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Cluster Synthesis. 1. The Use of Sulfido Ligands in the Synthesis of High Nuclearity Transition-Metal Cluster Compounds. The Synthesis and Crystal and Molecular Structures of $Os_6(CO)_{17}(\mu_4\text{-}S)_2$ and $Os_6(CO)_{16}(\mu_4\text{-}S)(\mu_3\text{-}S)$

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Abstract: By taking advantage of the multicoordination and donor capacity of sulfido ligands, the clusters $Os_3(CO)_9(\mu_3\text{-}S)_2$ (I) and $Os_3(CO)_{10}(NCMe)_2$ (II) have been combined by reaction to yield the high nuclearity cluster $Os_6(CO)_{17}(\mu_4\text{-}S)_2$ (III). III has been characterized by X-ray crystallographic methods: space group $P2_12_12_1$, a = 11.280 (5) Å, b = 14.622 (8) Å, c = 17.626 (5) Å, V = 2907 (4) Å^3, Z = 4, ρ_{calcd} = 3.84 g/cm^3. A total of 1726 reflections ($F^2 \geq 2.0\sigma(F^2)$) produced the final residuals R_1 = 0.037 and R_2 = 0.030. III consists of a pentagonal-bipyramidal cluster that includes five osmium atoms and two sulfido ligands with the sulfido ligands in equatorial sites. An $Os(CO)_4$ group bridges an edge of the cluster between apical and equatorial metal atoms. The apical–equatorial metal–metal bond distances in the cluster, which range from 2.898 (2)–2.988 (2) Å, are significantly longer than the one equatorial–equatorial bond distance at 2.833 (2) Å. When refluxed in octane solvent for 5 h, III loses 1 mol of CO and is transformed into new cluster complex $Os_6(CO)_{16}(\mu_4\text{-}S)(\mu_3\text{-}S)$ (IV). IV has also been analyzed by X-ray diffraction methods: space group $P2_1/c$, a = 10.083 (4) Å, b = 12.633 (4) Å, c = 21.383 (4) Å, β = 91.73 (2)°, V = 2722 (3) Å^3, Z = 4, ρ_{calcd} = 4.03 g/cm^3. A total of 2629 reflections ($F^2 \geq 2.0\sigma(F^2)$) produced the final residuals R_1 = 0.038 and R_2 = 0.039. IV contains a square-pyramidal cluster of five metal atoms with a quadruply bridging sulfido ligand spanning the square base. The sixth metal atom bridges an edge of the square base and that group of three contains a triply bridging sulfido ligand. This edge of the square base contains an unusually short metal–metal bond (2.686 (1) Å), which could be due to the fact that it contains four single atom bridges. The formation of III from the trinuclear units of I and II is described, as well as the transformation of III into IV. Via their adaptable, multicoordination character, the sulfido ligands play a major role in the initial linking of the trinuclear units and the subsequent reorganization of the metal–metal bonding.

The synthesis of high nuclearity transition-metal carbonyl cluster compounds has, in much of the past, depended as much on serendipity and good fortune as it has on the skill and patience of the investigator.[1-3] One highly successful synthetic method involves simple pyrolysis of low nuclearity metal carbonyl compounds.[3-4] Metal–metal bonds replace the expelled carbonyl ligands, and higher nuclearity clusters with various polyhedral structures are formed.[5] Unfortunately these syntheses are fairly nonspecific. Many products are formed and the yields of any given product are usually low.

It seems that heteroatoms with adaptable coordination numbers could serve as focal points for the aggregation of metal atoms and thus, in some cases, assist and control the formation of metal–metal bonds as the cluster is forming. In this regard heteroatoms from the main groups such as S, Se, N, P, As, and Ge have been widely used in the synthesis of new and interesting small clusters.[6-10] It seems reasonable to expect that the syntheses of higher nuclearity carbonyl clusters could be equally influenced by the presence of heteroatoms. A number of high nuclearity clusters containing heteroatoms are known.[11] We have recently presented an example of a condensation reaction between two sulfido triosmium clusters where it was shown that the sulfido ligand played a key role in the initial linking of the clusters and the subsequent reorganization of the metal–metal bonding.[12]

Table I. Interatomic Distances with Esds for $Os_6(CO)_{17}(\mu_4\text{-}S)_2$ (III)

atoms	distance, Å	atoms	distance, Å
Os(1)–Os(2)	2.945 (2)	Os(3)–C(8)	1.98 (3)
Os(1)–Os(3)	2.818 (2)	Os(4)–C(9)	1.92 (5)
Os(1)–Os(4)	2.940 (2)	Os(4)–C(10)	1.83 (3)
Os(1)–Os(5)	2.920 (2)	Os(4)–C(11)	1.73 (3)
Os(2)–Os(3)	2.770 (2)	Os(5)–C(12)	1.89 (3)
Os(2)–Os(6)	2.898 (2)	Os(5)–C(13)	1.86 (3)
Os(4)–Os(5)	2.833 (2)	Os(5)–C(14)	2.04 (3)
Os(4)–Os(6)	2.957 (2)	Os(6)–C(15)	1.91 (4)
Os(5)–Os(6)	2.988 (2)	Os(6)–C(16)	1.95 (2)
Os(1)–S(1)	2.489 (7)	Os(6)–C(17)	1.75 (3)
Os(1)–S(2)	2.475 (8)	C(1)–O(1)	1.12 (3)
Os(2)–S(1)	2.449 (7)	C(2)–O(2)	1.23 (3)
Os(2)–S(2)	2.439 (7)	C(3)–O(3)	1.16 (3)
Os(4)–S(2)	2.420 (7)	C(4)–O(4)	1.22 (4)
Os(5)–S(1)	2.430 (7)	C(5)–O(5)	1.16 (3)
Os(6)–S(1)	2.522 (8)	C(6)–O(6)	1.30 (5)
Os(6)–S(2)	2.496 (7)	C(7)–O(7)	1.15 (3)
S(1)···S(2)	3.335 (12)	C(8)–O(8)	1.19 (4)
Os(1)···Os(6)	3.557 (2)	C(9)–O(9)	1.18 (6)
Os(1)–C(1)	1.90 (3)	C(10)–O(10)	1.16 (3)
Os(1)–C(2)	1.81 (3)	C(11)–O(11)	1.22 (3)
Os(2)–C(3)	1.80 (3)	C(12)–O(12)	1.17 (3)
Os(2)–C(4)	1.83 (3)	C(13)–O(13)	1.15 (3)
Os(2)···C(16)	2.49 (2)	C(14)–O(14)	1.09 (4)
Os(3)–C(5)	1.92 (2)	C(15)–O(15)	1.21 (5)
Os(3)–C(6)	1.80 (3)	C(16)–O(16)	1.21 (3)
Os(3)–C(7)	1.92 (3)	C(17)–O(17)	1.24 (3)

