Volume 22
Number 19
September 14, 1983

Inorganic Chemistry

© Copyright 1983 by the American Chemical Society

Communications

Facile Synthesis of $Cp_2Mo_2(\mu\text{-}SH)_2(\mu\text{-}S)_2$ and Its Use in Heterobimetallic Cluster Synthesis

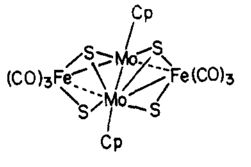
Sir:

Bimetallic sulfido clusters have become the focus of increased research activity, due in part to their potential as models for heterogeneous[1,2] and biological catalysts.[3-5] Sulfided clusters containing molybdenum and a group 8 metal, e.g. Fe, Co, and Ni, are especially interesting as models for the poorly understood hydrodesulfurization catalysts based on "sulfided" iron, cobalt, or nickel molybdates on oxide supports.[6,7]

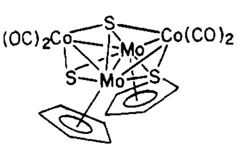
We have previously demonstrated that Mo–S clusters may be synthesized in a rational manner from the interaction of the Mo≡Mo triple bond in $Cp_2Mo_2(CO)_4$ and the sulfides $Fe_2(CO)_6S_2$ and $Cp_2Mo_2(SCH_2CHRS)_2$ (**1**).[8] By analogy with the rich chemistry displayed by derivatives of $Fe_2(\mu\text{-}SH)_2(CO)_6$,[9] we reasoned that $Cp_2Mo_2(\mu\text{-}S)_2(\mu\text{-}SH)_2$ (**2**) might be more reactive and useful in cluster synthesis than the bridging dithiolate **1**. However, any investigation of the chemistry of **2** is hampered by its tedious, 14-day preparation from $(Cp_2Mo_2S_x)_n$ and H_2.[1a] We here report an extremely facile synthesis of **2** and its use in rational synthesis of sulfided iron, cobalt, or nickel molybdenum clusters.

Complex **2** is easily prepared by reducing the readily available, polymeric sulfide $(Cp_2Mo_2S_x)_n$ (**3**)[1a] with $LiEt_3BH$ (ca. 11 equiv/g of **3**) in THF for several hours. The mixture is then carefully quenched with water and the THF stripped out of the mixture. The solid is filtered and washed with water until the washings are colorless. The dried solid is then extracted with CH_2Cl_2 to give a deep purple solution. Removal of the CH_2Cl_2 gives pure **2** as black crystals (yield 75% based on Mo used to prepare **3**).

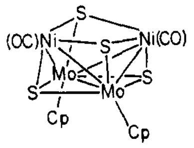
The hydrosulfide **2** reacts rapidly (≤2 h) at room temperature with the carbonyls $Fe_2(CO)_9$, $Co_2(CO)_8$, and $Ni(CO)_4$, affording products **4**–**6**, respectively. (Clusters **4** and **6** were formed in THF with reactant molar ratios of 1:1 (**4**) and 1:2.5 (**2**:$Ni(CO)_4$, **6**), whereas toluene was used as solvent for the formation of **5**, again with a 1:1 mole ratio of reactants.)



4



5



6

The compounds **4**–**6** were isolated by elution chromatography over alumina. In each case, the initial band contained the cluster. The eluant, color, and yield for each cluster are as follows: **4**, CH_2Cl_2, emerald green, 20%; **5**, hexane/toluene (4:1), black, 50%; **6**, CH_2Cl_2, pine green, 25%.

The structures of clusters **4**–**6** have been determined by X-ray crystallography.[10-12] Cluster **4** is centrosymmetric and displays two nonbonding (3.612 (3) Å) and two bonding (2.853 (3) Å) Mo–Fe distances. This cluster is closely related to $Cp_2Mo_2(\mu_3\text{-}S)_2(\mu\text{-}CO)_2Fe(CO)_6$ (**7**),[8] in that two μ-CO ligands in **7** are replaced by two μ_3-S ligands in **4**, resulting in an increase in the number of cluster framework electrons from 62 in **7** to 66 in **4**. The addition of two more antibonding electron pairs would be expected to break two metal–metal bonds as observed (in **7**, all four Mo–Fe bonds are ca. 2.8 Å long). The Mo–Mo bond length in **4** is 2.624 (2) Å, which

---

(1) (a) DuBois, M. R.; VanDerveer, M. C.; DuBois, D. L.; Haltiwanger, R. C.; Miller, W. K. *J. Am. Chem. Soc.* **1980**, *102*, 7456. (b) DuBois, M. R.; Haltiwanger, R. C.; Miller, D. J.; Glatzmaier, G. *Ibid.* **1979**, *101*, 5245.

