$ (IV) in 18% yield. The structure of III was determined by single-crystal X-ray diffraction methods: space group $P\bar{1}$, $a = 11.119$ (2) Å, $b = 11.357$ (3) Å, $c = 12.904$ (2) Å, $\alpha = 104.51$ (2)°, $\beta = 91.12$ (1)°, $\gamma = 108.80$ (1)°, $V = 1484.4$ (11) Å³, $Z = 2$, $\rho_{\text{calcd}} = 3.82$ g/m³. The structure was solved by direct methods and refined with 3847 reflections ($F^2 \geq 3.0\sigma(F^2)$) to yield the final residuals $R_1 = 0.038$ and $R_2 = 0.045$. The structure consists of a butterfly tetrahedron of four osmium atoms with two additional osmium tetracarbonyl groups bridging adjacent edges of the butterfly tetrahedron. A triply bridging sulfido ligand bridges one of the open triangular faces of the cluster. When refluxed in toluene solvent, III loses 2 mol of CO and is converted into the new cluster compound $\text{Os}_6(\text{CO})_{17}(\mu_4\text{-S})$ (V) in 23% yield. The structure of V was also determined by a single-crystal X-ray diffraction analysis: space group $Pna2_1$, $a = 11.371$ (3) Å, $b = 16.550$ (3) Å, $c = 14.140$ (3) Å, $V = 2661$ (2) Å³, $Z = 4$, $\rho_{\text{calcd}} = 4.12$ g/cm³. The structure was solved by direct methods and refined with 1887 reflections ($F^2 \geq 3.0\sigma(F^2)$) to yield the final residuals $R_1 = 0.029$ and $R_2 = 0.030$. The structure consists of a capped square pyramid of six osmium atoms with a quadruply bridging sulfido ligand spanning the base of the square pyramid. The observed structure is in accord with the skeletal electron pair theory, but the metal-metal bonding to the capping group is highly distorted. Both the shortest (2.625 (1) Å) and longest (2.930 (1) Å) metal-metal bonds in the molecule involve the capping group. This can be rationalized by a combination of resonance structures, one of which includes a multiple bond at the shortest bond distance and no bond at the longest distance.

Introduction

The widespread interest in the chemistry of transition-metal cluster compounds has stimulated efforts to synthesize them by systematic procedures.¹⁻⁴ While redox

condensation^{2,3} and pyrolytic decarbonylation processes⁵ have been employed with considerable success, condensation reactions promoted by bridging ligands have recently attracted attention.⁶⁻¹⁴

(1) "Transition Metal Clusters"; Johnson, B. F. G., Ed.; Wiley: New York, 1980.

(2) Chini, P.; Longoni, G.; Albano, V. G. *Adv. Organomet. Chem.* 1976, 14, 285.

(3) Chini, P. *J. Organomet. Chem.* 1980, 200, 37.

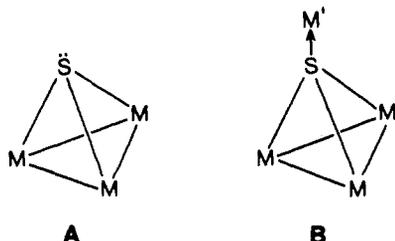
(4) King, R. B. *Prog. Inorg. Chem.* 1972, 15, 287.

(5) Eady, C. R.; Johnson, B. F. G.; Lewis, J. J. *Chem. Soc., Dalton Trans.*, 1975, 2606.

Table I. Crystallographic Data for X-ray Diffraction Studies

(A) Crystal Data		
compd	III	V
formula	Os ₆ SC ₁₉ O ₁₉	Os ₆ SC ₁₇ O ₁₇
temp, ± 3 °C	29	30
space group	P $\bar{1}$, No. 2	Pna2 ₁ , No. 33
a, Å	11.119 (2)	11.371 (3)
b, Å	11.357 (2)	16.550 (3)
c, Å	12.904 (3)	14.140 (3)
α, deg	104.51 (2)	90.0
β, deg	91.12 (1)	90.0
γ, deg	108.80 (1)	90.0
V, Å ³	1484.4 (11)	2661 (2)
M _r	1705.5	1649.4
Z	2	4
ρ _{calcd} , g/cm ³	3.82	4.12
(B) Measurement of Intensity Data		
radiation	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)
monochromator	graphite	graphite
detector aperture, mm		
horiz (A + B tan θ)		
A	3.0	3.0
B	1.0	1.0
vert	4.0	4.0
cryst faces	100, $\bar{1}00$, $1\bar{2}\bar{2}$	010, $0\bar{1}0$, 111, $\bar{1}\bar{1}\bar{1}$
	$\bar{1}\bar{2}\bar{2}$, $\bar{1}2\bar{1}$, $1\bar{2}\bar{3}$	$10\bar{2}$, $\bar{1}02$, $2\bar{1}\bar{1}$, $2\bar{1}1$
cryst size, mm	0.03 × 0.11 × 0.29	0.04 × 0.17 × 0.24
cryst orientation direction; deg from φ axis	normal to $1\bar{2}\bar{2}$; 8.6	normal to $10\bar{2}$, 10.3
reflectns measd	h±k±l	+h+k+l
max 2θ	50°	50°
scan type	moving crystal-stationary counter	moving crystal-stationary counter
ω scan width		
(A + 0.347 tan θ)	1.00	1.00
bkgd	1/4 additional scan at each end of scan	1/4 additional scan at each end of scan
ω scan rate (variable)		
max, deg/min	10.0	10.0
min, deg/min	1.4	1.4
no. reflectns measd	5208	2657
data used (F ² ≥ 3.0σ(F ²))	3847	1887
(C) Treatment of Data		
absorption correction		
coeff, cm ⁻¹	257.7	287.4
grid	4 × 12 × 18	14 × 4 × 16
transmission coefficient		
max	0.47	0.333
min	0.08	0.016
decay correction		
max	1.02	
min	0.93	
P factor	0.02	0.02
final residuals, R _F	0.038	0.029
	R _{wF}	0.030
esd of unit wt obsvn	2.15	1.36
largest shift/error value of final cycle	0.03	0.16
largest peak in final diff fourier, e ⁻ /Å ³	2.97	1.11

In recent studies we have shown that cluster compounds containing triply bridging sulfido ligands (A) can couple



readily with other metal carbonyl cluster compounds to form a variety of new high-nuclearity metal carbonyl clusters.¹³⁻¹⁷ Self-condensation reactions may also occur.¹⁸

(9) (a) Richter, F.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* 1980, 19, 65. (b) *Ibid.* 1979, 18, 531. (c) *Ibid.* 1978, 17, 864.

(10) (a) Huttner, G.; Mohr, G.; Pritzlaff, B.; von Seyler, J.; Zsolani, L. *Chem. Ber.* 1982, 115, 2044. (b) Huttner, G.; Sigwarth, B.; von Seyler, J.; Zsolani, L. *Ibid.* 1982, 115, 2035.

(11) Vahrenkamp, H.; Wucherer, E. J.; Wolters, D. *Chem. Ber.* 1983, 116, 1219.

(12) (a) Seyferth, D.; Henderson, R. S.; Fackler, J. P., Jr.; Mazany, A. *M. J. Organomet. Chem.* 1981, 213, C21.

(13) Adams, R. D.; Dawoodi, Z.; Foust, D. F.; Segmüller, B. E. *J. Am. Chem. Soc.* 1983, 105, 831.