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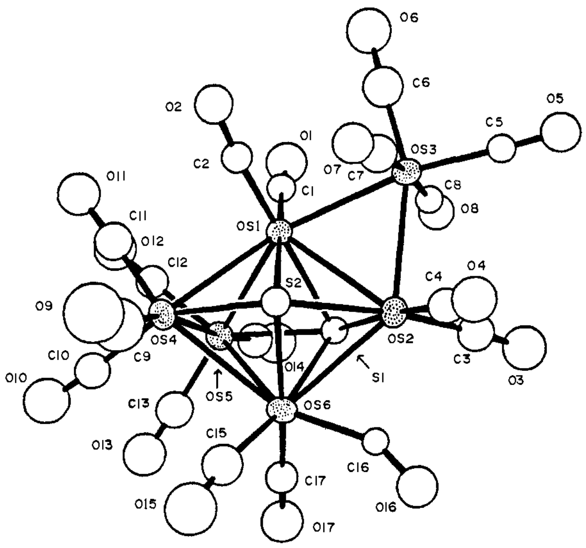
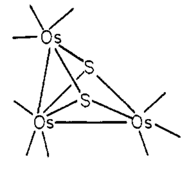
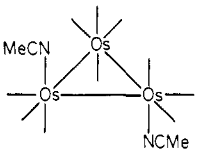


Figure 1. Perspective ORTEP drawing of $Os_6(CO)_{17}(\mu_4\text{-}S)_2$ (III) showing 50% probability thermal motion ellipsoids.

We have now investigated the reaction between the trinuclear clusters $Os_3(CO)_9(\mu_3\text{-}S)_2$ (I)[13-16] and $Os_3(CO)_{10}(NCMe)_2$ (II).[17]



I



II

The products $Os_6(CO)_{17}(\mu_4\text{-}S)_2$ (III) and $Os_6(CO)_{16}(\mu_4\text{-}S)(\mu_3\text{-}S)$ (IV) are formed sequentially, and the importance and role of the sulfido ligands in the condensation of the clusters and rearrangement of the metal–metal bonding are clearly revealed.[18]

Results

When I and II are allowed to react in refluxing hexane for 3 h, one of the major products is $Os_6(CO)_{17}(\mu_4\text{-}S)_2$ (III), which has been characterized by IR and single-crystal X-ray diffraction analysis. An ORTEP diagram of the molecular structure of III is shown in Figure 1. Tables I and II list interatomic distances and angles. Table III lists final fractional atomic coordinates and thermal parameters. The molecule contains a pentagonal-bipyramidal cluster consisting of five osmium atoms and two sulfido ligands. Osmium atoms Os(1) and Os(6) occupy the apical positions while osmium atoms Os(2), Os(4), and Os(5) and the two sulfido ligands define the equatorial plane. None of the equatorial atoms deviate from their least-squares plane by more than 0.023 Å. The Os(1)–Os(2) edge of the cluster is bridged by an $Os(CO)_4$ group. The metal–metal bonding within the cluster is not uniform, since the metal–metal bond distances between the apical and equatorial osmium atoms which range from 2.898 (2)–2.988 (2) Å are significantly longer than the one equatorial–equatorial metal–metal bond, Os(4)–Os(5) at 2.833 (2) Å, and

Table II. Interatomic Angles with Esds for $Os_6(CO)_{17}(\mu_4\text{-}S)_2$ (III)

