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# Characterization and Reaction Studies of Dimeric Molybdenum(III) Complexes with Bridging Dithiolate Ligands. Catalytic Reduction of Acetylene to Ethylene[1]

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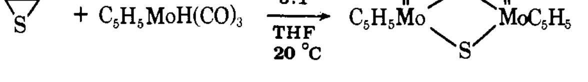
**Abstract:** The complexes $[C_5H_5MoSC_nH_{2n}S]_2$ (where $n = 2$ and 3) have been prepared by the reaction of ethylene sulfide and propylene sulfide, respectively, with $C_5H_5MoH(CO)_3$ or with $[C_5H_5Mo(CO)_3]_2$. Cyclic voltammetry shows that each complex undergoes two reversible oxidations at 0.13 and 0.79 V vs. SCE (in acetonitrile with 0.1 M $Bu_4NBF_4$). Both the one-electron and two-electron oxidation products have been synthesized and characterized by spectral and magnetic data. Electrochemical data for the oxidized complexes support the conclusion that the complexes have the same gross structural features in all three oxidation states. A single crystal of the monocation $[C_5H_5MoSC_3H_6S]_2BF_4$ has been characterized by an X-ray diffraction study. The compound crystallizes in the space group $C2/c$ with $a = 18.266$ (1) Å, $b = 9.206$ (4) Å, $c = 12.911$ (5) Å, $\beta = 100.83$ (3)°, and $V = 2128$ Å$^3$. The metal ions of the cation are bridged by two 1,2-propanedithiolate ligands. The four sulfur atoms of these ligands form a plane which bisects the metal-metal distance. The neutral dimeric complexes undergo a unique reaction with alkenes and alkynes in which the hydrocarbon portion of the bridging dithiolate ligands is exchanged. The reaction has been characterized with olefins with both electron-withdrawing and electron-donating substituents. When $[C_5H_5MoSC_2H_4S]_2$ (**1**) is reacted with acetylene at 25 °C, ethene is produced and the complex $[C_5H_5MoSC_2H_2S]_2$ is isolated. The latter complex is reduced by hydrogen (2 atm) at 60 °C to re-form **1**. The utility of these reactions in the catalytic reduction of acetylene to ethylene has been investigated. The role of the sulfur ligands in this catalytic cycle is discussed.

## Introduction

There is evidence that molybdenum ions coordinated, at least in part, by sulfur donor ligands participate in a number of catalytic reactions. These include the homogeneous reactions of several molybdoenzymes,[2-8] as well as heterogeneous processes in Fischer-Tropsch[9-11] and hydrodesulfurization[12,13] catalyst systems. Despite extensive synthetic studies of molybdenum complexes with sulfur ligands, relatively few of these homogeneous systems have been found to display catalytic activity.[14-21] We are extending the study of reactions of new sulfur-containing molybdenum complexes in the expectation that this will increase our understanding of structural and mechanistic features which are important in catalyst development.

Dimeric cyclopentadienylmolybdenum complexes containing sulfido and disulfido ligands have been reported as products of reactions of hydridomolybdenum complexes with propylene sulfide (reactions 1 and 2).[22] However, the reaction



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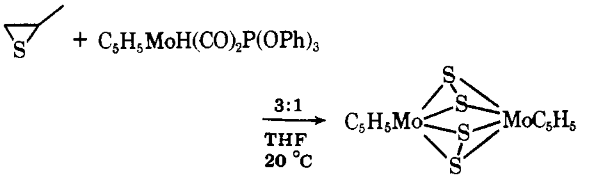

(2)

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**Table I.** Elemental Analyses for Dithiolate Bridged Complexes