(14) Adams, R. D.; Horváth, I. T.; Yang, L. W. *J. Am. Chem. Soc.* 1983, 105, 1533.

(15) Adams, R. D.; Foust, D. F.; Mathur, P. *Organometallics* 1983, 2, 990.

(16) Adams, R. D.; Horváth, I. T.; Mathur, P.; Segmüller, B. E.; Yang, L. W. *Organometallics*, 1983, 2, 1078.

(6) Marko, L. *Gazz. Chim. Ital.* 1979, 109, 247.

(7) (a) Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* 1975, 14, 322.

(b) Vahrenkamp, H.; Wucherer, E. J. *Ibid.* 1981, 20, 680.

(8) Day, V. W.; Lesch, D. A.; Ranchfuss, T. B. *J. Am. Chem. Soc.* 1982, 104, 1290.

Table II. Positional and Thermal Parameters^a and Their Estimated Standard Deviations for Os₆(CO)₁₅(μ₃-S) (III)

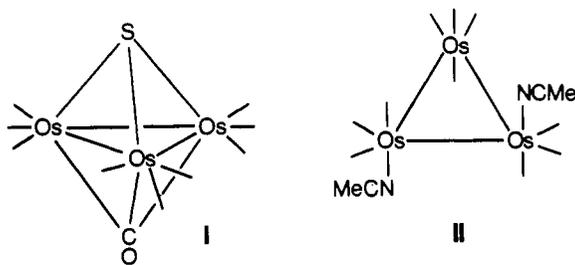
atom	x	y	z	B _{1,1}	B _{2,2}	B _{3,3}	B _{1,2}	B _{1,3}	B _{2,3}	R _{eqv}
Os1	0.78533 (6)	0.80050 (5)	0.80068 (5)	1.74 (2)	1.65 (2)	1.39 (2)	0.63 (2)	-0.05 (2)	0.21 (2)	1.62 (1)
Os2	0.80129 (7)	0.63625 (6)	0.92988 (5)	2.93 (3)	2.18 (2)	1.72 (2)	0.62 (2)	-0.10 (2)	0.68 (2)	2.32 (2)
Os3	0.82785 (7)	0.56805 (5)	0.70647 (5)	2.35 (3)	1.59 (2)	1.75 (2)	0.75 (2)	-0.00 (2)	0.28 (2)	1.91 (1)
Os4	0.94381 (7)	0.78943 (6)	0.63287 (5)	2.00 (3)	2.23 (2)	2.08 (2)	0.85 (2)	0.42 (2)	0.78 (2)	2.03 (1)
Os5	0.68793 (7)	0.78015 (6)	0.59111 (5)	2.14 (3)	2.28 (2)	1.68 (2)	0.73 (2)	-0.31 (2)	0.46 (2)	2.05 (1)
Os6	0.62573 (7)	0.94300 (6)	0.77302 (6)	2.15 (3)	2.31 (2)	2.57 (3)	1.12 (2)	0.08 (2)	0.50 (2)	2.29 (1)
S	0.6310 (4)	0.6136 (4)	0.6848 (3)	1.9 (2)	1.9 (1)	1.8 (1)	0.3 (1)	-0.2 (1)	0.1 (1)	2.06 (9)

atom	x	y	z	B, Å ²	atom	x	y	z	B, Å ²
O1	0.681 (1)	0.886 (1)	1.015 (1)	4.3 (3)	C1	0.716 (2)	0.846 (2)	0.934 (1)	3.0 (4)
O2	1.032 (1)	1.023 (1)	0.888 (1)	3.3 (3)	C2	0.940 (2)	0.939 (1)	0.853 (1)	2.0 (3)
O3	1.087 (1)	0.803 (1)	0.959 (1)	3.5 (3)	C3	0.982 (2)	0.741 (1)	0.948 (1)	2.7 (3)
O4	0.767 (2)	0.745 (1)	1.167 (1)	5.5 (4)	C4	0.783 (2)	0.707 (2)	1.076 (2)	3.5 (4)
O5	0.849 (2)	0.405 (1)	0.970 (1)	5.6 (4)	C5	0.830 (2)	0.497 (2)	0.959 (2)	3.6 (4)
O6	0.511 (2)	0.488 (1)	0.878 (1)	5.6 (4)	C6	0.621 (2)	0.545 (2)	0.895 (2)	3.6 (4)
O7	1.082 (1)	0.545 (1)	0.773 (1)	4.7 (3)	C7	0.989 (2)	0.560 (2)	0.747 (1)	3.0 (4)
O8	0.685 (1)	0.296 (1)	0.720 (1)	4.6 (3)	C8	0.740 (2)	0.400 (2)	0.716 (1)	3.2 (4)
O9	0.851 (1)	0.457 (1)	0.469 (1)	3.5 (3)	C9	0.844 (2)	0.510 (2)	0.559 (1)	2.9 (4)
O10	1.043 (1)	1.067 (1)	0.627 (1)	3.4 (3)	C10	1.000 (2)	0.960 (1)	0.625 (1)	2.6 (3)
O11	1.205 (2)	0.831 (1)	0.741 (1)	5.8 (4)	C11	1.104 (2)	0.810 (2)	0.699 (2)	3.5 (4)
O12	1.033 (1)	0.707 (1)	0.415 (1)	4.2 (3)	C12	1.003 (2)	0.742 (2)	0.500 (1)	2.8 (4)
O13	0.410 (2)	0.716 (1)	0.509 (1)	5.7 (4)	C13	0.516 (2)	0.741 (2)	0.543 (2)	3.9 (4)
O14	0.727 (2)	0.617 (1)	0.376 (1)	5.5 (4)	C14	0.715 (2)	0.679 (2)	0.462 (1)	3.3 (4)
O15	0.765 (1)	1.020 (1)	0.509 (1)	4.2 (3)	C15	0.738 (2)	0.929 (1)	0.540 (1)	2.3 (3)
O16	0.465 (2)	1.040 (2)	0.643 (1)	7.0 (5)	C16	0.529 (2)	1.012 (2)	0.699 (2)	5.4 (6)
O17	0.878 (1)	1.159 (1)	0.773 (1)	3.8 (3)	C17	0.789 (2)	1.075 (1)	0.770 (1)	2.6 (3)
O18	0.603 (2)	1.120 (1)	0.984 (1)	5.1 (4)	C18	0.610 (2)	1.049 (2)	0.905 (2)	4.1 (5)
O19	0.393 (2)	0.706 (1)	0.785 (1)	4.9 (3)	C19	0.478 (2)	0.791 (2)	0.779 (1)	2.8 (4)

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

It is believed that the first step in such condensations involves the formation of a coordinate bond between the sulfido ligand and the incoming metal atoms M' (B).⁶⁻¹⁸ Subsequent ligand eliminations can lead to metal-metal bond formations which may be influenced by the bridging sulfido ligand.

In this report we shall describe the nature of the coupling of the cluster compounds Os₃(CO)₁₀(μ₃-S) (I)¹⁹ and Os₃(CO)₁₀(CH₃CN)₂ (II)²⁰ which yields the new nido-cluster



Os₆(CO)₁₉(μ₃-S) (III) and the known compound Os₅(CO)₁₅(μ₄-S) (IV). III can be closed by decarbonylation to yield the new cluster Os₆(CO)₁₇(μ₄-S) (V). Both III and V have been characterized by single-crystal X-ray diffraction methods.