atoms	angle, deg	atoms	angle, deg
A. Angles within the Cluster			
Os(2)–Os(1)–Os(3)	57.42 (4)	Os(5)–Os(4)–S(2)	95.8 (2)
Os(2)–Os(1)–Os(4)	97.66 (5)	Os(6)–Os(4)–S(2)	54.2 (2)
Os(2)–Os(1)–Os(5)	98.21 (4)	Os(1)–Os(5)–Os(4)	61.45 (4)
Os(2)–Os(1)–S(1)	52.8 (2)	Os(1)–Os(5)–Os(6)	74.03 (4)
Os(2)–Os(1)–S(2)	52.6 (2)	Os(1)–Os(5)–S(1)	54.5 (2)
Os(3)–Os(1)–Os(4)	143.27 (6)	Os(4)–Os(5)–Os(6)	60.98 (4)
Os(3)–Os(1)–Os(5)	143.51 (5)	Os(4)–Os(5)–S(1)	96.1 (2)
Os(3)–Os(1)–S(1)	91.8 (2)	Os(6)–Os(5)–S(1)	54.3 (2)
Os(3)–Os(1)–S(2)	91.9 (2)	Os(2)–Os(6)–Os(4)	98.33 (5)
Os(4)–Os(1)–Os(5)	58.82 (4)	Os(2)–Os(6)–Os(5)	97.70 (5)
Os(4)–Os(1)–S(1)	92.2 (2)	Os(2)–Os(6)–S(1)	53.2 (2)
Os(4)–Os(1)–S(2)	52.2 (2)	Os(2)–Os(6)–S(2)	53.1 (2)
Os(5)–Os(1)–S(1)	52.7 (2)	Os(4)–Os(6)–Os(5)	56.92 (4)
Os(5)–Os(1)–S(2)	92.4 (2)	Os(4)–Os(6)–S(1)	91.1 (2)
S(1)–Os(1)–S(2)	84.4 (2)	Os(4)–Os(6)–S(2)	51.9 (2)
Os(1)–Os(2)–Os(3)	59.00 (4)	Os(5)–Os(6)–S(1)	51.5 (2)
Os(1)–Os(2)–Os(6)	75.01 (4)	Os(5)–Os(6)–S(2)	90.4 (2)
Os(1)–Os(2)–S(1)	54.0 (2)	S(1)–Os(6)–S(2)	83.3 (2)
Os(1)–Os(2)–S(2)	53.8 (2)	Os(1)–S(1)–Os(2)	73.2 (2)
Os(3)–Os(2)–Os(6)	134.01 (5)	Os(1)–S(1)–Os(5)	72.8 (2)
Os(3)–Os(2)–S(1)	93.8 (2)	Os(1)–S(1)–Os(6)	90.5 (2)
Os(3)–Os(2)–S(2)	93.9 (2)	Os(2)–S(1)–Os(5)	130.6 (3)
Os(6)–Os(2)–S(1)	55.5 (2)	Os(2)–S(1)–Os(6)	71.3 (2)
Os(6)–Os(2)–S(2)	55.0 (1)	Os(5)–S(1)–Os(6)	74.2 (2)
S(1)–Os(2)–S(2)	86.1 (2)	Os(1)–S(2)–Os(2)	73.6 (2)
Os(1)–Os(3)–Os(2)	63.59 (4)	Os(1)–S(2)–Os(4)	73.8 (2)
Os(1)–Os(4)–Os(5)	60.73 (4)	Os(1)–S(2)–Os(6)	91.4 (2)
Os(1)–Os(4)–Os(6)	74.21 (4)	Os(2)–S(2)–Os(4)	131.4 (3)
Os(1)–Os(4)–S(2)	54.0 (2)	Os(2)–S(2)–Os(6)	71.9 (2)
Os(5)–Os(4)–Os(6)	62.11 (4)	Os(4)–S(2)–Os(6)	73.9 (2)
B. Angles from the Cluster to the Carbonyl Ligands			
Os(2)–Os(1)–C(1)	126.8 (8)	Os(5)–Os(4)–C(10)	86.5 (10)
Os(3)–Os(1)–C(1)	90.1 (8)	Os(6)–Os(4)–C(10)	100.6 (8)
Os(4)–Os(1)–C(1)	126.2 (8)	S(2)–Os(4)–C(10)	148.0 (10)
Os(5)–Os(1)–C(1)	84.4 (8)	Os(1)–Os(4)–C(11)	85.6 (10)
S(1)–Os(1)–C(1)	92.8 (8)	Os(5)–Os(4)–C(11)	100.8 (11)
S(2)–Os(1)–C(1)	176.6 (8)	Os(6)–Os(4)–C(11)	158.1 (10)
Os(2)–Os(1)–C(2)	126.3 (9)	S(2)–Os(4)–C(11)	119.3 (11)
Os(3)–Os(1)–C(2)	88.4 (8)	Os(1)–Os(5)–C(12)	92.5 (9)
Os(4)–Os(1)–C(2)	86.7 (9)	Os(4)–Os(5)–C(12)	83.1 (9)
Os(5)–Os(1)–C(2)	127.3 (8)	Os(6)–Os(5)–C(12)	143.9 (9)
S(1)–Os(1)–C(2)	178.5 (10)	S(1)–Os(5)–C(12)	140.7 (9)
S(2)–Os(1)–C(2)	94.1 (10)	Os(1)–Os(5)–C(13)	157.9 (11)
Os(1)–Os(2)–C(3)	131.2 (11)	Os(4)–Os(5)–C(13)	98.1 (11)
Os(3)–Os(2)–C(3)	93.8 (10)	Os(6)–Os(5)–C(13)	89.0 (11)
Os(6)–Os(2)–C(3)	118.7 (10)	S(1)–Os(5)–C(13)	125.6 (10)
S(1)–Os(2)–C(3)	93.4 (10)	Os(1)–Os(5)–C(14)	115.1 (9)
S(2)–Os(2)–C(3)	172.3 (10)	Os(4)–Os(5)–C(14)	174.5 (10)
Os(1)–Os(2)–C(4)	130.2 (9)	Os(6)–Os(5)–C(14)	123.0 (9)
Os(3)–Os(2)–C(4)	91.2 (9)	S(1)–Os(5)–C(14)	84.4 (9)
Os(6)–Os(2)–C(4)	121.0 (0)	Os(2)–Os(6)–C(15)	130.2 (9)
S(1)–Os(2)–C(4)	174.9 (9)	Os(4)–Os(6)–C(15)	78.3 (9)
S(2)–Os(2)–C(4)	94.7 (9)	Os(5)–Os(6)–C(15)	119.1 (10)
Os(1)–Os(3)–C(5)	168.6 (8)	S(1)–Os(6)–C(15)	169.1 (10)
Os(2)–Os(3)–C(5)	105.0 (8)	S(2)–Os(6)–C(15)	91.9 (9)
Os(1)–Os(3)–C(6)	96.8 (10)	Os(2)–Os(6)–C(16)	58.0 (7)
Os(2)–Os(3)–C(6)	159.9 (10)	Os(4)–Os(6)–C(16)	148.5 (7)
Os(1)–Os(3)–C(7)	88.9 (8)	Os(5)–Os(6)–C(16)	139.4 (8)
Os(2)–Os(3)–C(7)	86.1 (9)	S(1)–Os(6)–C(16)	89.7 (8)
Os(1)–Os(3)–C(8)	86.4 (7)	S(2)–Os(6)–C(16)	97.0 (7)
Os(2)–Os(3)–C(8)	87.6 (8)	Os(2)–Os(6)–C(17)	128.5 (9)
Os(1)–Os(4)–C(9)	129.5 (12)	Os(4)–Os(6)–C(17)	124.3 (9)
Os(5)–Os(4)–C(9)	165.3 (12)	Os(5)–Os(6)–C(17)	85.3 (10)
Os(6)–Os(4)–C(9)	108.0 (13)	S(1)–Os(6)–C(17)	94.8 (11)
S(2)–Os(4)–C(9)	85.6 (12)	S(2)–Os(6)–C(17)	175.5 (10)
Os(1)–Os(4)–C(10)	145.6 (10)		
C. Angles of the Carbonyl Ligands			
Os(1)–C(1)–O(1)	175 (3)	Os(4)–C(9)–O(9)	163 (3)
Os(1)–C(2)–O(2)	172 (2)	Os(4)–C(10)–O(10)	175 (3)
Os(2)–C(3)–O(3)	175 (3)	Os(4)–C(11)–O(11)	173 (3)
Os(2)–C(4)–O(4)	174 (2)	Os(5)–C(12)–O(12)	173 (3)
Os(3)–C(5)–O(5)	177 (3)	Os(5)–C(13)–O(13)	173 (3)
Os(3)–C(6)–O(6)	169 (3)	Os(5)–C(14)–O(14)	175 (3)
Os(3)–C(7)–O(7)	174 (3)	Os(6)–C(15)–O(15)	171 (2)
Os(3)–C(8)–O(8)	174 (2)	Os(6)–C(16)–O(16)	152 (2)
		Os(6)–C(17)–O(17)	178 (3)

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(18) A preliminary report of the structure of **IV** was published.[14] This report was accidentally placed in the full papers section of the journal.

Table III. Final Fractional Atomic Coordinates and Thermal Parameters[a] with Esds for $Os_6(CO)_{17}(\mu_4\text{-}S)_2$ (III)

atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)
Os(1)	−0.7238 (1)	−0.43136 (8)	−0.19659 (8)	2.20 (5)	2.12 (5)	1.99 (6)	0.01 (5)	0.16 (5)	−0.07 (6)
Os(2)	−0.7456 (1)	−0.59184 (8)	−0.09663 (9)	2.93 (5)	2.28 (5)	2.10 (6)	0.07 (5)	−0.10 (6)	−0.02 (6)
Os(3)	−0.5450 (1)	−0.56512 (9)	−0.18452 (8)	2.17 (5)	2.69 (5)	2.55 (7)	−0.25 (6)	−0.11 (6)	0.37 (6)
Os(4)	−0.8718 (1)	−0.30526 (9)	−0.10763 (9)	2.66 (5)	2.30 (5)	2.52 (7)	0.20 (5)	0.03 (6)	−0.52 (6)
Os(5)	−0.9753 (1)	−0.40443 (9)	−0.22878 (8)	2.48 (5)	2.78 (5)	2.14 (7)	0.28 (6)	−0.31 (6)	−0.02 (6)
Os(6)	−0.9638 (1)	−0.49051 (9)	−0.07518 (8)	2.48 (5)	3.09 (6)	1.98 (6)	0.25 (6)	0.23 (6)	0.09 (6)

atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*	atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*
S(1)	−0.8821 (7)	−0.5499 (5)	−0.1989 (5)	2.5 (2)	O(17)	−1.211 (2)	−0.552 (2)	−0.109 (2)	5.8 (6)
S(2)	−0.7577 (7)	−0.4320 (5)	−0.0578 (5)	2.5 (2)	C(1)	−0.707 (2)	−0.432 (2)	−0.304 (2)	2.8 (7)
O(1)	−0.692 (2)	−0.438 (2)	−0.367 (2)	6.1 (7)	C(2)	−0.609 (2)	−0.345 (2)	−0.192 (2)	2.9 (7)
O(2)	−0.524 (2)	−0.293 (1)	−0.184 (1)	4.3 (5)	C(3)	−0.754 (3)	−0.712 (2)	−0.118 (2)	4.4 (8)
O(3)	−0.768 (2)	−0.789 (2)	−0.133 (2)	6.0 (7)	C(4)	−0.655 (3)	−0.627 (2)	−0.015 (2)	3.4 (8)
O(4)	−0.593 (2)	−0.639 (1)	0.040 (2)	5.2 (6)	C(5)	−0.444 (3)	−0.667 (2)	−0.162 (2)	2.5 (7)
O(5)	−0.382 (2)	−0.729 (1)	−0.152 (1)	4.6 (6)	C(6)	−0.439 (3)	−0.509 (2)	−0.244 (2)	5.0 (9)
O(6)	−0.373 (2)	−0.476 (2)	−0.298 (2)	6.3 (7)	C(7)	−0.482 (3)	−0.500 (2)	−0.099 (2)	4.1 (8)
O(7)	−0.451 (2)	−0.456 (1)	−0.049 (1)	4.4 (6)	C(8)	−0.628 (2)	−0.630 (2)	−0.268 (2)	2.6 (7)
O(8)	−0.678 (2)	−0.661 (1)	−0.321 (1)	4.6 (6)	C(9)	−0.839 (4)	−0.246 (3)	−0.012 (3)	7.7 (13)
O(9)	−0.790 (3)	−0.211 (2)	0.039 (2)	9.0 (9)	C(10)	−1.009 (3)	−0.239 (2)	−0.105 (2)	3.8 (8)
O(10)	−1.092 (2)	−0.192 (2)	−0.108 (2)	6.6 (7)	C(11)	−0.800 (3)	−0.219 (2)	−0.157 (2)	4.3 (9)
O(11)	−0.759 (2)	−0.159 (1)	−0.198 (2)	5.6 (6)	C(12)	−0.946 (3)	−0.296 (2)	−0.283 (2)	3.8 (8)
O(12)	−0.931 (2)	−0.234 (2)	−0.324 (2)	6.5 (7)	C(13)	−1.133 (3)	−0.374 (2)	−0.210 (2)	4.9 (9)
O(13)	−1.226 (2)	−0.351 (2)	−0.192 (2)	6.3 (7)	C(14)	−1.037 (3)	−0.472 (2)	−0.323 (2)	4.6 (9)
O(14)	−1.067 (2)	−0.512 (2)	−0.371 (2)	6.6 (7)	C(15)	−1.020 (3)	−0.423 (2)	0.011 (2)	4.7 (9)
O(15)	−1.058 (2)	−0.393 (2)	0.069 (2)	7.2 (8)	C(16)	−0.939 (2)	−0.610 (2)	−0.030 (2)	2.1 (7)
O(16)	−0.961 (2)	−0.669 (1)	0.017 (1)	4.7 (6)	C(17)	−1.110 (2)	−0.526 (2)	−0.093 (2)	3.3 (8)

[a] The form of the anisotropic thermal parameter is $B = \exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + B_{12}hka^*b^* + B_{13}hla^*c^* + B_{23}klb^*c^*)]$.

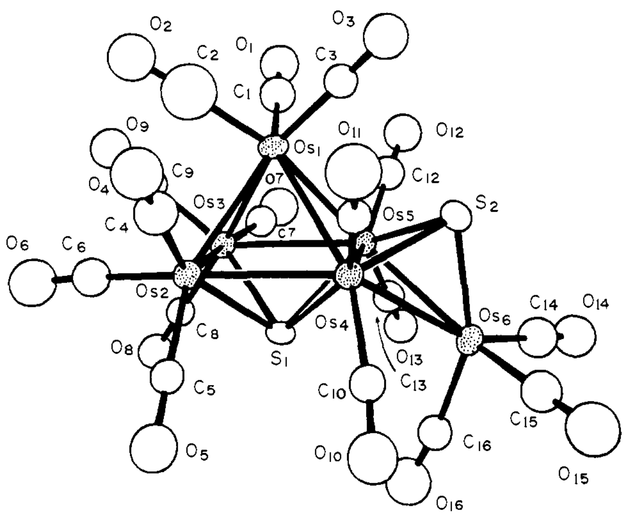

Figure 2. Perspective ORTEP drawing of $Os_6(CO)_{16}(\mu_4\text{-}S)(\mu_3\text{-}S)$ (IV) showing 50% probability thermal motion ellipsoids.

the metal–metal bonds to the bridging $Os(CO)_4$ group, Os(1)–Os(3) = 2.818 (2) and Os(2)–Os(3) = 2.770 (2) Å. The Os–Os bond distance in $Os_3(CO)_{12}$ is 2.877 (3) Å.[19] Each sulfido ligand is bonded to four metal atoms. The Os–S bonds to the apical metal atoms, 2.475(8)–2.522 (8) Å, are slightly longer than those to the equatorial metal atoms, 2.420 (7)–2.449 (7) Å. Os–S distances observed previously for triply bridging "capping" sulfido ligands lie generally in the range 2.35–2.45 Å.[20]

Assuming the sulfido ligands serve as four electron donors, this cluster is electron precise according to the 2c–2e bond theory and each metal atom achieves an 18-electron configuration. However, the Os(6)–Os(2) bond would have to be viewed as a heteropolar, donor bond from Os(6) to Os(2).

Table IV. Interatomic Distances with Esds for $Os_6(CO)_{16}(\mu_4\text{-}S)(\mu_3\text{-}S)$ (IV)

atoms	distance, Å	atoms	distance, Å
Os(1)–Os(2)	2.849 (1)	Os(3)–C(8)	1.90 (2)
Os(1)–Os(3)	2.833 (1)	Os(3)–C(9)	1.95 (2)
Os(1)–Os(4)	2.888 (1)	Os(4)–C(10)	1.91 (2)
Os(1)–Os(5)	2.843 (1)	Os(4)–C(11)	1.86 (2)
Os(2)–Os(3)	2.884 (1)	Os(5)–C(12)	1.86 (2)
Os(2)–Os(4)	2.781 (1)	Os(5)–C(13)	1.87 (2)
Os(3)–Os(5)	2.863 (1)	Os(6)–C(14)	1.88 (2)
Os(4)–Os(5)	2.686 (1)	Os(6)–C(15)	1.86 (2)
Os(4)–Os(6)	2.844 (1)	Os(6)–C(16)	1.87 (2)
Os(5)–Os(6)	2.828 (1)	C(1)–O(1)	1.23 (2)
Os(1)···S(1)	3.472 (4)	C(2)–O(2)	1.17 (3)
Os(2)–S(1)	2.432 (4)	C(3)–O(3)	1.18 (2)
Os(3)–S(1)	2.414 (4)	C(4)–O(4)	1.15 (2)
Os(4)–S(1)	2.440 (4)	C(5)–O(5)	1.16 (2)
Os(5)–S(1)	2.476 (4)	C(6)–O(6)	1.16 (2)
Os(4)–S(2)	2.352 (4)	C(7)–O(7)	1.20 (2)
Os(5)–S(2)	2.372 (4)	C(8)–O(8)	1.16 (2)
Os(6)–S(2)	2.285 (4)	C(9)–O(9)	1.15 (2)
Os(1)–C(1)	1.82 (2)	C(10)–O(10)	1.16 (2)
Os(1)–C(2)	1.87 (3)	C(11)–O(11)	1.20 (2)
Os(1)–C(3)	1.89 (2)	C(12)–O(12)	1.17 (2)
Os(2)–C(4)	1.87 (2)	C(13)–O(13)	1.19 (2)
Os(2)–C(5)	1.86 (2)	C(14)–O(14)	1.11 (2)
Os(2)–C(6)	1.87 (2)	C(15)–O(15)	1.16 (2)
Os(3)–C(7)	1.77 (2)	C(16)–O(16)	1.15 (2)