| compd | C (calcd C) | H (calcd H) | S (calcd S) |
|---|---|---|---|
| $[C_5H_5MoSC_2H_4S]_2$ | 33.38 (33.20) | 3.66 (3.56) | 25.40 (25.30) |
| $[C_5H_5MoSC_3H_6S]_2$ | 35.96 (35.96) | 4.07 (4.12) | 24.02 (23.97) |
| $[C_5H_5MoSC_2H_4S]_2BF_4$ | 28.38 (28.33) | 3.19 (3.04) | 21.56 (21.59) |
| $[C_5H_5MoSC_3H_6S]_2BF_4$ | 30.94 (30.92) | 3.49 (3.54) | 20.64 (20.61) |
| $[C_5H_5MoSC_2H_4S]_2(PF_6)_2$ | 21.19 (21.11) | 2.45 (2.26) | 16.11 (16.08) |
| $[C_5H_5MoSC_3H_6S]_2(PF_6)_2$ | 23.24 (23.30) | 2.70 (2.67) | 15.71 (15.53) |
| $[C_5H_5MoSCH_2CH(OC_2H_5)S]_2$ | 36.39 (36.36) | 4.47 (4.38) | 21.51 (21.55) |
| $[C_5H_5MoSCH_2CH(CN)S]_2$ | 34.40 (34.53) | 2.99 (2.88) | 22.82 (23.02) |
| $[C_5H_5MoSC_2H_2S]_2$ | 33.51 (33.47) | 2.78 (2.79) | 25.62 (25.50) |
| $[C_5H_5MoSCHC(C_6H_5)S]_2$ | 47.56 (47.71) | 3.33 (3.36) | 19.67 (19.57) |
| $[C_5H_5MoS_2]_n$ | 26.48 (26.67) | 2.20 (2.22) | 28.58 (28.44) |

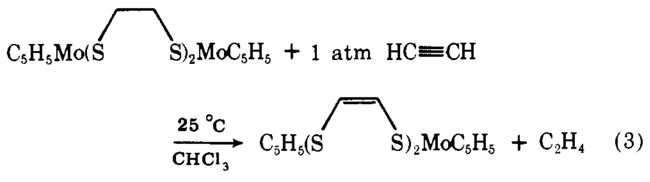
**Table II.** Cyclic Voltammetric Data for Oxidations of Neutral Dithiolate Bridged Complexes[a]

| complex | $E_{1/2}$, V vs. SCE | $\Delta E_p$, mV[b] | $i_{pa}/i_{pc}$ |
|---|---|---|---|
| $[C_5H_5MoSC_2H_4S]_2$ | 0.13 | 60 | 1.0 |
|  | 0.79 | 70 | 1.1 |
| $[C_5H_5MoSC_3H_6S]_2$ | 0.12 | 65 | 1.0 |
|  | 0.79 | 60 | 1.0 |
| $[C_5H_5MoSCH(CH_3)CH(CH_3)S]_2$ | 0.12 | 60 | 1.0 |
|  | 0.79 | 60 | 1.0 |
| $[C_5H_5MoSCH_2CH(OC_2H_5)S]_2$ | 0.14 | 70 | 0.9 |
|  | 0.71[c] |  |  |
| $[C_5H_5MoSCH_2CH(CN)S]_2$ | 0.47[d] | 60 | ~1 |
|  | 1.13 | 60 | ~1 |

[a] Millimolar solutions of complexes in $CH_3CN$/0.1 M $n$-$Bu_4NBF_4$ oxidized at a Pt wire electrode. Scan rate = 100 mV/s. [b] $\Delta E_p$ for a reversible one-electron oxidation of a standard compound $(Ni(Me_6[14]4,11\text{-diene-}N_4)(ClO_4)_2$[50] was found to be ~60 mV for this cell system (theory, 59 mV).[29] [c] An irreversible wave was observed. $E_{pa}$ is reported. [d] Reversible oxidations of a minor product (~30%) were also observed at 0.30 and 0.96 V.

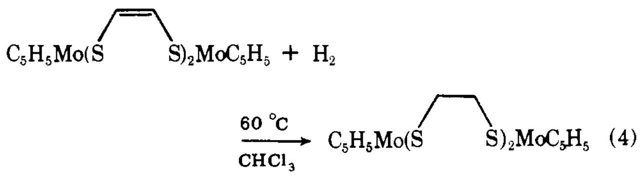
chemistry of these products has not been reported. In our efforts to repeat these syntheses and study the products in more detail, we have isolated from both reactions 1 and 2 an isomeric mixture of products with the formulation $[C_5H_5MoSC_3H_6S]_2$. Spectral studies suggest that the two molybdenum ions are bridged by two 1,2-propanedithiolate ligands. The analogous complex with 1,2-ethanedithiolate bridges has also been prepared. An unusual characteristic of these dimers is their ability to undergo two reversible one-electron oxidations. The syntheses and characterizations of both the one- and two-electron oxidation products are included in this paper.

