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Synthesis and Structural Characterization of an Organometallic $Mo_2Fe_2S_4$ Cluster

Brett Cowans, Jan Noordik, and M. Rakowski DuBois*[1]

Department of Chemistry, University of Colorado
Boulder, Colorado 80309

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Summary: The reaction of $[MeCpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$ (MeCp = $CH_3C_5H_4$) with $Fe(CO)_5$ in the presence of Me_3NO has resulted in the synthesis of $[MeCpMoS_2Fe(CO)_3]_2$, I. The structure and reactivity of I have been compared with those of organodithiolate-bridged dimers of molybdenum.

We have reported that the sulfido ligands in many dimers of the general type $[CpMo(\mu\text{-}S)(\mu\text{-}SR)]_2$ react with hydrogen and with unsaturated molecules such as alkenes and alkynes.[2,3] A molecular orbital description of this structural type indicated that the LUMO includes a pair of in-phase vacant p orbitals on the bridging sulfido ligands which can function as an acceptor site in reactions with electron donors.[4] Reactions with several types of electron donors are being investigated in order to understand factors which lead to reversibility in these interactions. In this communication we report our initial studies of the reactions of the sulfido ligands in the dimers with low-valent metal centers. The reaction of iron pentacarbonyl with $[MeCpMo(S)SH]_2$ has led to the incorporation of two iron tricarbonyl fragments into a molybdenum dimer. The $Fe_2Mo_2S_4$ core of the resulting cluster is significantly distorted from the cubane-type structures characterized for most other M_4S_4 systems. Similar reactions of $Cp_2M_2S_4$ dimers with metal carbonyls have been reported recently,[5,6] and related $Mo_2Fe_2S_2$ clusters have also been synthesized.[7,8] In each case a different structural variation has been characterized or proposed. These are compared with the present system in the following discussion.

The reaction of $[MeCpMo(S)SH]_2$ with 2 equiv of iron carbonyl in the presence of anhydrous trimethylamine oxide proceeds at room temperature according to eq 1.

$$[MeCpMo(S)SH]_2 + 2Fe(CO)_5 \xrightarrow[CH_2Cl_2]{4Me_3NO} \underset{\textstyle I}{[MeCpMoS_2Fe(CO)_3]_2} \quad (1)$$

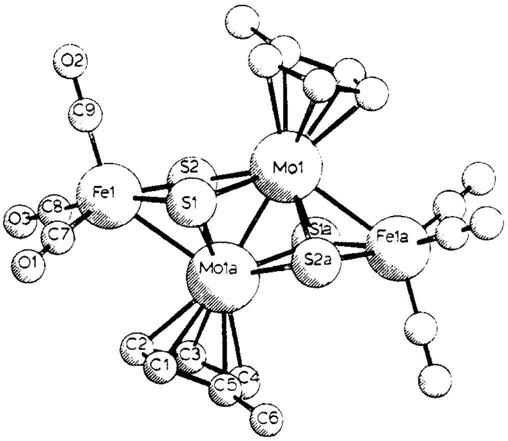

Figure 1. A perspective view and numbering scheme for $[CH_3C_5H_4MoS_2Fe(CO)_3]_2$.

Table I. Selected Bond Distances and Angles for $[CH_3C_5H_4MoS_2Fe(CO)_3]_2$

A. Distances (Å)

Mo_1-Mo_{1A}	2.624 (2)	Fe_1-C_7	1.801 (4)
Mo_1-S_1	2.456 (3)	Fe_1-C_8	1.806 (4)
Mo_1-S_2	2.458 (2)	Fe_1-C_9	1.784 (5)
Mo_1-S_{1A}	2.395 (3)	Mo_1-Fe_{1A}	2.853 (3)
Mo_1-S_{2A}	2.393 (2)	$Mo_1 \cdots Fe_1$	3.612 (3)
Fe_1-S_2	2.232 (3)	$S_1 \cdots S_{2A}$	2.808 (3)
Fe_1-S_1	2.237 (2)	$S_1 \cdots S_2$	2.961 (3)

B. Angles (deg)

S_1-Mo_1-S_2	74.11 (6)	Fe_1-S_1-Mo_{1A}	75.94 (7)
S_1-Mo_1-S_{2A}	70.75 (8)	Fe_1-S_2-Mo_{1A}	76.07 (9)
Fe_1-S_1-Mo_1	100.55 (7)	S_1-Fe_1-S_2	82.99 (7)
Fe_1-S_2-Mo_1	100.64 (7)		