According to the skeletal electron pair theory, a pentagonal-bipyramidal cluster would be stable in the presence of eight skeletal electron pairs.[21] According to this theory $Os(CO)_3$ groups contribute two electrons to cluster bonding; thus, the three $Os(CO)_3$ groups will provide a total of six electrons. The two sulfido ligands provide an additional eight, while metal atoms Os(1) and Os(2) provide only one each since one of the two electrons normally used for cluster bonding from an $Os(CO)_3$ group is instead used to form a bond to the bridging $Os(CO)_4$ group. The total number of skeletal electrons is thus 16, or 8 pairs, as predicted.

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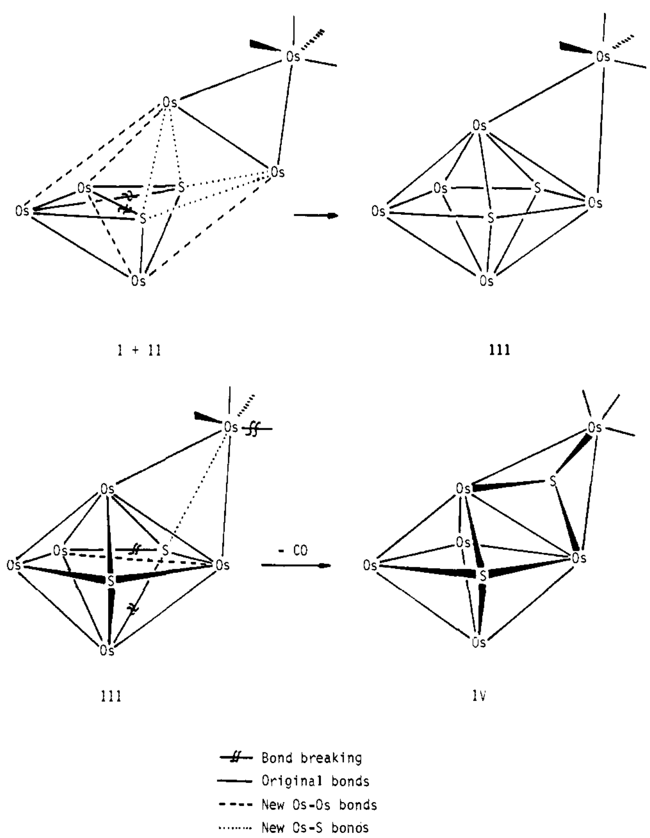
Table V. Interatomic Angles with Esds for $Os_6(CO)_{16}(\mu_4\text{-}S)(\mu_3\text{-}S)$ (IV)