Although cyclopentadienylmolybdenum dimers with other bridging thiolate ligands have been reported previously,[23-28] we have found that the neutral complexes of this study display exceptional reactivity at the site of the bridging ligands. Under mild conditions the hydrocarbon linkage of the dithiolate ligands undergoes an exchange reaction with alkenes and alkynes (e.g., reaction 3). We have investigated the potential



$$C_5H_5Mo(S\quad S)_2MoC_5H_5 + 1\ \text{atm}\ HC{\equiv}CH \xrightarrow[CHCl_3]{25\ °C} C_5H_5(S\quad S)_2MoC_5H_5 + C_2H_4 \quad (3)$$

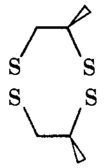
utility of these reactions in the development of a catalytic cycle. The product of alkyne substitution, shown in reaction 3, reacts with hydrogen to form the ethanedithiolate bridged complex (reaction 4). No further reduction occurs under these conditions. Reactions 3 and 4 comprise a catalytic cycle which effects the reduction of acetylene to ethylene under mild homogeneous conditions. These complexes represent a novel catalytic system in which bridging sulfur ligands play an active role in the catalytic cycle. In this paper we report the scope and characteristics of this unique series of reactions. Results of mechanistic studies will be presented in a later paper.



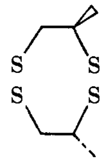
$$C_5H_5Mo(S\quad S)_2MoC_5H_5 + H_2 \xrightarrow[CHCl_3]{60\ °C} C_5H_5Mo(S\quad S)_2MoC_5H_5 \quad (4)$$

## Results and Discussion

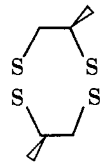
**Characterization of Neutral Dithiolate Bridged Complexes.** When propylene sulfide is reacted with cyclopentadienylmolybdenum tricarbonyl hydride according to the conditions shown in reaction 1, a red-brown product is isolated in 50–60% yield. The mass spectrum of the product shows the previously reported peaks centered at *m/e* 450 and below, which correspond to the $[C_5H_5MoS_2]_2{}^+$ ion and its fragmentation products, respectively.[22] In addition, weak envelopes (relative intensities ~2%) with the characteristic dimolybdenum isotope pattern are observed at *m/e* 492 and 534. The spectrum is consistent with a product formulated as $[C_5H_5MoSC_3H_6S]_2$. Analytical data for the complex, included in Table I, also fit this formulation. Complex resonances observed at 1.2 and 2.2 ppm in the NMR spectrum suggest that the molybdenum ions are bridged by 1,2-propanedithiolate ligands. The splitting of an apparent triplet at 5.18 ppm in the spectrum is field dependent, confirming that the cyclopentadienyl resonance is not split by coupling. Different environments for the Cp ligands can be attributed to the presence of isomers. Since the four sulfur atoms form a plane perpendicular to the M–M bond of the molecule (vide infra), four distinct isomers can result from different orientations of the methyl groups of the bridging ligands. Isomers represented by I and III have inequivalent cyclopentadienyl rings (resonances observed at 5.11 and 5.24 ppm) while a single Cp resonance is expected in the spectra of isomers II and IV (5.18 ppm).



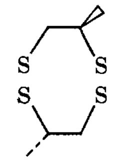
I



II



III



IV

The reaction of $C_5H_5Mo(H)(CO)_3$ with ethylene sulfide produces the analogous dimeric product with 1,2-ethanedithiolate bridges. No isomers are expected for this product, and the NMR spectrum consists of two singlets at 5.1 and 1.8 ppm with relative intensities of 5:4. The same products can also be prepared in 60–80% yields by reaction of the appropriate episulfide with bis(cyclopentadienylmolybdenum tricarbonyl).