(2) Adams, R. D.; Dawoodi, Z.; Foust, D. F.; Segmüller, B. F. *Organometallics* **1983**, *2*, 315. Adams, R. D. *Acc. Chem. Res.* **1983**, *16*, 67.

(3) Muller, A.; Diemann, E.; Jostes, R.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 934.

(4) Coucouvanis, D. *Acc. Chem. Res.* **1981**, *14*, 201.

(5) Averill, B. A. *Structure Bonding (Berlin)* **1983**, *53*, 59.

(6) (a) Furmisky, E. *Catal. Rev.—Sci. Eng.* **1980**, *22*, 371. (b) Ratnasamy, P.; Sivasanker, S. *Ibid.* **1980**, *22*, 401. (c) Schuman, S. C.; Shalit, H. *Ibid.* **1980**, *4*, 245. (d) Grange, P. *Ibid.* **1980**, *21*, 135.

(7) Massoth, F. E. *Adv. Catal.* **1978**, *27*, 265.

(8) Williams, P. D.; Curtis, M. D.; Duffy, D. N.; Butler, W. M. *Organometallics* **1983**, *2*, 165.

(9) Seyferth, D.; Henderson, R. S.; Song, L.-C. *Organometallics* **1982**, *1*, 125.

(10) During the course of our structure solution for **4**, we became aware of its independent synthesis from **2** and $Fe(CO)_5$ in the presence of Me_3NO: Cowan, B.; Noordik, J.; DuBois, M. R. *Organometallics* **1983**, *2*, 931. These authors also determined the structure of **4**, and their values for its structural parameters are quoted here since we did not finish our refinement.

(11) For **5**: $a = 10.404$ (3), $b = 11.015$ (3), $c = 9.962$ (2) Å; $\alpha = 99.78$ (2), $\beta = 96.99$ (2), $\gamma = 63.11$ (2)°; $V = 1002.0$ (4) Å^3; $\rho_{calcd} = 2.24$, $\rho_{obsd} = 2.3$ g/mL; $Z = 2$; space group $P\bar{1}$ (No. 2); ν_{CO}(KBr) = 1990 (s), 1960 (s) cm^{-1}; mp 177 °C. The structure was refined with use of anisotropic temperature factors on non-hydrogen atoms to $R = 0.036$, $R_w = 0.053$ for 2988 unique reflections with $I \geq 3\sigma(I)$.

(12) For **6**: $a = 9.712$ (2), $b = 20.303$ (4), $c = 9.787$ (1) Å; $\beta = 98.30$ (1)°; $V = 1909.5$ (6) Å^3; $\rho_{calcd} = 2.27$, $\rho_{obsd} = 2.24$ g/mL; $Z = 4$, space group $P2_1/n$ (nonstandard setting of $P2_1/c$, No. 14); ν_{CO}(KBr) = 1990 (vs), 1968 (s) cm^{-1}. The structure was refined with use of anisotropic temperature factors for all nonhydrogen atoms to $R = 0.049$, $R_w = 0.066$ for 2179 unique reflections with $I \geq 3\sigma(I)$.