atoms	angles, deg	atoms	angle, deg
Os(2)–Os(1)–Os(5)	87.42 (3)	Os(1)–Os(3)–C(7)	105.6 (6)
Os(3)–Os(1)–Os(4)	87.47 (3)	Os(1)–Os(3)–C(8)	163.1 (5)
Os(1)–Os(4)–Os(6)	120.49 (3)	Os(1)–Os(3)–C(9)	86.3 (5)
Os(1)–Os(5)–Os(6)	122.68 (3)	Os(2)–Os(3)–C(7)	162.8 (6)
Os(3)–Os(2)–Os(4)	88.54 (3)	Os(2)–Os(3)–C(8)	103.6 (5)
Os(2)–Os(3)–Os(5)	87.42 (3)	Os(2)–Os(3)–C(9)	94.1 (5)
Os(2)–Os(4)–Os(5)	93.15 (3)	Os(5)–Os(3)–C(7)	76.7 (6)
Os(3)–Os(5)–Os(4)	90.86 (3)	Os(5)–Os(3)–C(8)	126.4 (5)
Os(2)–Os(4)–Os(6)	136.75 (3)	Os(5)–Os(3)–C(9)	139.6 (5)
Os(3)–Os(5)–Os(6)	134.55 (3)	Os(1)–Os(4)–C(10)	159.3 (5)
Os(1)–Os(2)–Os(3)	59.22 (2)	Os(1)–Os(4)–C(11)	87.8 (5)
Os(1)–Os(3)–Os(2)	59.77 (2)	Os(2)–Os(4)–C(10)	99.7 (5)
Os(1)–Os(3)–Os(5)	59.89 (2)	Os(2)–Os(4)–C(11)	95.4 (5)
Os(1)–Os(5)–Os(3)	59.53 (2)	Os(5)–Os(4)–C(10)	129.9 (5)
Os(1)–Os(4)–Os(5)	61.21 (2)	Os(5)–Os(4)–C(11)	137.6 (5)
Os(1)–Os(5)–Os(4)	62.89 (2)	Os(6)–Os(4)–C(10)	77.0 (5)
Os(2)–Os(1)–Os(3)	61.01 (2)	Os(6)–Os(4)–C(11)	127.3 (5)
Os(2)–Os(1)–Os(4)	57.98 (2)	Os(1)–Os(5)–C(12)	89.1 (6)
Os(3)–Os(1)–Os(5)	60.58 (2)	Os(1)–Os(5)–C(13)	157.6 (5)
Os(4)–Os(1)–Os(5)	55.89 (2)	Os(3)–Os(5)–C(12)	102.2 (6)
Os(5)–Os(4)–Os(6)	61.43 (2)	Os(3)–Os(5)–C(13)	99.5 (5)
Os(4)–Os(5)–Os(6)	62.04 (3)	Os(4)–Os(5)–C(12)	137.3 (6)
Os(4)–Os(6)–Os(5)	56.53 (2)	Os(4)–Os(5)–C(13)	130.3 (5)
Os(2)–S(1)–Os(3)	73.05 (12)	Os(6)–Os(5)–C(12)	122.7 (6)
Os(2)–S(1)–Os(4)	69.62 (12)	Os(6)–Os(5)–C(13)	77.1 (5)
Os(2)–S(1)–Os(5)	108.03 (15)	Os(4)–Os(6)–C(14)	155.9 (3)
Os(3)–S(1)–Os(4)	109.14 (16)	Os(4)–Os(6)–C(15)	99.5 (6)
Os(3)–S(1)–Os(5)	71.65 (11)	Os(4)–Os(6)–C(16)	107.0 (5)
Os(4)–S(1)–Os(5)	66.24 (11)	Os(5)–Os(6)–C(14)	104.8 (6)
Os(4)–S(2)–Os(5)	69.32 (12)	Os(5)–Os(6)–C(15)	153.7 (6)
Os(4)–S(2)–Os(6)	75.67 (13)	Os(5)–Os(6)–C(16)	102.8 (5)
Os(5)–S(2)–Os(6)	74.76 (13)	S(1)–Os(2)–C(4)	149.9 (6)
Os(1)–Os(2)–S(1)	81.80 (10)	S(1)–Os(2)–C(5)	90.0 (5)
Os(1)–Os(3)–S(1)	82.43 (10)	S(1)–Os(2)–C(6)	114.8 (6)
Os(1)–Os(4)–S(1)	80.86 (10)	S(1)–Os(2)–C(7)	118.8 (6)
Os(1)–Os(5)–S(1)	81.16 (10)	S(1)–Os(3)–C(8)	89.7 (5)
Os(1)–Os(4)–S(2)	83.78 (11)	S(1)–Os(3)–C(9)	147.2 (5)
Os(1)–Os(5)–S(2)	84.42 (11)	S(1)–Os(4)–C(10)	91.7 (5)
S(1)–Os(4)–S(2)	110.43 (15)	S(1)–Os(4)–C(11)	150.2 (5)
S(1)–Os(5)–S(2)	108.51 (15)	S(1)–Os(5)–C(12)	155.1 (6)
Os(4)–Os(5)–S(2)	54.98 (11)	S(1)–Os(5)–C(13)	92.6 (6)
Os(5)–Os(4)–S(2)	55.70 (11)	S(2)–Os(4)–C(10)	116.9 (5)
Os(4)–Os(6)–S(2)	52.23 (11)	S(2)–Os(4)–C(11)	95.5 (5)
Os(5)–Os(6)–S(2)	54.02 (11)	S(2)–Os(5)–C(12)	93.2 (6)
Os(2)–Os(1)–C(1)	140.7 (6)	S(2)–Os(5)–C(13)	117.9 (6)
Os(2)–Os(1)–C(2)	83.4 (8)	S(2)–Os(5)–C(14)	104.4 (6)
Os(2)–Os(1)–C(3)	127.3 (5)	S(2)–Os(6)–C(15)	104.4 (6)
Os(3)–Os(1)–C(1)	84.8 (6)	S(2)–Os(6)–C(16)	154.5 (5)
Os(3)–Os(1)–C(2)	104.8 (8)	Os(1)–C(1)–O(1)	179 (1)
Os(3)–Os(1)–C(3)	162.1 (5)	Os(1)–C(2)–O(2)	177 (2)
Os(4)–Os(1)–C(1)	144.9 (6)	Os(1)–C(3)–O(3)	177 (1)
Os(4)–Os(1)–C(2)	127.3 (8)	Os(2)–C(4)–O(4)	174 (2)
Os(4)–Os(1)–C(3)	85.9 (5)	Os(2)–C(5)–O(5)	179 (2)
Os(5)–Os(1)–C(1)	90.9 (6)	Os(2)–C(6)–O(6)	175 (2)
Os(5)–Os(1)–C(2)	165.4 (8)	Os(3)–C(7)–O(7)	175 (2)
Os(5)–Os(1)–C(3)	102.2 (5)	Os(3)–C(8)–O(8)	178 (1)
Os(1)–Os(2)–C(4)	84.7 (6)	Os(3)–C(9)–O(9)	178 (2)
Os(1)–Os(2)–C(5)	153.0 (5)	Os(4)–C(10)–O(10)	174 (1)
Os(1)–Os(2)–C(6)	114.9 (6)	Os(4)–C(11)–O(11)	177 (1)
Os(3)–Os(2)–C(4)	136.8 (6)	Os(5)–C(12)–O(12)	177 (1)
Os(3)–Os(2)–C(5)	133.0 (5)	Os(5)–C(13)–O(13)	178 (2)
Os(3)–Os(2)–C(6)	81.2 (6)	Os(6)–C(14)–O(14)	180 (2)
Os(4)–Os(2)–C(4)	94.6 (6)	Os(6)–C(15)–O(15)	179 (2)
Os(4)–Os(2)–C(5)	92.5 (5)	Os(6)–C(16)–O(16)	173 (2)
Os(4)–Os(2)–C(6)	169.1 (6)		

The molecule contains 17 carbonyl ligands. All are of the linear terminal type except C(16)–O(16).[22] C(16)–O(16) is significantly bent, Os(6)–C(16)–O(16) = 152 (2)°, and carbon C(16) makes a close approach the neighboring metal atom Os(2), Os(2)–C(16) = 2.49 (2) Å. C(16)–O(16) is best described as a semibridge and may have formed as a result of the heteropolar character of the Os(6)–Os(2) bond.[23]

Scheme I



When heated to reflux in octane solvent for 5 h, III loses 1 mol of CO and is converted into $Os_6(CO)_{16}(\mu_4\text{-}S)(\mu_3\text{-}S)$ (IV). This compound is also a principal product of the pyrolysis of $HOs_3(CO)_{10}(\mu\text{-}SPh)$.[14] IV has been characterized by IR and single-crystal X-ray diffraction analysis, and its molecular structure is shown in Figure 2.[18] Tables IV and V list interatomic distances and angles. Table VI lists final fractional atomic coordinates and thermal parameters. IV is a hexanuclear cluster which consists of a square-pyramidal group of five metal atoms with a quadruply bridging sulfido ligand, S(1), spanning the square base. The sixth metal atom bridges an edge of the square base and that group of three is bridged by the second sulfido ligand. Except for the Os(4)–Os(5) bond distance, all the metal–metal bond distances are within 0.1 Å of the 2.877 (3) Å found in $Os_3(CO)_{12}$.[19] The Os(4)–Os(5) bond is considerably shorter at 2.686 (1) Å. The reason for this is not clear, but it should be pointed out that this bond contains four single-atom bridges. A similar shortening was observed in the structurally related molecule $Os_6(CO)_{16}(\mu_4\text{-}CMe)(\mu_3\text{-}CMe)$.[24] Quadruply bridging sulfido ligands have been observed previously.[25] The Os–S distances to the quadruply bridging sulfido ligand, $Os\text{–}\mu_4\text{-}S_{av}$ = 2.44 (1) Å, are significantly longer than those to the triply bridging ligand, $Os\text{–}\mu_3\text{-}S_{av}$ = 2.34 (2) Å. The Os(1)···S(1) distance at 3.472 (4) Å is probably completely nonbonding. There are sixteen linear, terminal carbonyl ligands. Overall the molecule has no symmetry, mirror symmetry being destroyed by the arrangement of the CO ligands on metal atoms Os(1), Os(2), and Os(3).

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[22] Although not as much as C(16)–O(16), C(9)–O(9) also deviates from linearity, Os(4)–C(9)–O(9) = 163 (3)°, much more than the others. We do not wish to describe C(9)–O(9) as a semibridge because it does not make a close approach to any of the other metal atoms. The observed deviation from linearity may reflect some weakness in the structure determination (i.e., adsorption effects on the data, or poor refinement).

