Table II. Positional Parameters with Esd's for $\mathrm{Os_4(CO)_{12}(NHMe_2)(\mu_3\text{-}S)}$ (**3**)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Os(1)	0.91771 (6)	0.32088 (2)	0.35289 (4)	O(12)	0.794 (1)	0.5390 (5)	0.1680 (9)
Os(2)	0.68330 (6)	0.28182 (2)	0.44840 (4)	N	0.737 (1)	0.3942 (5)	0.0500 (9)
Os(3)	0.68332 (6)	0.38843 (2)	0.37774 (4)	C(1)	0.971 (2)	0.2489 (6)	0.361 (1)
Os(4)	0.90045 (6)	0.42542 (2)	0.24259 (4)	C(2)	1.078 (2)	0.3324 (6)	0.519 (1)
S	0.6331 (4)	0.3132 (1)	0.2297 (3)	C(3)	1.050 (2)	0.3282 (6)	0.249 (1)
O(1)	1.008 (1)	0.2037 (5)	0.3607 (10)	C(4)	0.789 (2)	0.2909 (6)	0.629 (1)
O(2)	1.169 (1)	0.3402 (5)	0.6230 (8)	C(5)	0.711 (2)	0.2088 (6)	0.441 (1)
O(3)	1.145 (1)	0.3227 (5)	0.1952 (9)	C(6)	0.487 (2)	0.2697 (6)	0.471 (1)
O(4)	0.852 (1)	0.3007 (5)	0.7383 (9)	C(7)	0.793 (2)	0.4186 (6)	0.543 (1)
O(5)	0.730 (1)	0.1619 (5)	0.4429 (9)	C(8)	0.595 (2)	0.4528 (6)	0.294 (1)
O(6)	0.364 (1)	0.2605 (5)	0.4887 (9)	C(9)	0.496 (2)	0.3821 (6)	0.423 (1)
O(7)	0.860 (1)	0.4353 (5)	0.6465 (9)	C(10)	1.035 (1)	0.4444 (6)	0.410 (1)
O(8)	0.472 (1)	0.5076 (5)	0.7428 (9)	C(11)	1.066 (2)	0.4360 (7)	0.173 (1)
O(9)	0.380 (1)	0.3845 (6)	0.4529 (10)	C(12)	0.830 (2)	0.4951 (6)	0.195 (1)
O(10)	1.127 (1)	0.4575 (4)	0.5114 (8)	C(13)	0.579 (2)	0.4211 (7)	−0.005 (1)
O(11)	1.179 (1)	0.4434 (5)	0.1405 (10)	C(14)	0.814 (2)	0.3924 (8)	−0.054 (1)

Table III. Interatomic Distances (Å) with Esd's for $\mathrm{Os_4(CO)_{12}(NHMe_2)(\mu_3\text{-}S)}$ (**3**)

Os(1)–Os(2)	2.770 (1)	Os(4)–C(11)	1.867 (13)
Os(1)–Os(3)	2.750 (1)	Os(4)–C(12)	1.875 (13)
Os(1)–Os(4)	2.870 (1)	Os(4)–N	2.238 (9)
Os(2)–Os(3)	2.789 (1)	Os(4)⋯C(3)	2.767 (13)
Os(3)–Os(4)	2.911 (1)	C(1)–O(1)	1.184 (16)
Os(1)–S	2.418 (3)	C(2)–O(2)	1.156 (12)
Os(2)–S	2.386 (2)	C(3)–O(3)	1.165 (13)
Os(3)–S	2.422 (3)	C(4)–O(4)	1.149 (12)
Os(1)–C(1)	1.865 (14)	C(5)–O(5)	1.192 (15)
Os(1)–C(2)	1.900 (11)	C(6)–O(6)	1.178 (13)
Os(1)–C(3)	1.877 (11)	C(7)–O(7)	1.159 (13)
Os(2)–C(4)	1.876 (10)	C(8)–O(8)	1.158 (13)
Os(2)–C(5)	1.858 (13)	C(9)–O(9)	1.165 (14)
Os(2)–C(6)	1.847 (12)	C(10)–O(10)	1.168 (12)
Os(3)–C(7)	1.879 (12)	C(11)–O(11)	1.169 (14)
Os(3)–C(8)	1.890 (13)	C(12)–O(12)	1.157 (15)
Os(3)–C(9)	1.875 (12)	N–C(13)	1.479 (15)
Os(4)–C(10)	1.865 (11)	N–C(14)	1.490 (16)