The green, air-stable product is purified by eluting it through an alumina column with a 30:70 mixture of CH_2Cl_2/hexane and is isolated in 20% yield. The same tetrameric product is produced in lower yields when only 1 equiv of iron carbonyl is used. The low yields appear to result from a competing oxidation of the starting molybdenum dimer by the amine oxide. The composition of I is supported by spectral data.[9] Single crystals were grown by slow evaporation of a dichloromethane solution and characterized by an X-ray diffraction study.[10] The molecule crystallizes in the centrosymmetric space group $P\bar{1}$. A perspective view of the cluster is shown in Figure 1, and selected bond distances and angles are presented in Table I. The molecule contains four metal ions which lie in a plane and which are bridged by four μ_3-sulfido ligands. The plane of the sulfur atoms intersects the metal ion plane with a dihedral angle of 90°.[11] The $(MeCp)_2Mo_2S_4$ core of the molecule is similar to those characterized previously in dimeric structures.[12] However some slight distortions can be attributed to a change in the electronic environment of the core resulting from the sulfur coordination of the tricarbonyl iron fragments. For example, the Mo–Mo distance is 0.02–0.04 Å longer than those observed previously in neutral bis(dithiolate)bridged

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(9) IR (CH_2Cl_2): 2032, 1978 cm^{-1} ($\nu_{C{=}O}$). NMR ($CDCl_3$): δ 2.36 (s, 6, CH_3Cp), 6.15 (2m, 8, C_5H_4). Mass spectrum: m/e^+ 758 (P), 730 (P – CO), 702 (P – 2CO), 646 (P – 4CO); 618 (P – 5CO), 590 (P – 6CO), 295 $(MeCpMo_2S_4Fe_2)^{2+}$. Electronic spectrum: λ 652 nm (ϵ 4.2 × 10^3), 452 (sh), 345 nm (sh).

(10) Crystal data: space group $P\bar{1}$; cell dimensions at 25 °C, $a = 6.598$ (2) Å, $b = 10.168$ (3) Å, $c = 10.203$ (3) Å, $\alpha = 99.81$ (2)°, $\beta = 107.55$ (2)°, $\gamma = 108.99$ (2)°; $V = 589.1$ (3) $Å^3$, $Z = 1$, $\rho_{calcd} = 2.14$ g/cm^3. Mo was located in a Patterson synthesis and used as input to DIRDIF[22] which gave the remaining 15 non-hydrogen atoms as the top 15 peaks. Least-squares refinement on 3069 reflections ($F^2 > 3.0\sigma(F^2)$) with a weighting scheme $\sigma^2(F) = \sigma_c{}^2 + 10^{-4}F^2$ ($\sigma_c{}^2$ from counting statistics), a constrained cyclopentadienyl ring, and anisotropic thermal parameters for all non-hydrogen atoms converged to a final residual $R_F = 0.041$ ($R_{wF} = 0.039$). Data were collected on a Nicolet $P\bar{1}$ autodiffractometer (crystal-monochromated Mo Kα radiation). The SHELX76 program system was used for all routine crystallographic calculations.

(11) Plane calculated for Mo_1–Mo_{1A}–Fe_1–Fe_{1A}: $6.043x - 5.951y + 0.503z = 0$; plane calculated for S_1–S_{1A}–S_2–S_{2A}: $2.638x + 4.968y + 9.087z = 0$, where x, y, and z are the fractional cell coordinates.

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dimers. Unlike the previously characterized structures, each sulfur ligand is unsymmetrically bridged between the two Mo ions with Mo–S distances of 2.457 (3) and 2.394 (3) Å.

The most notable feature of the iron interaction is its unsymmetrical coordination to the Mo_2S_4 core. Although the Fe–S distances of 2.232 (1) and 2.237 (1) Å are nearly equivalent, Fe_1 is displaced from the plane of the sulfur atoms and tilted toward Mo_{1A}. As a result, the molecule contains a relatively short Fe–Mo distance of 2.853 (3) Å and acute Fe_1–S–Mo_{1A} angles of 76°. The second Mo ion and Fe_1 are bridged by two sulfido ligands in an approximately planar configuration with a much longer metal–metal distance. The short Mo–Fe distance is 0.08–0.15 Å longer than the distances between these metal ions in most of the previously reported sulfido-bridged Mo–Fe clusters.[13-18] However it seems reasonable to assume some bonding interaction between Fe_1Mo_{1A} in I because of the strong tendency of low-spin Fe(II) to be six-coordinate. If this oxidation state formalism is used, the 18-electron Mo(III) ion can be viewed as an electron pair donor to the iron center. This structure provides the first evidence for additional bond formation at the molybdenum ion in the series of tetrasulfido-bridged dimolybdenum complexes.