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Table VI. Final Fractional Atomic Coordinates and Thermal Parameters with Esds for $Os_6(CO)_{16}(\mu_4\text{-}S)(\mu_3\text{-}S)$ (IV)

atoms	*x*/*a*	*y*/*b*	*z*/*c*	*B*	atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*
Os(1)	0.81175 (10)	0.21724 (8)	0.30992 (4)	[a]	O(13)	0.351 (2)	0.392 (1)	0.4278 (8)	4.3 (4)
Os(2)	0.96642 (9)	0.34763 (8)	0.39277 (4)	[a]	O(14)	0.269 (2)	0.147 (2)	0.5172 (9)	5.3 (5)
Os(3)	0.73485 (10)	0.43069 (8)	0.32723 (4)	[a]	O(15)	0.642 (2)	0.053 (2)	0.6165 (8)	5.2 (5)
Os(4)	0.80589 (10)	0.19332 (8)	0.44413 (4)	[a]	O(16)	0.549 (2)	0.395 (2)	0.5771 (9)	5.9 (5)
Os(5)	0.58701 (9)	0.26317 (8)	0.38239 (4)	[a]	C(1)	0.711 (3)	0.225 (2)	0.238 (1)	4.1 (6)
Os(6)	0.55991 (10)	0.18709 (8)	0.50573 (5)	[a]	C(2)	0.962 (4)	0.225 (3)	0.261 (2)	8.2 (10)
S(1)	0.7503 (6)	0.3809 (5)	0.4362 (3)	[a]	C(3)	0.809 (2)	0.068 (2)	0.307 (1)	2.8 (5)
S(2)	0.6178 (6)	0.0887 (5)	0.4211 (3)	[a]	C(4)	1.104 (3)	0.254 (2)	0.375 (1)	3.9 (6)
O(1)	0.643 (2)	0.232 (2)	0.1899 (9)	5.3 (5)	C(5)	1.048 (2)	0.379 (2)	0.470 (1)	2.4 (5)
O(2)	1.055 (2)	0.234 (2)	0.2296 (9)	5.6 (5)	C(6)	1.044 (3)	0.465 (2)	0.355 (1)	3.8 (6)
O(3)	0.812 (2)	−0.025 (1)	0.3068 (8)	4.7 (4)	C(7)	0.576 (3)	0.442 (2)	0.290 (1)	3.7 (6)
O(4)	1.188 (2)	0.194 (1)	0.3704 (8)	4.8 (4)	C(8)	0.733 (2)	0.575 (2)	0.351 (1)	2.8 (5)
O(5)	1.097 (2)	0.396 (1)	0.5183 (8)	4.1 (4)	C(9)	0.829 (2)	0.461 (2)	0.251 (1)	3.5 (6)
O(6)	1.099 (2)	0.539 (2)	0.3360 (9)	5.9 (5)	C(10)	0.858 (2)	0.208 (2)	0.530 (1)	2.6 (5)
O(7)	0.472 (2)	0.457 (2)	0.2625 (9)	6.4 (5)	C(11)	0.928 (2)	0.084 (2)	0.437 (1)	2.3 (5)
O(8)	0.734 (2)	0.663 (1)	0.3666 (8)	4.1 (4)	C(12)	0.478 (3)	0.219 (2)	0.316 (1)	4.0 (6)
O(9)	0.885 (2)	0.475 (2)	0.2059 (9)	5.5 (5)	C(13)	0.443 (3)	0.341 (2)	0.411 (1)	3.4 (6)
O(10)	0.899 (2)	0.221 (1)	0.5810 (8)	4.5 (4)	C(14)	0.378 (3)	0.162 (2)	0.513 (1)	4.6 (7)
O(11)	1.010 (2)	0.017 (2)	0.4310 (9)	5.2 (5)	C(15)	0.609 (3)	0.104 (2)	0.574 (1)	3.6 (6)
O(12)	0.409 (2)	0.187 (2)	0.2750 (9)	5.4 (5)	C(16)	0.548 (2)	0.314 (2)	0.553 (1)	3.1 (5)

General Temperature Factor Expressions[b]

name	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)
Os(1)	2.37 (4)	2.62 (4)	1.76 (4)	0.02 (4)	0.09 (3)	−0.49 (4)
Os(2)	1.81 (4)	2.56 (4)	1.94 (4)	−0.19 (4)	0.05 (3)	−0.08 (4)
Os(3)	2.13 (4)	2.40 (4)	1.93 (4)	0.00 (4)	0.10 (3)	0.32 (4)
Os(4)	2.31 (4)	1.97 (4)	1.89 (4)	−0.07 (4)	0.02 (3)	0.13 (4)
Os(5)	1.79 (4)	2.28 (4)	2.04 (4)	−0.21 (4)	0.09 (3)	−0.03 (4)
Os(6)	2.98 (5)	2.53 (4)	2.30 (4)	−0.53 (4)	0.66 (4)	−0.10 (4)
S(1)	2.5 (3)	2.5 (3)	1.8 (2)	−0.3 (2)	−0.2 (2)	−0.5 (2)
S(2)	3.2 (3)	2.3 (3)	2.8 (3)	−0.5 (3)	0.1 (3)	−0.3 (3)

[a] See under appropriate columns in General Temperature Factor Expressions section of this table. [b] The form of the anisotropic thermal parameter is $B = \exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + B_{12}hka^*b^* + B_{13}hla^*c^* + B_{23}klb^*c^*)]$.

Assuming the sulfido ligands serve as 4-electron donors, each metal atom can achieve an 18-electron configuration and the cluster is thus electron precise. The bonding can also be rationalized within the framework of the skeletal electron pair theory as was done for the isoelectronic and structurally related molecule $Os_6(CO)_{16}(\mu_5\text{-}C)(\mu_3\text{-}MeC_2Me)$.[24]

Discussion

The formation of III is most reasonably explained by the combination of one trinuclear cluster of I and one of II and is accompanied by the loss of 2 mol of CO. Most likely, the labile nitrile ligands in II are dislodged[26] and replaced by donor bonds from the lone pairs of electrons on the sulfur atoms in I. The triangular group Os(1)–Os(2)–Os(3) is probably derived from II while the remaining group Os(4)–Os(5)–Os(6)–S(1)–S(2) is probably derived from I. Scheme I shows the relationship between the trinuclear cluster groups in III and the locations where bonds are formed and cleaved in the course of their condensation. Clearly, unobserved intermediates must have been transversed as the 2 mol of CO were evolved, but the nature of these species cannot be accurately speculated upon at this time.

The conversion of III into IV involves the loss of 1 mol of CO and is mechanistically more obvious. CO loss in III probably occurs at the edge-bridging osmium atom Os(3) (Figure 1). The $Os(CO)_3$ group then folds toward one of the sulfur atoms and forms a coordinate bond to the lone pair residing on it (Scheme I). Cleavage of two metal–sulfur bonds then yields the triosmium group with the triply bridging sulfido ligand (Figure 2). The formation of the square pyramid is accomplished by the formation of one metal–metal bond (e.g., Os(5)–Os(2), Figure 1). The remaining sulfido ligand becomes the quadruple bridge on the base of the pyramid. It is somewhat surprising but IV will not add 1 mol of CO to reform III, even under a CO pressure of 165 atm at 210 °C.