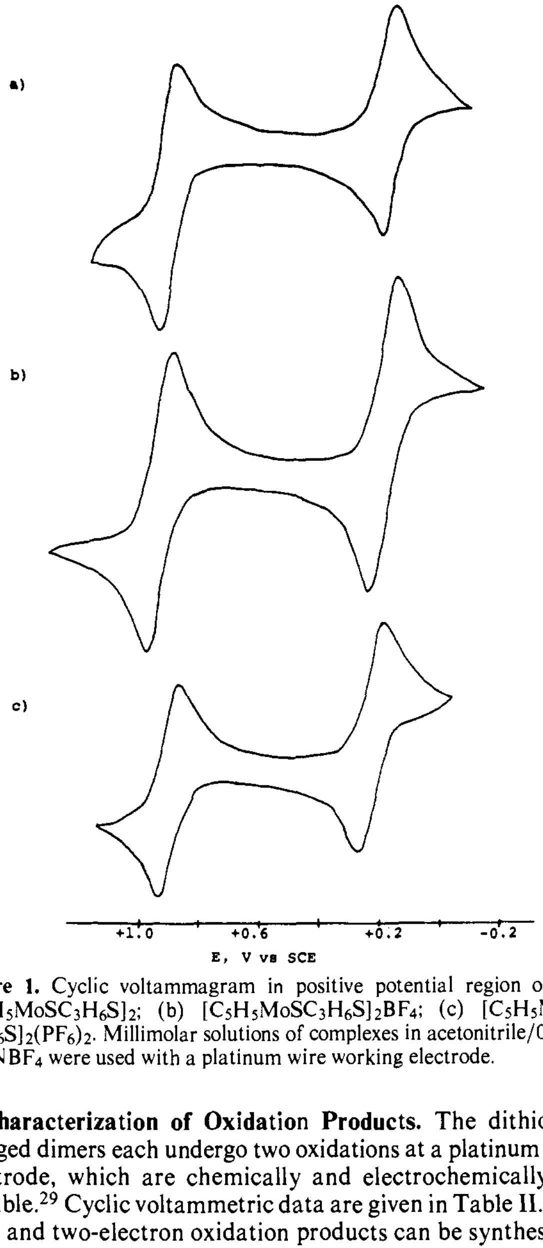


**Figure 1.** Cyclic voltammagram in positive potential region of (a) $[C_5H_5MoSC_3H_6S]_2$; (b) $[C_5H_5MoSC_3H_6S]_2BF_4$; (c) $[C_5H_5MoSC_3H_6S]_2(PF_6)_2$. Millimolar solutions of complexes in acetonitrile/0.1 M $Bu_4NBF_4$ were used with a platinum wire working electrode.

**Characterization of Oxidation Products.** The dithiolate bridged dimers each undergo two oxidations at a platinum wire electrode, which are chemically and electrochemically reversible.[29] Cyclic voltammetric data are given in Table II. The one- and two-electron oxidation products can be synthesized according to the reactions

$$[C_5H_5MoSC_nH_{2n}S]_2 + Ag^+ \rightarrow [C_5H_5MoSC_nH_{2n}S]_2{}^+ \quad (5a)$$

$$[C_5H_5MoSC_nH_{2n}S]_2{}^+ + Ce^{4+} \rightarrow [C_5H_5MoSC_nH_{2n}S]_2{}^{2+} \quad (5b)$$

and have been isolated as tetrafluoroborate or hexafluorophosphate salts. These cationic complexes have also been characterized electrochemically, and two reversible electron transfers are observed for each complex at 0.13 and 0.79 V vs. SCE (Figure 1).[30] The data support the conclusion that the dithiolate bridged dimers have the same gross structural features in all three oxidation states. Results of conductivity and magnetic susceptibility measurements for the cationic dimers are included in the Experimental Section. The room temperature magnetic moments for $[C_5H_5MoSC_nH_{2n}S]^+$ of 1.68 $\mu_B$ are consistent with the presence of a single unpaired electron in each complex.[31] The effective magnetic moments of the dicationic complexes ($\sim$2.5 $\mu_B$) are in the range of those observed for molybdenum complexes with triplet ground states.[8] Complete characterization of possible magnetic interactions in these dimers must await variable temperature susceptibility measurements.

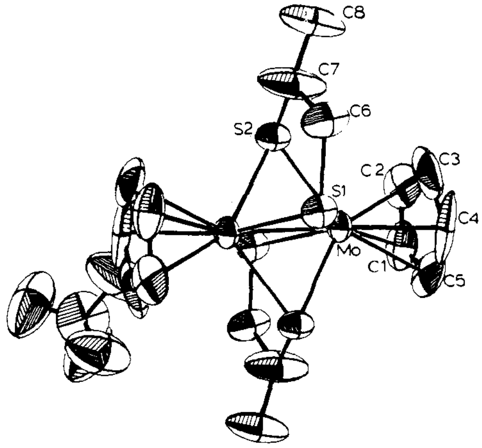


**Figure 2.** Perspective drawing of $[C_5H_5MoSC_3H_6S]_2BF_4$.

**Structural Characterization.** A single crystal of $[C_5H_5Mo(SC_3H_6S)]_2BF_4$ has been characterized by an X-ray diffraction study. The four sulfur atoms of the propanedithiolate ligands form a plane which bisects the metal-metal bond of the cation. The two equivalent halves of the molecule are related by a crystallographic inversion center. The tetrafluoroborate anions are positioned on a twofold axis of symmetry. A perspective view of the molecular structure and the numbering scheme used are shown in Figure 2. Final structural parameters and selected bond distances and angles are listed in Tables III and IV, respectively. Examination of intra- and intermolecular contacts shows no significant interactions.