0020-1669/83/1322-2661$01.50/0 © 1983 American Chemical Society

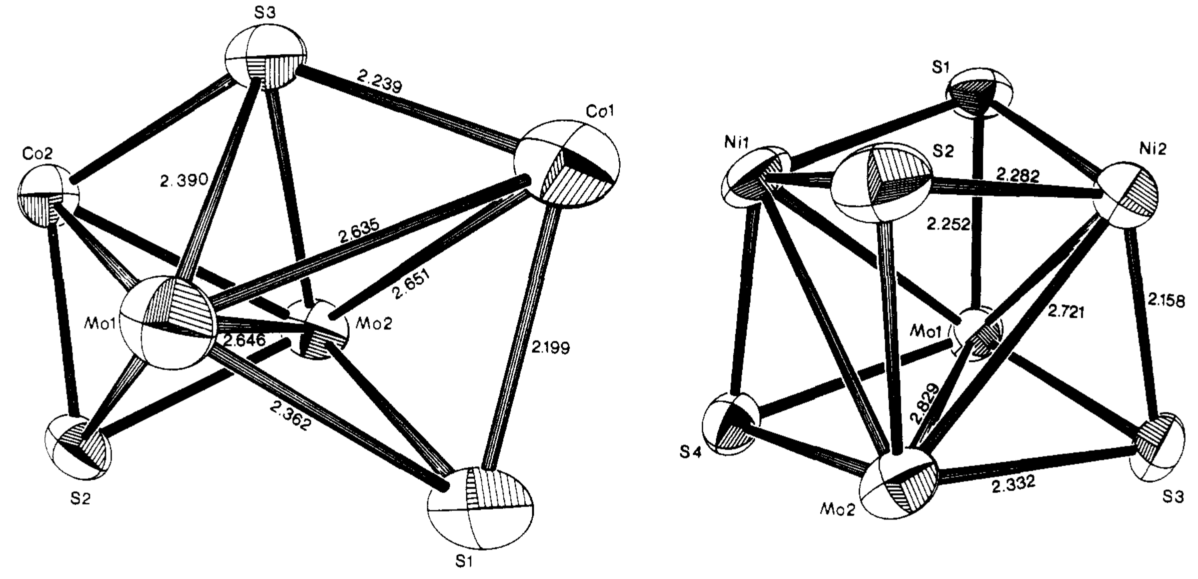


Figure 1. Molecular cores of the clusters $Cp_2Mo_2(\mu_3\text{-}S)_4Ni_2(CO)_2$ (**6**) (right) and $Cp_2Mo_2(\mu_4\text{-}S)(\mu_3\text{-}S)_2Co_2(CO)_4$ (**5**) (left). Representative distances are noted on the drawings.

is 0.20 Å shorter than the Mo–Mo bond in **7**. In **4**, the Mo–Mo bond is bridged by four sulfido ligands whereas there are only two such bridges in **7**. Apparently, the metal orbitals used in Mo–S bridge bonds are also metal–metal bonding.[13]

The structure of **6** (Figure 1) is also easily rationalized as a cubane with five metal–metal bonds, i.e. a 62e butterfly with Ni at the wingtips (Ni···Ni = 2.962 (2) Å, Mo–Ni = 2.720 (1)–2.724 (1) Å, Mo–Mo = 2.829 (1) Å). In this complex, the Mo–Mo bond, bridged by two sulfido groups, has essentially the same length as the Mo–Mo bond in **7**, 2.821 (1) Å (vide supra).

The structure of **5** contains a relatively rare μ_4-S ligand (Figure 1). The geometry of the μ_4-S ligand observed here has been found previously in Chevrel chalcogenides[14] and in two other clusters.[15] Square-pyramidal[16] and tetrahedral[17] geometries have been observed also for μ_4-S bridges.

Clusters **4**, **6**, and **7** are electron precise, but the μ_4-S ligand demands a delocalized description of the bonding in the electron-deficient cluster **5**. If it is assumed that the Mo uses 4 AO's for cluster bonding, then 5 AO's are left for ligand bonding and nonbonding electrons. The CpMo fragment thus donates $6 + 5 - 10 = 1e$ to the cluster framework, as does the $Co(CO)_2$ fragment (assuming Co uses only 3 AO's for cluster framework bonding, $9 + 4 - 12 = 1e$).[18a] If each sulfur then donates 4e to the framework, there is a total of 16e, which predicts a closo structure for the seven-vertex $Mo_2Co_2S_3$ cluster. The closo, seven-vertex structure adopted by $B_7H_7^{2-}$ and $C_2B_5H_7$ is the pentagonal bipyramid.[18b] However, in these examples, the B and C atoms use only 3 AO's each for cluster bonding. Apparently, the greater connectivity permitted by the use of 4 AO's in the CpMo fragment favors the bicapped-trigonal-bipyramidal structure observed here. Alternatively, if Mo is considered to use only 3 AO's in cluster framework bonding, then there are only 12e (6 *pairs* = *S*) available for cluster bonding. In this case, $S = N - 1$, which correctly predicts the bicapped-trigonal-bipyramidal structure but fails to account for the high connectivity of Mo.[18c]