Experimental Section

Although the products are air stable, all reactions were performed under a prepurified nitrogen atmosphere. Os₃(CO)₁₀

(17) Adams, R. D.; Horváth, I. T.; Segmüller, B. E. *J. Organomet. Chem.*, in press.

(18) Adams, R. D.; Männig, D.; Segmüller, B. E. *Organometallics*, 1983, 2, 149.

(19) Adams, R. D.; Horváth, I. T.; Kim, H. S. *Organometallics*, in press.

(20) (a) Johnson, B. F. G.; Lewis, J.; Pippard, D. A. *J. Chem. Soc., Dalton Trans.* 1981, 407. (b) Dawson, P. A.; Johnson, B. F. G.; Lewis, J.; Puga, J.; Raithby, R. R.; Rosales, M. *J. Chem. Soc., Dalton Trans.* 1982, 233.

Table III. Interatomic Distances (Å) with Esd's for Os₆(CO)₁₉(μ₃-S) (III)

atoms	distance	atoms	distance
Os(1)-Os(2)	2.837 (1)	Os(5)-C(14)	1.860 (14)
Os(1)-Os(3)	2.809 (1)	Os(5)-C(15)	1.883 (11)
Os(1)-Os(4)	2.822 (1)	Os(6)-C(16)	1.880 (18)
Os(1)-Os(5)	2.820 (1)	Os(6)-C(17)	1.954 (17)
Os(1)-Os(6)	2.830 (1)	Os(6)-C(18)	1.866 (16)
Os(2)-Os(3)	2.839 (1)	Os(6)-C(19)	1.979 (14)
Os(3)-Os(4)	2.836 (1)	C(1)-O(1)	1.160 (15)
Os(4)-Os(5)	2.849 (1)	C(2)-O(2)	1.138 (14)
Os(5)-Os(6)	2.850 (1)	C(3)-O(3)	1.129 (15)
Os(1)-S	2.376 (3)	C(4)-O(4)	1.190 (16)
Os(3)-S	2.432 (3)	C(5)-O(5)	1.173 (15)
Os(5)-S	2.417 (3)	C(6)-O(6)	1.170 (18)
Os(1)-C(1)	1.923 (14)	C(7)-O(7)	1.162 (16)
Os(1)-C(2)	1.890 (13)	C(8)-O(8)	1.155 (15)
Os(2)-C(3)	1.954 (13)	C(9)-O(9)	1.183 (14)
Os(2)-C(4)	1.893 (14)	C(10)-O(10)	1.150 (14)
Os(2)-C(5)	1.840 (14)	C(11)-O(11)	1.160 (18)
Os(2)-C(6)	1.922 (17)	C(12)-O(12)	1.162 (15)
Os(3)-C(7)	1.893 (14)	C(13)-O(13)	1.160 (18)
Os(3)-C(8)	1.886 (14)	C(14)-O(14)	1.193 (16)
Os(3)-C(9)	1.885 (13)	C(15)-O(15)	1.158 (13)
Os(4)-C(10)	1.865 (12)	C(16)-O(16)	1.170 (19)
Os(4)-C(11)	1.875 (16)	C(17)-O(17)	1.126 (15)
Os(4)-C(12)	1.860 (13)	C(18)-O(18)	1.163 (16)
Os(4)-C(13)	1.876 (17)	C(19)-O(19)	1.137 (15)

(NCMe)₂²⁰ and Os₃(CO)₁₀(μ₃-S)¹⁹ were prepared by reported procedures. Reagent grade solvents were used without further purification. IR spectra were recorded on a Nicolet 5SX FT-IR.

Preparation of Os₆(CO)₁₉(μ₃-S) (III). In a typical preparation a solution of 0.100 g of Os₃(CO)₁₀(NCMe)₂ and 0.070 g of Os₃(CO)₁₀(μ₃-S) (I) in 50 mL of benzene solvent was heated to reflux. After 15 min a solution of 0.050 g of Os₃(CO)₁₀(NCMe)₂ in 20 mL of benzene was added via syringe and heating was continued a further 45 min. The solution turned red-brown and the solvent was removed in vacuo. The brown residue was put

Table IV. Selected Interatomic Angles (deg) with Esd's for Os₆(CO)₁₉(μ₃-S) (III)

atoms	angle	atoms	angle
Os(2)-Os(1)-Os(3)	60.37 (2)	Os(1)-Os(4)-C(10)	101.9 (4)
Os(2)-Os(1)-Os(4)	112.04 (2)	Os(1)-Os(4)-C(11)	105.2 (4)
Os(2)-Os(1)-Os(5)	138.91 (2)	Os(1)-Os(4)-C(12)	162.4 (4)
Os(2)-Os(1)-Os(6)	136.98 (2)	Os(3)-Os(4)-C(10)	161.2 (4)
Os(3)-Os(1)-Os(4)	60.47 (2)	Os(3)-Os(4)-C(11)	90.6 (4)
Os(3)-Os(1)-Os(5)	85.37 (2)	Os(3)-Os(4)-C(12)	110.3 (4)
Os(3)-Os(1)-Os(6)	141.43 (2)	Os(5)-Os(4)-C(10)	88.7 (4)
Os(4)-Os(1)-Os(5)	60.65 (2)	Os(5)-Os(4)-C(11)	164.5 (4)
Os(4)-Os(1)-Os(6)	110.10 (2)	Os(5)-Os(4)-C(12)	107.1 (4)
Os(5)-Os(1)-Os(6)	60.58 (2)	Os(1)-Os(5)-S	53.30 (7)
Os(1)-Os(2)-Os(3)	59.32 (2)	Os(1)-Os(5)-C(13)	126.0 (4)
Os(1)-Os(3)-Os(2)	60.32 (2)	Os(1)-Os(5)-C(14)	127.2 (4)
Os(1)-Os(3)-Os(4)	60.00 (2)	Os(1)-Os(5)-C(15)	118.4 (4)
Os(1)-Os(4)-Os(3)	59.53 (2)	Os(4)-Os(5)-S	85.26 (8)
Os(1)-Os(4)-Os(5)	59.63 (2)	Os(4)-Os(5)-C(13)	167.9 (4)
Os(1)-Os(5)-Os(4)	59.72 (2)	Os(4)-Os(5)-C(14)	77.3 (4)
Os(1)-Os(5)-Os(6)	59.90 (2)	Os(4)-Os(5)-C(15)	93.5 (4)
Os(1)-Os(6)-Os(5)	59.52 (2)	Os(6)-Os(5)-S	87.24 (7)
Os(2)-Os(1)-S	85.75 (7)	Os(6)-Os(5)-C(13)	82.4 (5)
Os(2)-Os(1)-C(1)	69.8 (4)	Os(6)-Os(5)-C(14)	172.9 (4)
Os(2)-Os(1)-C(2)	100.0 (3)	Os(6)-Os(5)-C(15)	84.5 (4)
Os(3)-Os(1)-S	55.19 (8)	Os(1)-Os(6)-C(16)	157.8 (5)
Os(3)-Os(1)-C(1)	127.7 (4)	Os(1)-Os(6)-C(17)	82.8 (4)
Os(3)-Os(1)-C(2)	111.7 (4)	Os(1)-Os(6)-C(18)	111.1 (5)
Os(4)-Os(1)-S	86.61 (8)	Os(1)-Os(6)-C(19)	87.8 (4)
Os(4)-Os(1)-C(1)	164.9 (4)	Os(5)-Os(6)-C(16)	98.5 (5)
Os(4)-Os(1)-C(2)	74.0 (3)	Os(5)-Os(6)-C(17)	87.4 (4)
Os(5)-Os(1)-S	54.64 (7)	Os(5)-Os(6)-C(18)	170.1 (5)
Os(5)-Os(1)-C(1)	128.5 (4)	Os(5)-Os(6)-C(19)	87.8 (4)
Os(5)-Os(1)-C(2)	114.2 (3)	Os(1)-S-Os(3)	71.46 (9)
Os(6)-Os(1)-S	88.48 (8)	Os(1)-S-Os(5)	72.05 (8)
Os(6)-Os(1)-C(1)	71.9 (4)	Os(3)-S-Os(5)	103.78 (12)
Os(6)-Os(1)-C(2)	99.4 (3)	Os(1)-C(1)-O(1)	173.4 (11)
Os(1)-Os(2)-C(3)	81.9 (3)	Os(1)-C(2)-O(2)	177.7 (10)
Os(1)-Os(2)-C(4)	111.7 (4)	Os(2)-C(3)-O(3)	179.7 (12)
Os(1)-Os(2)-C(5)	155.6 (4)	Os(2)-C(4)-O(4)	176.8 (13)
Os(1)-Os(2)-C(6)	89.6 (4)	Os(2)-C(5)-O(5)	175.6 (13)
Os(3)-Os(2)-C(3)	86.0 (4)	Os(2)-C(6)-O(6)	176.9 (13)
Os(3)-Os(2)-C(4)	171.0 (4)	Os(3)-C(7)-O(7)	174.7 (12)
Os(3)-Os(2)-C(5)	96.4 (4)	Os(3)-C(8)-O(8)	178.7 (14)
Os(3)-Os(2)-C(6)	88.3 (4)	Os(3)-C(9)-O(9)	170.6 (11)
Os(1)-Os(3)-S	53.34 (7)	Os(4)-C(10)-O(10)	174.2 (11)
Os(1)-Os(3)-C(7)	116.2 (4)	Os(4)-C(11)-O(11)	175.4 (13)
Os(1)-Os(3)-C(8)	129.5 (4)	Os(4)-C(12)-O(12)	175.9 (13)
Os(1)-Os(3)-C(9)	123.9 (4)	Os(5)-C(13)-O(13)	177.4 (14)
Os(4)-Os(3)-S	85.27 (7)	Os(5)-C(14)-O(14)	175.8 (13)
Os(4)-Os(3)-C(7)	91.9 (4)	Os(5)-C(15)-O(15)	177.6 (12)
Os(4)-Os(3)-C(8)	164.9 (4)	Os(6)-C(16)-O(16)	170.9 (17)
Os(4)-Os(3)-C(9)	72.5 (4)	Os(6)-C(17)-O(17)	174.2 (11)
		Os(6)-C(18)-O(18)	176.5 (12)
		Os(6)-C(19)-O(19)	178.1 (12)