The complex is similar in structure to the neutral and cationic cyclopentadienylmolybdenum dimers with bridging methyl thiolate ligands, reported previously.[23,26] Most of the bond lengths and angles involved in the molybdenum-sulfur framework of $[C_5H_5MoSC_3H_6S]_2{}^+$ are in close agreement with those reported for $[C_5H_5Mo(SCH_3)_2]_2{}^{0,1}$.[26] The Mo-Mo bond length is consistent with a single bond between metal ions.[32] The two-carbon bridge between sulfur atoms in the former complex results in inequivalent S-S distances. The distance between bridged sulfur atoms is 2.939 (3) Å, while the adjacent sulfurs from two different dithiolate ligands are separated by 2.838 (3) Å. Comparable sulfur-sulfur distances in other compounds have been associated with partial bonding interactions.[33-36] Extended Hückel calculations are in progress to assess the nature and extent of the interligand S-S interaction in the molecule of this study.

**Reactions of the Dithiolate Bridged Complexes.** We were interested in determining whether the dithiolate bridged complexes can be converted to the dimer with bridging disulfide ligands originally proposed as the product of reaction 2.[22] The low intensities of the parent ion and P − 42 peaks in the mass spectrum of $[C_5H_5MoSC_3H_6S]_2$ indicate that propene is readily lost under the ionizing conditions of the spectrometer. When the neutral complexes with dithiolate bridges are heated in the solid state in a sealed evacuated tube at 150-170 °C, ethene or propene is quantitatively evolved. The gaseous products have been identified by gas chromatography and mass spectroscopy. The remaining black molybdenum complex has the composition $[C_5H_5MoS_2]_n$, established by elemental analysis; the mass spectrum of the complex is consistent with a dimeric formulation. However, spectral characteristics originally reported for the disulfide bridged complex have not been observed.[22,37] The thermal product of this study is insoluble in common solvents; a polymeric rather than a dimeric structure may be formed during the heating process. The product does not react with olefins (vide infra).

The neutral dithiolate bridged complexes are also unstable in solution in organic solvents such as benzene, chloroform, and

**Table III.** Positional and Thermal Parameters for the Atoms of $[C_5H_5MoSC_3H_6S]_2BF_4$

| atom | $x^a$ | $y$ | $z$ | $B_{11}{}^b$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Mo | 0.319 37(4) | 0.282 69(8) | 0.036 82(5) | 2.56(4) | 3.57(4) | 2.78(4) | −0.29(3) | 0.14(3) | 0.04(3) |
| S1 | 0.226 43(13) | 0.264 53(24) | 0.148 41(16) | 4.78(12) | 3.74(12) | 2.53(10) | 0.15(9) | 1.03(9) | 0.15(8) |
| S2 | 0.226 64(13) | 0.464 54(24) | −0.028 91(16) | 4.91(12) | 3.08(11) | 3.07(11) | 0.61(9) | 1.19(8) | 0.30(8) |
| C1 | 0.4099(6) | 0.3741(22) | 0.1733(10) | 4.3(6) | 10.3(10) | 6.1(7) | −2.9(7) | −1.5(5) | −1.4(7) |
| C2 | 0.4282(8) | 0.2334(18) | 0.1520(16) | 4.2(6) | 7.6(10) | 10.2(11) | −0.3(6) | −4.1(7) | 0.7(8) |
| C3 | 0.4425(6) | 0.2263(24) | 0.0529(22) | 2.3(5) | 13.3(14) | 14.1(16) | −1.0 (7) | 1.2(8) | −4.5(13) |
| C4 | 0.4337(9) | 0.364(4) | 0.0082(12) | 5.7(8) | 17.4(17) | 7.2(9) | −8.0(10) | 0.6(6) | 1.5(12) |
| C5 | 0.4141(7) | 0.4564(15) | 0.0817(18) | 4.7(6) | 7.1(8) | 11.2(11) | −2.9(6) | −2.4(7) | 0.5(9) |
| C6 | 0.1948(6) | 0.4471(11) | 0.1733(7) | 9.6(7) | 3.8(5) | 4.5(5) | 0.4(5) | 3.4(5) | 0.1(4) |
| C7 | 0.2056(8) | 0.5532(13) | 0.0898(9) | 15.7(11) | 5.6(7) | 6.3(6) | 5.1(7) | 6.3(7) | 0.6(5) |
| C8 | 0.1591 | 0.6749(14) | 0.0691(10) | 15.7(11) | 6.2(7) | 6.9(7) | 6.3(8) | 4.1(7) | 0.5(5) |
| B1 | 0 | 0.312(4) | ¼ | 17.7(31) | 14.0(27) | 14.3(26) | 0 | 14.6(26) | 0 |
| F1 | 0.0626(7) | 0.2394(15) | 0.2611(13) | 14.6(10) | 15.9(11) | 21.5(13) | 8.4(8) | 11.3(9) | 11.4(10) |
| F2 | −0.0044(7) | 0.4020(13) | 0.3325(9) | 16.7(9) | 13.1(8) | 14.6(8) | −7.7(8) | 9.3(7) | −6.7(7) |