Clearly, the sulfur atoms have played a key role in the initial linking of the clusters I and II and later in reorganization of the cluster framework of III to form IV. The ability of the sulfur atom to do this undoubtedly derives from its ability to interconvert between different multicoordinate bridging modes and also to serve as a variable multielectron donor. The ultimate value of heteroatoms in cluster synthesis has yet to be realized, but its scope may rival and bear analogy to the known ability of metal atoms to restructure the bonding of ligands via the so-called template reactions.[27]

Experimental Section

Although the products are air stable, all reactions were performed under a prepurified nitrogen atmosphere. The products were isolated by TLC on silica gel by using a methylene chloride/hexane 1/9 solvent mixture. $Os_3(CO)_{10}(NCMe)_2$[17] and $Os_3(CO)_9(\mu_3\text{-}S)_2$[14] were prepared by reported procedures. Melting points were obtained on a Thomas-Hoover apparatus and are uncorrected. Infrared spectra were recorded on a Nicolet 7199 FT-IR.

Preparation of $Os_6(CO)_{17}(\mu_4\text{-}S)_2$ (III). In a typical preparation a solution of 0.05 g of $Os_3(CO)_{10}(NCMe)_2$ and 0.022 g of $Os_3(CO)_9(\mu_3\text{-}S)_2$ in 40 mL of hexane solvent was refluxed 3 h. The solution turned brownish-green and the solvent was removed in vacuo. The major green fraction (TLC) was crystallized from hexane to give $Os_6(CO)_{17}(\mu_4\text{-}S)_2$: Yield 0.013 g, 29%; mp 186–188 °C IR (ν_{CO} in hexane); 2119 w, 2089 m, 2069 vs, 2062 s, 2044 m, 2036 vs, 2016 s, 2004 m, 1986 w, 1948 w cm^{-1}.

Preparation of $Os_6(CO)_{16}(\mu_4\text{-}S)(\mu_3\text{-}S)$ (IV). III (0.014 g) was refluxed in 10 mL of octane solvent for 5 h. The brown product IV was isolated by TLC: yield 100%; mp 172 °C dec; IR (ν_{CO} in hexane) 2079 vs, 2065 sh, 2059 s, 2044 s, 2030 s, 2018 m.

Attempted Carbonylation of IV. IV (0.02 g) was dissolved in 80 mL of octane, placed in a high-pressure apparatus (Autoclave Engineers Model APB-300 Magnedrive), and treated with CO at 165 atm/210 °C

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Table VII. Crystallographic Data for X-ray Diffraction Studies

	A. Crystal Structure Data	
formula	$Os_6S_2O_{17}C_{17}$	$Os_6S_2O_{16}C_{16}$
temp, ±3 °C	24	27
space group	$P2_12_12_1$, no. 19	$P2_1/c$, no. 14
a, Å	11.280 (5)	10.083 (4)
b, Å	14.622 (8)	12.633 (4)
c, Å	17.626 (5)	21.383 (4)
α, deg	90.0	90.0
β, deg	90.0	91.73 (2)
γ, deg	90.0	90.0
V, Å^3	2907 (4)	2722 (3)
M_r	1681.5	1653.5
Z	4	4
ρ_{calcd} g/cm	3.84	4.03
	B. Measurement of Intensity Data	
radiatn	Mo K$\bar{\alpha}$ (0.710 73 Å)	Mo K$\bar{\alpha}$ (0.710 73 Å)
monochromator	graphite	graphite
detector aperture, mm		
horizontal (A + B tan θ) A	3.0	3.0
B	1.0	1.0
vertical	4.0	4.0
crystal faces	001, $00\bar{1}$, $\bar{1}\bar{1}0$ 110, $1\bar{2}0$, $\bar{1}20$	$0\bar{1}\bar{2}$, 012, $0\bar{1}2$ $01\bar{2}$, $\bar{1}\bar{1}1$, 111
crystal size, mm	0.05 × 0.126 × 0.208	0.12 × 0.14 × 0.20
crystal orientatn direction; deg from θ axis	normal to $\bar{1}10$; 12.2	a^*; 8.5
max 2θ, deg	48	48
scan type	moving crystal–stationary counter	
ω scan width, A + 0.347 tan θ	0.95	0.85
background	1/4 additional scan at each end of scan	
ω scan rate (variable),		
max, deg min^{-1}	10.0	10.0
min, deg min^{-1}	1.5	1.25
no. of reflctns measd	2571	4971
data used ($F^2 \geqslant 2.0\sigma(F)^2$)	1726	2629
	C. Treatment of Data	
absorptn corrctn coeff, cm^{-1}	279.9	298.8
grid	14 × 16 × 4	14 × 8 × 8
transmissn coeff,		
max	0.26	0.10
min	0.04	0.04
P factor	0.01	0.005
final residuals, R_1	0.037	0.038
R_2	0.030	0.039
esd of unit weight	1.49	2.14
largest shift/error value of final cycle	0.16	0.01
largest peaks in final diff Fourier, e/Å^3	0.90	1.07

for 2 days. After this treatment the only compound found in the apparatus was IV.

Crystallographic Analyses. Crystals III suitable for diffraction measurements were obtained by cooling hexanes solutions to −20 °C. Crystals of IV were obtained as described previously.[14] The 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 K$\bar{\alpha}$ radiation. Unit cells were determined and refined from 25 randomly selected reflections obtained by using the CAD-4 automatic search, center, index and least-squares routines.

The space groups for both III and IV were uniquely identified by the unit cell shapes and systematic absences in the data. 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 done for both structures. Neutral atom scattering factors were calculated by the standard procedures.[28a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[28b] Full-matrix least-squares refinements minimized the function $\sum_{hkl} w(||F_{obsd}| - |F_{calcd}||)^2$, where $w = 1/(\sigma(F)^2)$, $\sigma(F) = \sigma(F^2_{obsd})/2F_{obsd}$, and $\sigma(F^2_{obsd}) = [\sigma(I_{raw})^2 + (PF^2_{obsd})^2]^{1/2}/Lp$.

The structure of III was solved by a combination of direct methods and difference Fourier techniques. The six metal atoms were located in an electron density map based on the phasing (MULTAN) of 171 reflections ($E \geq 1.75$). Only the osmium and sulfur atoms were refined anisotropically. The enantiomorph corresponding to positive fractional coordinates was selected originally, and with this model the values of residuals R_1 and R_2 upon convergence of the refinement were 0.042 and 0.037, respectively. At this point the other enantiomorph was tested by transforming all atomic coordinates to their negative values and refining again. With this enantiomorph refinement produced the residuals R_1 = 0.037 and R_2 = 0.030 upon convergence. This is a significant improvement and the latter enantiomorph was deemed to be correct. The values of the fractional coordinates listed in Table III correspond to those of the latter enantiomorph.[29] Tables I and II list interatomic distances and angles with errors obtained from the inverse matrix obtained on the final cycle of refinement.

The structure of IV was also solved by a combination of direct methods and difference Fourier techniques. The six metal atoms were located in an electron density map based on the phasing (MULTAN) of 167 reflections ($E \geq 2.00$). Only the osmium and sulfur atoms were refined anisotropically. Tables IV and V list interatomic distances and angles for IV. Final fractional atomic coordinates and thermal parameters for IV are listed in Table VI. Tables of structure factor amplitudes are available.[29]

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Supplementary Material Available: Tables of structure factor amplitudes for both structures (20 pages). Ordering information is given on any current masthead page.

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(28) "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.

(29) See supplementary material.