Table IV. Selected Interatomic Angles (deg) with Esd's for $\mathrm{Os_4(CO)_{12}(NHMe_2)(\mu_3\text{-}S)}$ (**3**)

Os(2)–Os(1)–Os(3)	60.69 (2)	Os(2)–S–Os(3)	70.91 (7)
Os(2)–Os(1)–Os(4)	122.41 (2)	Os(1)–Os(4)–N	89.60 (26)
Os(1)–Os(2)–Os(3)	59.30 (2)	Os(3)–Os(4)–N	91.69 (23)
Os(1)–Os(3)–Os(2)	60.0 (2)	Os(1)–C(1)–O(1)	176 (1)
Os(1)–Os(3)–Os(4)	60.85 (2)	Os(1)–C(2)–O(2)	175 (1)
Os(2)–Os(3)–Os(4)	120.26 (2)	Os(1)–C(3)–O(3)	165 (1)
Os(1)–Os(4)–Os(3)	56.81 (1)	Os(2)–C(4)–O(4)	174 (1)
Os(3)–Os(1)–Os(4)	62.35 (2)	Os(2)–C(5)–O(5)	176.9 (9)
Os(2)–Os(1)–S	54.25 (6)	Os(2)–C(6)–O(6)	177 (1)
Os(3)–Os(1)–S	55.44 (7)	Os(3)–C(7)–O(7)	177 (1)
Os(4)–Os(1)–S	86.74 (7)	Os(3)–C(8)–O(8)	169 (1)
Os(1)–Os(2)–S	55.31 (7)	Os(3)–C(9)–O(9)	172 (1)
Os(3)–Os(2)–S	55.14 (7)	Os(4)–C(10)–O(10)	175.5 (9)
Os(1)–Os(3)–S	55.30 (6)	Os(4)–C(11)–O(11)	174 (1)
Os(2)–Os(3)–S	53.95 (6)	Os(4)–C(12)–O(12)	177 (1)
Os(4)–Os(3)–S	85.74 (7)	Os(4)–N–C(13)	116.1 (7)
Os(1)–S–Os(2)	70.43 (7)	Os(4)–N–C(14)	113.7 (8)
Os(1)–S–Os(3)	69.27 (1)		

Table V. Final Positional Parameters with Esd's for $\mathrm{Os_4(CO)_{12}(\mu\text{-}H)_2(\mu_3\text{-}S)}$ (**5**)

atom	*x*	*y*	*z*
Os(1)	0.3243 (1)	0.13472 (5)	0.1728 (1)
Os(2)	0.0670 (2)	0.250	0.2199 (2)
Os(3)	0.4318 (2)	0.250	0.4547 (2)
S	0.248 (1)	0.250	0.012 (1)
C(1)	0.140 (3)	0.089 (1)	−0.009 (3)
O(1)	−0.030 (3)	−0.064 (1)	0.120 (2)
C(2)	0.533 (3)	0.092 (1)	0.102 (4)
O(2)	0.652 (2)	0.070 (1)	0.046 (3)
C(3)	0.315 (3)	0.046 (1)	0.311 (4)
O(3)	0.300 (3)	−0.006 (1)	0.397 (3)
C(4)	−0.162 (5)	0.250	0.043 (5)
O(4)	−0.308 (3)	0.250	−0.056 (3)
C(5)	−0.010 (4)	0.336 (2)	0.333 (4)
O(5)	−0.066 (3)	0.383 (1)	0.410 (3)
C(6)	0.373 (4)	0.331 (2)	0.597 (4)
O(6)	0.345 (3)	0.376 (1)	0.691 (2)
C(7)	0.696 (5)	0.250	0.568 (4)
O(7)	−0.150 (3)	0.250	−0.361 (3)

Table VI. Interatomic Distances (Å) with Esd's for $\mathrm{Os_4(CO)_{12}(\mu_3\text{-}S)(\mu\text{-}H)_2}$ (**5**)