The triply bridged Mo–Mo bond in **5** is short (2.646 (1) Å) as it is in **4**, again suggesting the presence of multiple-bond character. The bonds between the metals and the μ_4-S ligand are all statistically longer than the corresponding M–(μ_3-S) bonds, consistent with 5-center–6e delocalization around the μ_4-S ligand compared to the 4-center–6e bonding around the μ_3-S ligand (see Figure 1) (we assume that the $3s^2$ electrons on sulfur are too low in energy to be used effectively in bonding). It is also interesting to note that the sulfhydryl complex **2** shows a reactivity with $Co_2(CO)_8$ different from that reported for $Cp^*{}_2Mo_2S_4$.[19]

These results and others[8,19,20] show that the reaction between organometal sulfides and reactive carbonyls constitutes an attractive pathway to heterobimetallic clusters. The surface chemistry and catalytic properties of these clusters are currently under investigation.

Acknowledgment. We thank the National Science Foundation for support through Grant No. CHE8206153. P.D.W. thanks the Department of Chemistry and the donors of the Samuel H. Baer Fellowship for support. We are especially grateful to Professor M. R. DuBois for a preprint of her work. X-ray data collection by Dr. W. M. Butler is also gratefully acknowledged.

Supplementary Material Available: Listings of fractional atomic coordinates (Tables I and II), F_o vs. F_c (Tables III and IV), thermal parameters (Tables V and VI), bond distances (Tables VII and VIII), bond angles (Tables IX and X), and crystal and data collection statistics (Tables XI and XII) for **5** and **6**, respectively (31 pages). Ordering information is given on any current masthead page.

Department of Chemistry
The University of Michigan
Ann Arbor, Michigan 48109

M. David Curtis*
P. Douglas Williams

Received May 19, 1983

---

(13) Triplett, K.; Curtis, M. D. *J. Am. Chem. Soc.* **1975**, *97*, 5747.

(14) Potel, M.; Chevrel, R.; Sergent, M.; Armici, J. C.; Deroux, M.; Fischer, O. *J. Solid State Chem.* **1980**, *35*, 286.

(15) (a) $Cp_4Cr_2Ni_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)$: Pasynskii, A. A.; Eremenko, I. L.; Ellert, O. G.; Novoturtsev, V. M.; Rakitin, Y. V.; Kalinnikov, V. T.; Shklover, V. E.; Struchov, Y. T. *J. Organomet. Chem.* **1982**, *234*, 315. (b) $Ni_9(\mu_4\text{-}S)_3(\mu_3\text{-}S)_6(PEt_3)_6^{2+}$: Ghilardi, C. A.; Midollini, S.; Sacconi, L. *J. Chem. Soc., Chem. Commun.* **1981**, 47.

(16) (a) Vahrenkamp, H.; Wucheres, E. J. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 680. (b) Ryan, R. C.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6904. (c) Adams, R. D.; Horvath, I. T.; Yang, L. W. *Ibid.* **1983**, *105*, 1533.

(17) (a) Adams, R. D.; Forest, D. F. *Organometallics* **1983**, *2*, 323 and references therein. (b) Adams, R. D.; Dawoodi, Z.; Forest, D. F.; Segmüller, B. E. *J. Am. Chem. Soc.* **1983**, *105*, 831.

(18) (a) Wade, K. "Transition Metal Clusters"; Johnson, B. F. G., Ed.; Wiley: New York, 1980; pp 193–264. (b) Rudolph, R. W. *Acc. Chem. Res.* **1976**, *9*, 446 and references therein. (c) Johnson, B. F. G.; Lewis, J. *Adv. Inorg. Chem. Radiochem.* **1981**, *24*, 225–355.

(19) Brunner, H.; Wachter, J. *J. Organomet. Chem.* **1982**, *240*, C41.

(20) Bolinger, C. M.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1982**, *104*, 7313.