on silica gel TLC plates and eluted with hexane/CH₂Cl₂ (90/10). Orange Os₅(CO)₁₅(μ-S) (IV) (0.020 g, 18%) readily separated from the boron Os₆(CO)₁₉(μ₃-S) (III) (0.042 g, 31%); IR (ν(CO)CH₂Cl₂) 2128 w, 2105 s, 2073 vs, 2049 s, 2039 s, 2004 w sh, 2001 w cm⁻¹.

Preparation of Os₆(CO)₁₇(μ₃-S) (V). A solution of III (0.030 g) in 50 mL of toluene was heated to reflux for 50 min. The solvent was removed in vacuo and the residue was placed on silica gel TLC plates. Elution with hexane/CH₂Cl₂ (85/15) separated the following bands: orange Os₅(CO)₁₅(μ₄-S) (IV) (0.011 g, 50%); brown Os₆(CO)₁₇(μ₄-S) (V) (0.006 g, 23%), IR (ν(CO)CH₂Cl₂) 2105 w, 2072 vs, 2065 s, 2051 m, 2038 s, 2012 w cm⁻¹ and untreated I (0.003 g).

Crystallographic Analyses. Dark brown crystals of III suitable for diffraction measurements were obtained by slowly evaporating hexane/CH₂Cl₂ (80/20) solutions at 4 °C. Dark brown crystals of V were obtained by slowly evaporating hexane/CH₂Cl₂ (50/50) solutions at 4 °C. The data crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on an Enraf-Nonius CAD-4 fully automated diffractometer using graphite monochromatized Mo Kα radiation. Unit cells were determined and refined from 25 randomly selected reflections obtained by using the CAD-4 automatic search, center, index, and least-squares routines. Crystal data and data collection parameters

are listed in Table I. All data processing was performed on a Digital Equipment Corp. PDP 11/45 computer using the Enraf-Nonius SDP program library (version 18). An absorption correction of a Gaussian integration type was performed for each structure. Neutral atom scattering factors were calculated by standard procedures.^{21a} Anomalous dispersion corrections were applied to all non-hydrogen atoms.^{21b} Full-matrix least-squares refinements minimized the function $\sum_{hkl} w(|F_{\text{obsd}}| - |F_{\text{calcd}}|)^2$, where $w = 1/(\sigma(F)^2)$, $\sigma(F) = \sigma(F_{\text{obsd}}^2)/(2F_{\text{obsd}})$, and $\sigma(F_{\text{obsd}}^2) = \{\sigma(I_{\text{raw}})^2 + (PF_{\text{obsd}})^2\}^{1/2}/Lp$.

For III the space group $P\bar{1}$ was selected and confirmed by the successful solution and refinement of the structure. The structure was solved by a combination of direct methods (MULTAN) and difference Fourier techniques. The coordinates of the six osmium atoms were obtained from an E map calculated on the basis of 272 reflections ($E \geq 1.94$). The remaining atoms were located in subsequent difference Fourier syntheses. Only the osmium and sulfur atoms were refined anisotropically. Fractional atomic coordinates, thermal parameters, and interatomic distances and

(21) "International Tables for X-ray Crystallography" Kynoch Press: Birmingham, England, 1975; Vol. 4, (a) Table 2.2B, pp 99-101, (b) Table 2.3.1, pp 149-150.