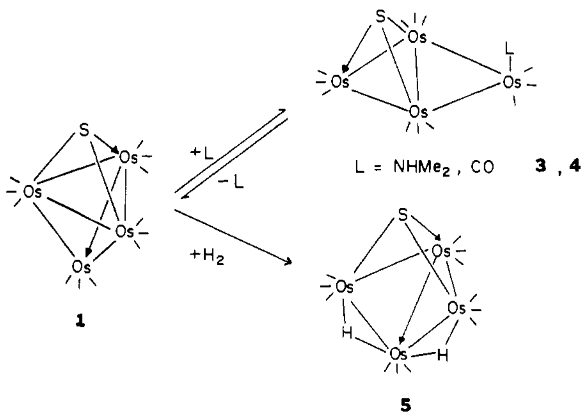
Os(1)–Os(2)	2.815 (1)	Os(3)–C(6)	1.92 (2)
Os(1)–Os(3)	2.970 (1)	Os(3)–C(7)	1.91 (2)
Os(2)–Os(3)	2.858 (1)	C(1)–O(1)	1.13 (2)
Os(1)–S	2.348 (3)	C(2)–O(2)	1.15 (2)
Os(2)–S	2.405 (4)	C(3)–O(3)	1.15 (2)
Os(1)–C(1)	1.895 (15)	C(4)–O(4)	1.17 (3)
Os(1)–C(2)	1.911 (15)	C(5)–O(5)	1.16 (2)
Os(1)–C(3)	1.894 (15)	C(6)–O(6)	1.14 (2)
Os(2)–C(4)	1.91 (3)	C(7)–O(7)	1.13 (2)
Os(2)–C(5)	1.89 (2)	Os(1)⋯Os(1′)	3.930 (1)

Table VII. Selected Interatomic Angles (deg) with Esd's for $\mathrm{Os_4(CO)_{12}(\mu_3\text{-}S)(\mu\text{-}H)_2}$ (**5**)

Os(2)–Os(1)–Os(3)	59.14 (2)	Os(1)–Os(2)–Os(1′)	88.53 (3)
Os(1)–Os(2)–Os(3)	63.14 (2)	Os(1)–Os(3)–Os(1′)	82.84 (3)
Os(1)–Os(3)–Os(2)	57.73 (2)	Os(1)–Os(3)–C(6)	152.3 (5)
Os(2)–Os(1)–S	54.6 (1)	Os(1)–Os(3)–C(7)	114.0 (4)
Os(3)–Os(1)–S	81.69 (9)	Os(2)–Os(3)–C(6)	95.0 (4)
Os(1)–Os(2)–S	52.75 (5)	Os(2)–Os(3)–C(7)	167.4 (5)
Os(3)–Os(2)–S	83.2 (1)	Os(1)–C(1)–O(1)	177 (1)
Os(1)–S–Os(2)	72.6 (1)	Os(1)–C(2)–O(2)	173 (1)
Os(1)–S–Os(1′)	113.6 (2)	Os(1)–C(3)–O(3)	176 (1)
Os(2)–Os(1)–C(1)	91.5 (4)	Os(2)–C(4)–O(4)	175 (2)
Os(2)–Os(1)–C(2)	157.3 (4)	Os(2)–C(5)–O(5)	173 (2)
Os(2)–Os(1)–C(3)	110.4 (4)	Os(3)–C(6)–O(6)	175 (1)
Os(3)–Os(1)–C(1)	150.4 (4)	Os(3)–C(7)–O(7)	178 (1)
Os(3)–Os(1)–C(2)	114.3 (4)	S–Os(1)–C(1)	83.8 (4)
Os(3)–Os(1)–C(3)	96.3 (4)	S–Os(1)–C(2)	104.2 (4)
Os(1)–Os(2)–C(4)	112.7 (4)	S–Os(1)–C(3)	163.6 (4)
Os(1)–Os(2)–C(5)	154.2 (5)	S–Os(2)–C(4)	90.4 (6)
Os(3)–Os(2)–C(4)	173.5 (6)	S–Os(2)–C(5)	129.1 (5)
Os(3)–Os(2)–C(5)	91.0 (5)		

of the adduct $\mathrm{Os_4(CO)_{12}(\mu\text{-}H)_2(\mu_3\text{-}S)}$ (**5**) was determined by a single-crystal X-ray diffraction analysis. Final positional parameters are given in Table V, and interatomic distances and angles are given in Tables VI and VII. An ORTEP diagram of the molecular structure of **5** is shown in Figure 2. The molecule consists of a butterfly tetrahedral cluster of four osmium atoms with a triply bridging sulfido ligand spanning one of the open triangular faces, Os(1)–Os(2)–Os(1′). The molecule contains a plane of symmetry that is imposed by the crystal lattice and passes through the atoms S, Os(2), Os(3), C(4), O(4), C(7), and O(7). The sulfur-bridged Os(1)–Os(2) distance of 2.815 (1) Å is very similar to those in **2** and **3**. The hinge bond Os(2)–Os(3) at 2.858 (1) Å is typical of an osmium–osmium single bond (e.g. $\mathrm{Os_3(CO)_{12}}$, Os–Os = 2.877 (3) Å).[16] The Os(1)–Os(3) distance is much