Different structures have been characterized or proposed when the metal sulfide or the metal carbonyl in eq 1 has been varied. In the reaction of $(MeCp)_2V_2S_4$ with excess iron carbonyl,[5] only one iron was incorporated into the cluster to form $(MeCp)_2V_2S_4Fe(CO)_3$ (II). Sulfur abstraction from II led to the formation of $(MeCp)_2V_2S_3Fe(CO)_3$ which was characterized by an X-ray diffraction study. The trigonal-bipyramidal $M_3(\mu_3\text{-}S)_2$ core involved two equivalent Fe–V distances (2.82 Å) and relatively short $V(\mu\text{-}S)$ distances as a means of alleviating electron deficiency associated with the vanadium ions. The reaction of $[(CH_3)_5C_5MoS_2]_2$ with $Co_2(CO)_8$ has led to the tetrameric product $[(CH_3)_5C_5MoS_2Co(CO)]_2$.[6] The latter complex has been proposed to have a cubane-type structure on the basis of its diamagnetic nature and by analogy to other sulfido-bridged systems. Two clusters with butterfly and planar Mo_2Fe_2 geometries with the formulas $Cp_2Mo_2Fe_2(\mu_3\text{-}S)_2(\mu_{2or3}\text{-}CO)_2(CO)_6$ have been synthesized by the reaction of $Cp_2Mo_2(CO)_4$ with $Fe_2S_2(CO)_6$.[7,8] The cluster reported here is related to the planar isomer by the replacement of two μ-CO ligands with μ_3-sulfido bridges. This results in a formal oxidation of the M_4 system and in the disruption of two of the four Mo–Fe bonds which were present in the carbonyl-bridged cluster.[8]

The reactivity of I is being compared to that of the structurally related Mo dimers with two equivalent organodithiolate bridges. Electrochemical studies suggest that the introduction of additional metal centers into the molybdenum dimers will enable us to develop the chemistry of electron-rich clusters. While complexes of the type $[CpMoSC_nH_{2n}S]_2$ do not show any tendency for electrochemical reduction in the negative potential range up to −2 V vs. SCE, the cyclic voltammetry of I in acetonitrile reveals that it undergoes a reversible reduction at −1.06 V vs. SCE and a second quasi-reversible reduction at −1.45 V. A largely irreversible oxidation is observed near +0.6 V.[19] The dithiometalate bridge of I does not show the lability exhibited by the organodithiolate ligands.[20] For example, no reaction is observed between I and acetylene at 25 °C except in the presence of an oxidizing agent (Me_3NO). Under the latter conditions $[MeCpMoSC_2H_2S]_2$ is formed. The competitive reaction of phenylacetylene and iron carbonyl with $[MeCpMoSSH]_2$ yields primarily the bis(alkenedithiolate) complex, but spectral data[21] suggest that the mixed bridge derivative $(MeCpMo)_2(SCHC(Ph)S)(S_2Fe(CO)_3)$ may also be produced in low yields. Further investigations of the reactivity of both the sulfur ligands and the metal ions in these systems are in progress.

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Registry No. I, 85534-08-3; $[MeCpMo(S)SH]_2$, 75675-65-9; $Fe(CO)_5$, 13463-40-6.

Supplementary Material Available: Tables of interatomic distances and angles, experimental conditions, solution and refinement details, final positional and thermal parameters, and structure factor amplitudes (20 pages). Ordering information is given on any current masthead page.

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Cyclometalation of (3-Chloropropyl)dicyclohexylphosphine on Rhodium and a Facile, Stoichiometric Rhodium-Assisted Synthesis of the Chelating Triphosphine Ligand $PhP(CH_2CH_2CH_2P\text{-}c\text{-}Hx_2)_2$

Robert D. Wald and Devon W. Meek*

Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

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Summary: Facile cyclometalation of (3-chloropropyl)dicyclohexylphosphine occurs when $RhCl(COD)(c\text{-}Hx_2PCH_2CH_2CH_2Cl)$ is treated with the secondary–tertiary diphosphine $c\text{-}Hx_2PCH_2CH_2CH_2P(Ph)H$ in the absence of a stronger base. On the other hand, if the same reagents are combined at −78 °C in the presence of NEt_3 and allowed to warm to room temperature over a 2-h period, a clean synthesis of the chelated triphosphine ligand $PhP(CH_2CH_2CH_2P\text{-}c\text{-}Hx_2)_2$ results.

Triphosphines that contain trimethylene chains are valuable chelating ligands with the larger transition-metal

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