Table V. Positional and Thermal Parameters^a and Their Estimated Standard Deviations for Os₆(CO)₁₇(μ₄-S) (V)

atom	x	y	z	B _{1,1}	B _{2,2}	B _{3,3}	B _{1,2}	B _{1,3}	B _{2,3}	R _{eqv}
Os1	0.28298 (8)	-0.03981 (7)	0.93466 (0)	2.05 (3)	1.72 (4)	1.50 (3)	0.08 (4)	-0.19 (3)	0.00 (4)	1.76 (2)
Os2	0.10647 (7)	-0.12654 (6)	0.84910 (8)	2.03 (3)	1.69 (4)	1.89 (3)	-0.15 (3)	-0.02 (4)	0.10 (5)	1.87 (2)
Os3	0.02019 (8)	0.01759 (7)	0.76166 (7)	1.73 (3)	2.14 (5)	2.30 (3)	0.11 (4)	-0.36 (3)	0.32 (4)	2.06 (2)
Os4	0.25922 (8)	-0.02637 (7)	0.73478 (6)	1.90 (3)	1.73 (4)	1.42 (3)	-0.02 (4)	0.01 (3)	0.00 (4)	1.68 (2)
Os5	0.20041 (7)	0.10750 (6)	0.85094 (7)	1.96 (3)	1.47 (4)	1.80 (3)	0.09 (3)	-0.03 (3)	-0.03 (4)	1.74 (2)
Os6	0.44230 (7)	0.04662 (6)	0.84509 (8)	1.68 (3)	2.11 (4)	2.15 (3)	-0.14 (3)	-0.05 (4)	-0.02 (5)	1.98 (2)

atom	x	y	z	B, Å ²	atom	x	y	z	B, Å ²
S	0.0807 (5)	0.0022 (4)	0.9339 (4)	2.1 (1)	C1	0.389 (2)	-0.124 (2)	0.957 (2)	2.9 (5)
O1	0.453 (2)	-0.176 (2)	0.969 (1)	5.1 (5)	C2	0.314 (2)	-0.011 (2)	1.061 (2)	3.3 (6)
O2	0.662 (2)	-0.010 (2)	0.640 (2)	5.8 (5)	C3	0.155 (2)	-0.189 (2)	0.956 (2)	2.5 (5)
O3	0.173 (2)	-0.235 (1)	1.014 (1)	4.3 (4)	C4	-0.051 (2)	-0.157 (2)	0.868 (2)	2.3 (5)
O4	-0.148 (2)	-0.177 (1)	0.880 (1)	4.3 (4)	C5	0.138 (2)	-0.214 (2)	0.768 (2)	3.3 (6)
O5	0.170 (2)	-0.265 (2)	0.717 (1)	5.3 (5)	C6	-0.063 (2)	-0.062 (2)	0.696 (2)	4.4 (7)
O6	-0.108 (2)	-0.111 (1)	0.651 (1)	3.9 (4)	C7	-0.123 (2)	0.063 (2)	0.805 (2)	3.6 (6)
O7	-0.207 (2)	0.094 (1)	0.833 (2)	5.2 (5)	C8	0.036 (2)	0.092 (2)	0.663 (2)	3.6 (6)
O8	0.053 (2)	0.131 (2)	0.600 (1)	5.3 (5)	C9	0.331 (2)	0.043 (2)	0.645 (2)	3.0 (5)
O9	0.371 (2)	0.076 (2)	0.583 (1)	4.7 (5)	C10	-0.184 (2)	0.077 (2)	1.135 (2)	2.6 (5)
O10	-0.146 (2)	0.107 (1)	1.068 (1)	4.9 (5)	C11	0.371 (2)	-0.112 (2)	0.739 (2)	3.3 (5)
O11	0.432 (2)	-0.167 (1)	0.739 (1)	4.2 (4)	C12	0.265 (2)	0.184 (2)	0.767 (2)	3.4 (6)
O12	0.301 (2)	0.230 (1)	0.710 (1)	4.6 (5)	C13	0.273 (2)	0.159 (2)	0.962 (2)	3.0 (5)
O13	-0.188 (2)	0.306 (2)	1.028 (1)	4.8 (5)	C14	0.070 (2)	0.177 (2)	0.873 (2)	4.2 (7)
O14	-0.008 (2)	0.223 (2)	0.886 (1)	5.7 (5)	C15	0.518 (2)	0.091 (2)	0.954 (2)	2.6 (5)
O15	0.563 (2)	0.119 (2)	1.018 (2)	5.8 (6)	C16	0.514 (2)	0.117 (2)	0.760 (2)	3.1 (5)
O16	0.564 (2)	0.164 (1)	0.709 (1)	4.1 (4)	C17	0.570 (2)	-0.022 (2)	0.843 (2)	3.6 (5)
O17	0.646 (2)	-0.073 (1)	0.840 (2)	4.7 (4)					

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

Table VI. Interatomic Distances (Å) with Esd's for Os₆(CO)₁₇(μ₄-S) (V)

atoms	distance	atoms	distance
Os(1)-Os(2)	2.756 (1)	Os(4)-C(11)	1.91 (3)
Os(1)-Os(4)	2.847 (1)	Os(5)-C(12)	1.89 (3)
Os(1)-Os(5)	2.855 (1)	Os(5)-C(13)	1.97 (2)
Os(1)-Os(6)	2.625 (1)	Os(5)-C(14)	1.90 (3)
Os(2)-Os(3)	2.860 (1)	Os(6)-C(15)	1.91 (2)
Os(2)-Os(4)	2.895 (1)	Os(6)-C(16)	1.86 (3)
Os(3)-Os(4)	2.839 (1)	Os(6)-C(17)	1.84 (2)
Os(3)-Os(5)	2.830 (1)	C(1)-O(1)	1.14 (3)
Os(4)-Os(5)	2.838 (1)	C(2)-O(2)	1.20 (3)
Os(4)-Os(6)	2.868 (1)	C(3)-O(3)	1.15 (3)
Os(5)-Os(6)	2.930 (1)	C(4)-O(4)	1.17 (2)
Os(1)-S	2.398 (5)	C(5)-O(5)	1.17 (3)
Os(2)-S	2.462 (6)	C(6)-O(6)	1.16 (3)
Os(3)-S	2.544 (5)	C(7)-O(7)	1.15 (3)
Os(5)-S	2.503 (6)	C(8)-O(8)	1.12 (3)
Os(1)-C(1)	1.88 (3)	C(9)-O(9)	1.13 (3)
Os(1)-C(2)	1.88 (2)	C(10)-O(10)	1.15 (3)
Os(2)-C(3)	1.90 (2)	C(11)-O(11)	1.14 (3)
Os(2)-C(4)	1.88 (2)	C(12)-O(12)	1.18 (3)
Os(2)-C(5)	1.89 (3)	C(13)-O(13)	1.18 (3)
Os(3)-C(6)	1.87 (3)	C(14)-O(14)	1.18 (3)
Os(3)-C(7)	1.90 (3)	C(15)-O(15)	1.15 (3)
Os(3)-C(8)	1.86 (3)	C(16)-O(16)	1.21 (3)
Os(4)-C(9)	1.90 (3)	C(17)-O(17)	1.20 (3)
Os(4)-C(10)	1.85 (2)		

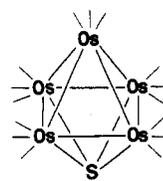
angles, with errors obtained from the inverse matrix obtained from the final cycle of least-squares refinement, are listed in Tables II-IV. A table of structure factor amplitudes is available (see supplementary material).

For V the systematic absences observed in the data set are consistent with either of the space groups *Pna2*₁ or *Pnma*. The space group *Pna2*₁ was selected because it was suspected that the structure of V would not contain either a reflection plane or a center of symmetry. This was confirmed by the subsequent analysis. The structure of V was obtained by a combination of direct methods (MULTAN) and difference Fourier techniques. The coordinates of the six osmium atoms were obtained from an E map calculated on the basis of 264 reflections (*E* ≥ 1.58). The remaining atoms were located in subsequent difference Fourier syntheses. Because of the limited number of data only the osmium

atoms were refined anisotropically. Fractional atomic coordinates and thermal parameters are listed in Table V. Interatomic distances and angles are listed in Tables VI and VII. A table of structure factor amplitudes is available. See supplementary material. The largest peaks in the final difference Fourier maps of both structures were residual electron density of the metal atoms.