Scheme I



longer, 2.970 (1) Å. This bond and its symmetry-related one probably contain the bridging hydride ligands, which were not observed crystallographically. Bridging hydride ligands are known to produce significant increases in the lengths of unsupported metal–metal bonds.[17] A tabulation of hydride-bridged osmium–osmium distances for a variety of osmium structures shows a range of 2.930–3.066 Å.[17] The Os(1)···Os(1′) distances of 3.930 (1) Å is clearly nonbonding. The dihedral angle between the Os(1)–Os(2)–Os(3) and Os(1′)–Os(2)–Os(3) planes is 103°. The osmium–sulfur distances are significantly different, 2.348 (3) and 2.405 (4) Å, with the shorter distance being associated with the widely separated wing-tip metal atoms, Os(1) and Os(1′). Each metal atom contains three linear carbonyl ligands. The hydridic character of the hydrogen atoms was confirmed by the very high field chemical shift, −16.47 ppm, observed in the ^{1}H NMR spectrum.

Discussion

In this study the reactivity of the tetraosmium clusters **1** and **2** toward the addition of selected Lewis donors and hydrogen was investigated. For compound **1** the addition of the donors proceeds under unusually mild conditions to yield the butterfly tetrahedral clusters **3** and **4**. Although all three metal–metal bonds to the unique osmium atom are equivalent, the opening process could be viewed formally as a cleavage of a heteropolar bond that is accompanied by the addition of the donor ligand to the unique osmium atom (Scheme I). This pathway is different from that found for the addition of primary and secondary amines to the clusters $M_3(CO)_{12}$ (M = Ru, Os), where amine addition occurs at the carbon atom of one of the carbonyl ligands.[18] The comparative unreactivity of **2** is surprising since structurally compounds **1** and **2** are extremely similar. Since the adducts of **2** corresponding to **3** and **4** have never been made, it cannot be decided if the lack of reactivity of **2** is due to thermodynamic or kinetic factors. Intuitively, however, it seems that the adducts of **2** corresponding to **3** and **4** should be stable and therefore kinetic factors are believed to be responsible. Since it appears that steric factors cannot explain the significant differences in reactivity, an electronic effect would seem to be implied. The details of such an effect will have to await the formulation of a more detailed understanding of the bonding in these molecules.

The activation of hydrogen is an integral step in most catalytic hydrogenation cycles.[19] Polynuclear metal complexes are capable of performing this reaction,[20] and some even do it reversibly.[21] The addition of hydrogen to **1** proceeds to yield butterfly tetrahedral cluster compound **5**, in which the sulfido ligand bridges one of the open triangular faces. This could be viewed as a cleavage of one of the homopolar, sulfur-bridged osmium–osmium bonds (Scheme I). Mechanistically, however, the addition could also proceed by the opening of a bond to the unique osmium atom vide supra with the product **5** being formed after a rearrangement that could include the cleavage of the hydrogen–hydrogen bond. The cleavage of a homopolar metal–metal bond would seem to be in accord with the fate of the hydrogen molecule, which is homolytically separated into two equivalent hydride ligands. As with the addition of donors, compound **2** also failed to add hydrogen.

It is believed that the much greater reactivity of **1** compared to **2** is a significant feature and must in some way be associated with the character of the sulfido ligand. It could be valuable to determine if this is a general property of the sulfido ligand that could be used to advantage in the development of cluster compounds as catalysts.

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Registry No. **1**, 82080-90-8; **2**, 78770-95-3; **3**, 102575-93-9; **4**, 86437-18-5; **5**, 102575-94-0.

Supplementary Material Available: Tables of general temperature factor expressions for both structural analyses (2 pages). Ordering information is given on any current masthead page.

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