Results

When benzene solutions of I and II are refluxed for approximately 1 h, the compounds Os₆(CO)₁₉(μ₃-S) (III) and Os₅(CO)₁₅(μ₄-S) (IV) can be isolated by TLC in yields of 31% and 18%, respectively. Compound IV was ob-



(IV)

tained by us previously as one of several compounds obtained in the pyrolysis of HOs₃(CO)₁₀(μ-SPh).²² Its structure consists of a cluster of five osmium atoms arranged in the form of a square pyramid with a quadruply bridging sulfido ligand spanning the square base.

The structure of III has been determined by a single-crystal X-ray diffraction analysis, and an ORTEP diagram of its structure is shown in Figure 1. Final fractional atomic coordinates and thermal parameters are listed in Table II. Interatomic distances and angles are listed in Tables III and IV, respectively. The cluster consists of a central group of four osmium atoms (Os(1), Os(3), Os(4), and Os(5)) arranged in the shape of a "butterfly" tetrahedron. A triply bridging sulfido ligand bridges the open

(22) Adams R. D.; Horváth, I. T.; Segmüller, B. E.; Yang, L. W. *Organometallics* 1983, 2, 1301.

Table VII. Selected Interatomic Angles (deg) with Esd's for Os₆(CO)₁₇(μ₄-S) (V)

atoms	angle	atoms	angle
Os(2)-Os(1)-Os(4)	62.19 (3)	Os(1)-Os(4)-C(9)	131.8 (7)
Os(2)-Os(1)-Os(5)	91.44 (4)	Os(1)-Os(4)-C(10)	140.4 (8)
Os(2)-Os(1)-Os(6)	125.07 (4)	Os(1)-Os(4)-C(11)	81.4 (8)
Os(4)-Os(1)-Os(5)	59.69 (3)	Os(2)-Os(4)-C(9)	168.4 (7)
Os(4)-Os(1)-Os(6)	63.07 (3)	Os(2)-Os(4)-C(10)	83.8 (8)
Os(5)-Os(1)-Os(6)	64.49 (3)	Os(2)-Os(4)-C(11)	87.5 (8)
Os(1)-Os(2)-Os(3)	90.04 (4)	Os(3)-Os(4)-C(9)	110.4 (8)
Os(1)-Os(2)-Os(4)	60.45 (3)	Os(3)-Os(4)-C(10)	77.1 (7)
Os(3)-Os(2)-Os(4)	59.12 (3)	Os(3)-Os(4)-C(11)	145.6 (8)
Os(2)-Os(3)-Os(4)	61.04 (3)	Os(5)-Os(4)-C(9)	91.0 (8)
Os(2)-Os(3)-Os(5)	89.84 (3)	Os(5)-Os(4)-C(10)	133.3 (7)
Os(4)-Os(3)-Os(5)	60.08 (3)	Os(5)-Os(4)-C(11)	136.1 (8)
Os(1)-Os(4)-Os(2)	57.37 (3)	Os(6)-Os(4)-C(9)	78.2 (7)
Os(1)-Os(4)-Os(3)	88.66 (3)	Os(6)-Os(4)-C(10)	160.0 (7)
Os(1)-Os(4)-Os(5)	60.30 (3)	Os(6)-Os(4)-C(11)	79.2 (8)
Os(1)-Os(4)-Os(6)	54.68 (3)	Os(1)-Os(5)-S	52.67 (12)
Os(2)-Os(4)-Os(3)	59.84 (3)	Os(1)-Os(5)-C(12)	134.6 (8)
Os(2)-Os(4)-Os(5)	89.00 (3)	Os(1)-Os(5)-C(13)	84.2 (8)
Os(2)-Os(4)-Os(6)	111.90 (3)	Os(1)-Os(5)-C(14)	134.5 (8)
Os(3)-Os(4)-Os(5)	59.79 (3)	Os(3)-Os(5)-S	56.58 (12)
Os(3)-Os(4)-Os(6)	120.94 (3)	Os(3)-Os(5)-C(12)	110.8 (7)
Os(5)-Os(4)-Os(6)	61.80 (3)	Os(3)-Os(5)-C(13)	152.6 (7)
Os(1)-Os(5)-Os(3)	88.68 (3)	Os(3)-Os(5)-C(14)	79.8 (8)
Os(1)-Os(5)-Os(4)	60.01 (3)	Os(4)-Os(5)-S	81.71 (14)
Os(1)-Os(5)-Os(6)	53.94 (3)	Os(4)-Os(5)-C(12)	93.8 (8)
Os(4)-Os(5)-Os(6)	59.61 (3)	Os(4)-Os(5)-C(13)	134.5 (7)
Os(1)-Os(6)-Os(4)	62.25 (3)	Os(4)-Os(5)-C(14)	138.4 (8)
Os(1)-Os(6)-Os(5)	61.57 (3)	Os(6)-Os(5)-S	106.51 (13)
Os(4)-Os(6)-Os(5)	58.59 (3)	Os(6)-Os(5)-C(12)	81.1 (8)
Os(2)-Os(1)-S	56.56 (14)	Os(6)-Os(5)-C(13)	77.2 (7)
Os(2)-Os(1)-C(1)	98.4 (8)	Os(6)-Os(5)-C(14)	161.0 (8)
Os(2)-Os(1)-C(2)	133.0 (8)	Os(1)-Os(6)-C(15)	97.6 (7)
Os(4)-Os(1)-S	83.3 (1)	Os(1)-Os(6)-C(16)	162.2 (7)
Os(4)-Os(1)-C(1)	106.4 (7)	Os(1)-Os(6)-C(17)	102.5 (8)
Os(4)-Os(1)-C(2)	160.9 (4)	Os(4)-Os(6)-C(15)	158.2 (7)
Os(5)-Os(1)-S	56.10 (14)	Os(4)-Os(6)-C(16)	103.4 (7)
Os(5)-Os(1)-C(1)	156.4 (7)	Os(4)-Os(6)-C(17)	107.4 (8)
Os(5)-Os(1)-C(2)	104.5 (9)	Os(5)-Os(6)-C(15)	105.7 (7)
Os(6)-Os(1)-S	120.46 (15)	Os(5)-Os(6)-C(16)	102.6 (8)
Os(6)-Os(1)-C(1)	92.5 (8)	Os(5)-Os(6)-C(17)	161.8 (8)
Os(6)-Os(1)-C(2)	101.5 (8)	Os(1)-S-Os(2)	69.08 (15)
Os(1)-Os(2)-S	54.37 (12)	Os(1)-S-Os(3)	106.99 (20)
Os(1)-Os(2)-C(3)	74.1 (7)	Os(1)-S-Os(5)	71.22 (14)
Os(1)-Os(2)-C(4)	140.4 (6)	Os(2)-S-Os(3)	69.67 (15)
Os(1)-Os(2)-C(5)	122.3 (7)	Os(2)-S-Os(5)	108.03 (20)
Os(3)-Os(2)-S	56.51 (13)	Os(3)-S-Os(5)	68.20 (15)
Os(3)-Os(2)-C(3)	152.9 (7)	Os(1)-C(1)-O(1)	179 (2)
Os(3)-Os(2)-C(4)	87.6 (7)	Os(1)-C(2)-O(2)	176 (2)
Os(3)-Os(2)-C(5)	116.4 (8)	Os(2)-C(3)-O(3)	170 (2)
Os(4)-Os(2)-S	81.25 (13)	Os(2)-C(4)-O(4)	179 (2)
Os(4)-Os(2)-C(3)	125.4 (7)	Os(2)-C(5)-O(5)	173 (2)
Os(4)-Os(2)-C(4)	143.7 (7)	Os(3)-C(6)-O(6)	175 (2)
Os(4)-Os(2)-C(5)	89.3 (8)	Os(3)-C(7)-O(7)	177 (2)
Os(2)-Os(3)-S	53.82 (14)	Os(3)-C(8)-O(8)	173 (3)
Os(2)-Os(3)-C(6)	78.5 (9)	Os(4)-C(9)-O(9)	170 (3)
Os(2)-Os(3)-C(7)	119.1 (8)	Os(4)-C(10)-O(10)	174 (2)
Os(2)-Os(3)-C(8)	147.1 (8)	Os(4)-C(11)-O(11)	175 (3)
Os(4)-Os(3)-S	80.99 (11)	Os(5)-C(12)-O(12)	176 (2)
Os(4)-Os(3)-C(6)	103.9 (9)	Os(5)-C(13)-O(13)	176 (2)
Os(4)-Os(3)-C(7)	165.1 (8)	Os(5)-C(14)-O(14)	177 (3)
Os(4)-Os(3)-C(8)	88.8 (8)	Os(6)-C(15)-O(15)	179 (3)
Os(5)-Os(3)-S	55.22 (13)	Os(6)-C(16)-O(16)	176 (2)
Os(5)-Os(3)-C(6)	163.6 (9)	Os(6)-C(17)-O(17)	174 (2)
Os(5)-Os(3)-C(7)	105.4 (8)		
Os(5)-Os(3)-C(8)	85.3 (8)		

triangular face Os(1), Os(3), Os(5). Two adjacent edges of the butterfly tetrahedron are bridged by osmium tetracarbonyl groups. The osmium-osmium bond distances range from 2.809 (1) to 2.850 (1) Å and all are slightly shorter than the osmium-osmium internuclear separation of 2.877 (3) Å found in Os₃(CO)₁₂. There does not appear to be any systematic or chemically significant pattern in their variations. The dihedral angle between the Os(1), Os(3), Os(4) and Os(1), Os(4), Os(5) planes is 102.2°. The

osmium-sulfur bond distances range from 2.376 (3) to 2.432 (3) Å, and are typical of those found for triply bridging sulfido ligands in related sulfido osmium carbonyl cluster compounds.²³ There are 19 linear terminal carbonyl ligands arranged such that Os(1) contains two, Os(2)

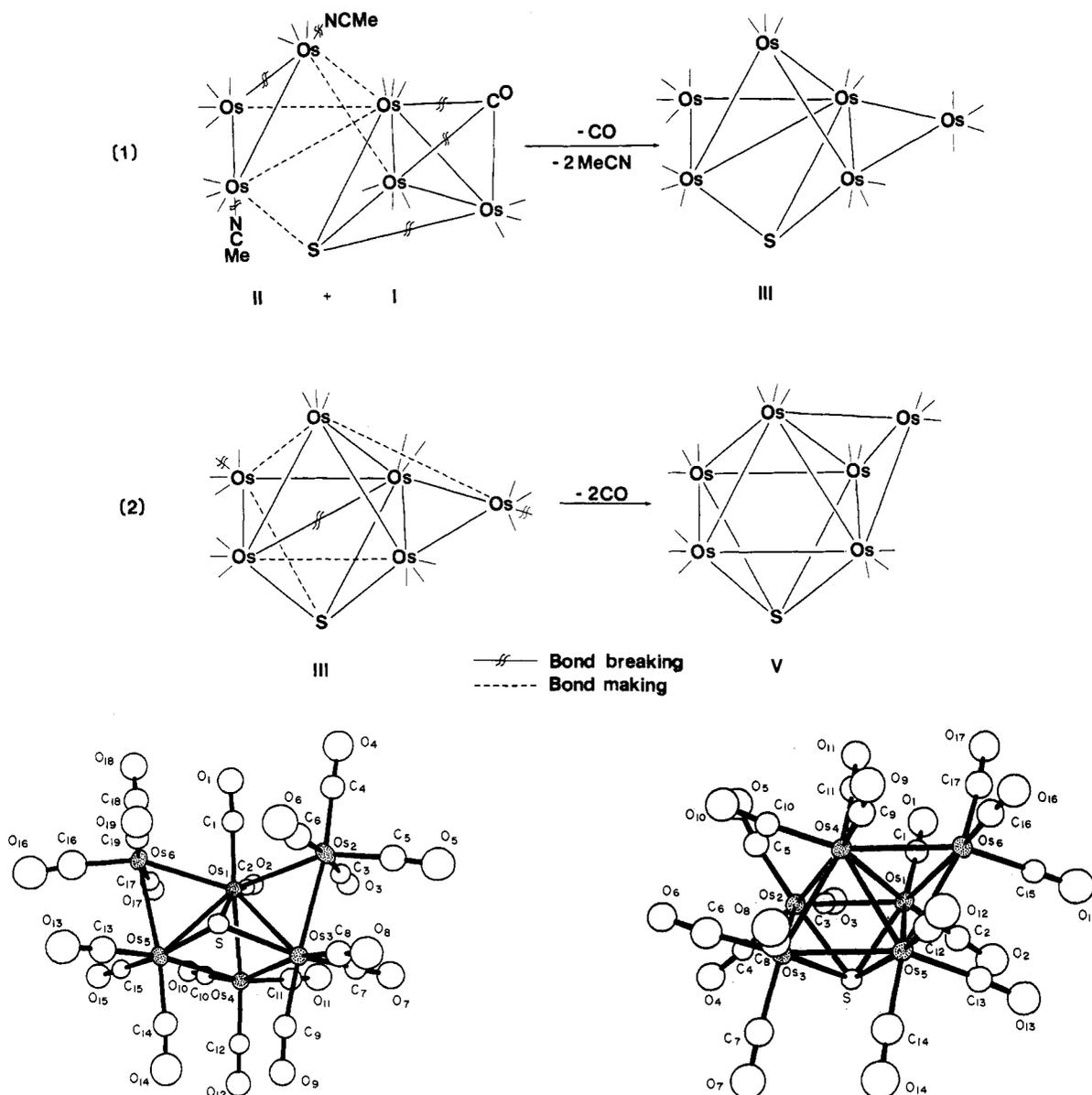


Figure 1. An ORTEP diagram of Os₆(CO)₁₉(μ₃-S) (III) showing 50% probability thermal ellipsoids.

Figure 2. An ORTEP diagram of Os₆(CO)₁₇(μ₄-S) (V) showing 50% probability thermal ellipsoids.

and Os(6) contain four each, and the remainder have three each.

Mingos has recently rationalized the tendency of Os(CO)₄ groups to adopt edge bridging positions in cluster compounds and predicted that 90-electron clusters like III would possess the doubly edge-bridged butterfly tetrahedral structure.²⁴ Compound III can also be viewed as "electron precise", but one of the osmium-osmium bonds to Os(4) must be viewed as a donor-acceptor bond.

When refluxed in toluene solvent, III loses 2 mol of CO and is converted into the new cluster Os₆(CO)₁₇(μ₄-S) (V). The structure of V was determined by a single-crystal diffraction analysis, and an ORTEP diagram of V is shown in Figure 2. Final fractional atomic coordinates and thermal parameters are listed in Table V. Interatomic distances and angles are listed in Tables VI and VII, respectively. The cluster consists of a square pyramid of five osmium atoms with a quadruply bridging sulfido ligand spanning the square base. On one of the triangular faces is a triply bridging "capping" osmium tricarbonyl group.

The osmium-osmium bond distances span the wide range from 2.625 (1) to 2.930 (1) Å. The shortest bond, Os(1)-Os(6), is 0.252 Å shorter than the osmium-osmium bond distances found in Os₃(CO)₁₂, 2.877 (3) Å.²⁵ The osmium-sulfur distances also span a wide range, 2.398 (5)-2.544 (5) Å, with the shortest bond being Os(3)-S. Similarly coordinated quadruply bridging sulfido ligands were also observed in the osmium clusters Os₅(CO)₁₅(μ₄-S),²² Os₆(CO)₁₆(μ₄-S)(μ₃-S),¹⁴ and Os₇(CO)₁₉(μ₄-S).¹⁵ The osmium-sulfur distances in these compounds all lay within the range observed in III. Each osmium atom contains three linear terminal carbonyl ligands, except Os(1) which has only two.

The structure of V can be rationalized within the framework of the skeletal electron pair (SEP) theory. According to this theory, V contains 14 cluster valence electrons (i.e., seven pairs). The predicted polyhedral

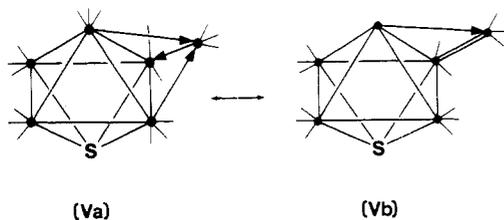
(25) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* 1977, 16, 878.

(26) (a) Wade, K. In "Transition Metal Clusters"; Johnson, B. F. G., Ed.; Wiley: New York, 1980. (b) Johnson, B. F. G.; Benfield, R. E. In "Topics in Stereochemistry"; Geoffroy, G. L., Ed.; Wiley: New York, 1981; Vol. 12.

shape of the cluster is that of an $\text{Os}(\text{CO})_3$ "capped" octahedron if the sulfido ligand is considered as a part of the cluster. Mingos has shown recently that capping groups should not change the number of bonding cluster valence orbitals so the observed structure of V is also an acceptable one.²⁷

Of further interest is the highly unsymmetrical bonding of the capping group to the cluster. For example, both the shortest ($\text{Os}(1)-\text{Os}(6) = 2.625(1) \text{ \AA}$) and longest ($\text{Os}(5)-\text{Os}(6) = 2.930(1) \text{ \AA}$) metal-metal bonds in the molecule involve the capping metal atom $\text{Os}(6)$. While the metal-metal bonds to capping groups are usually shorter than those within the polyhedron, the distortion observed in V is unprecedented.^{15,28-30}

The bonding in V can also be described with two-center two-electron metal-metal bonds if one employs a series of heteropolar bonds such as those indicated in structure Va



(27) Mingos, D. M. P.; Forsyth, M. I. *J. Chem. Soc., Dalton Trans.* 1977, 610.

(28) John, G. R.; Johnson, B. F. G.; Lewis, J. J. *Organomet. Chem.* 1979, 181, 143.

(29) Eady, C. R.; Johnson, B. F. G.; Lewis, J. J. *J. Chem. Soc., Chem. Commun.* 1977, 385.

(30) Lin, Y. C.; Knobler, C. B.; Kaez, H. D. *J. Organomet. Chem.* 1981, 213, C41.

by the double-headed arrows.²⁸ In addition, a component of the resonance form Vb which implies the absence of a bond between $\text{Os}(5)$ and $\text{Os}(6)$ and a double bond between $\text{Os}(1)$ and $\text{Os}(6)$ would explain the observed distortions.

Discussion

The condensation of I and II to yield III is clearly a multistep process involving ligand loss and metal-metal bond formation. It is believed that this process is initiated via the formation of a coordinate bond between the sulfido ligand in I and a metal atom in II, but in the absence of isolated intermediates further steps cannot be delineated at this time. Equation 1 shows schematically where bonds in I and II must be made and broken in order to produce III.

The formation of V from III is less complex; see eq 2. One carbonyl ligand is probably lost from each of the edge bridging $\text{Os}(\text{CO})_4$ groups. One $\text{Os}(\text{CO})_3$ group then becomes the capping group while the other inserts into one of the metal-metal bonds of the cluster and leads to its enlargement.

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Registry No. I, 88746-45-6; II, 61817-93-4; III, 88730-74-9; IV, 86437-19-6; V, 88730-75-0.

Supplementary Material Available: A table of structure factor amplitudes and a listing of interatomic angles for each structural analysis (30 pages). Ordering information is given on any current masthead page.

Communications

Monoalkylation of Dichloroarenes with Grignard Reagents Catalyzed by a Nickel Complex[†]

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Summary: Dichloroarenes react with Grignard reagents in the presence of a catalytic amount of $[\text{Ni}(\text{triphos})\text{Cl}]\text{PF}_6$ (triphos = bis(2-(diphenylphosphino)ethyl)phenylphosphine) to give mainly monoalkylated products.

Although the cross coupling of aromatic halides with Grignard reagents catalyzed by transition metals has been known for several years,¹ the desired monoalkylation of dichloroarenes has not been successfully accomplished. Cross-coupling reactions of dichlorobenzene using conventional nickel catalysts give predominant formation of

dialkylated products.² While dibromobenzene can be selectively monoalkylated with Grignard reagents in the presence of palladium catalysts,³ the use of chlorinated arenes is preferred because they are more readily available than their brominated analogues. Specifically, monoalkylation of dichloroarenes would be a useful route to pharmaceutical and agricultural intermediates.⁴

We have discovered that $[\text{Ni}(\text{triphos})\text{Cl}]\text{PF}_6$ (triphos = bis(2-(diphenylphosphino)ethyl)phenylphosphine) is an effective catalyst for the monoalkylation of dichloroarenes. Some examples are shown in Table I.⁶ In a typical reaction, 4.7 mL (13.6 mmol) of 2.9 M EtMgBr in ether was added to 2.00 g (13.60 mmol) of *o*-dichlorobenzene and 0.050 g (0.065 mmol) of $[\text{Ni}(\text{triphos})\text{Cl}]\text{PF}_6$ in 35 mL of

(2) Tamao, K.; Sumitani, K.; Kisco, Y.; Zembayashi, M.; Fujioka, A.; Kodama, S.-I.; Nakajima, I.; Kumada, M. *Bull. Chem. Soc. Jpn.* 1976, 49, 1958.

(3) Minato, A.; Tamao, K.; Hayashi, T.; Suzuki, K.; Kumada, M. *Tetrahedron Lett.* 1980, 21, 845.

(4) See for example: Hogel, E.; Tschape, T. *Pharmazie* 1975, 30, H3, 147.

(5) King, R. B.; Kapoor, P. N.; Kapoor, R. N. *Inorg. Chem.* 1971, 10, 1841.

(6) $[\text{Ni}(\text{triphos})\text{Cl}]\text{PF}_6$ catalyzes the reaction of chlorobenzene and EtMgBr to yield 88% ethylbenzene.

[†] Contribution No. 3409.

(1) Negishi, E.-I. *Acc. Chem. Res.* 1982, 15, 340 and references therein.