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. [b] The form of the anisotropic thermal ellipsoid is $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. The quantities given in the table are the thermal coefficients ×10 in units of Å$^2$.

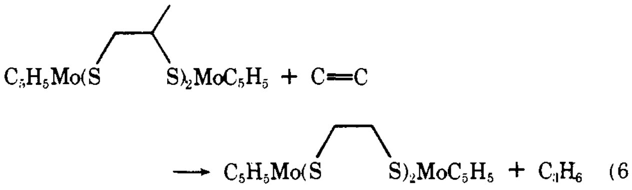
**Table IV.** Selected Bond Lengths and Angles for $[C_5H_5MoSC_3H_6S]_2BF_4$

| | | | |
|---|---|---|---|
| | | A. Bond Lengths (Å) | |
| Mo-Mo | 2.599(1) | S(1)-C(6) | 1.82(1) |
| Mo-S(1) | 2.427(2) | S(2)-C(7) | 1.84(1) |
| Mo-S(1)′[a] | 2.420(2) | C(6)-C(7) | 1.50(1) |
| Mo-S(2) | 2.421(2) | C(7)-C(8) | 1.40(2) |
| Mo-S(2)′ | 2.417(2) | $C-C_{(av)}$ | 1.38(2) |
| $Mo-C_{(av)}$[b] | 2.31(1) | $B-F_{av}$ | 1.34(2) |
| | | B. Bond Angles (deg) | |
| S(1)-Mo-S(1)′ | 115.14(6) | Mo-S(2)-C(7) | 109.1(4) |
| S(1)-Mo-S(2)′ | 71.67(7) | Mo′-S(2)-C(7) | 104.9(4) |
| S(1)-Mo-S(2) | 74.70(8) | S(1)-C(6)-C(7) | 112.7(7) |
| S(2)-Mo-S(2)′ | 115.00(6) | S(2)-C(7)-C(6) | 112.8(7) |
| Mo-S(1)-Mo′ | 64.86(6) | S(2)-C(7)-C(8) | 114.2(9) |
| Mo-S(1)-C(6) | 108.7(3) | C(6)-C(7)-C(8) | 120(1) |
| Mo′-S(1)-C(6) | 106.1(3) | $F-B-F_{av}$ | 112(2) |
| Mo-S(2)-Mo′ | 65.00(7) | $C-C-C_{av}$ | 108(2) |

[a] Atoms in symmetry position ½ − $x$, ½ − $y$, −$z$ are marked with a prime. All other atoms are at positions given in Table III. [b] Average bond lengths are given for the cyclopentadiene ring and for the tetrafluoroborate anion.

acetonitrile. Spectral and electrochemical changes are observed for solutions of $[C_5H_5MoSC_3H_6S]_2$ after ~10 h at room temperature and after 5-10 min at 60 °C both in air and under a nitrogen atmosphere. The nature of these new products is the subject of a detailed study and will be discussed in a later paper.

**Reactions with Alkenes and Alkynes.** We have found that the neutral molybdenum dimers with dithiolate bridges react with olefins in an unusual exchange reaction. For example, when a chloroform or benzene solution of $[C_5H_5MoSC_3H_6S]_2$ is stirred at 25 °C under 1-2 atm of ethylene for 24 h, the 1,2-*ethane*dithiolate bridged complex is the isolated product in 75% yield (reaction 6). The product molybdenum complex

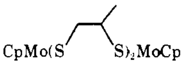
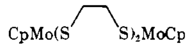
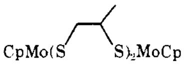
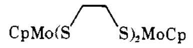
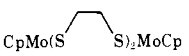
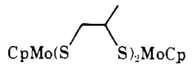
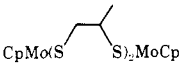
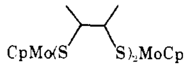
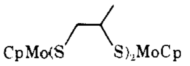
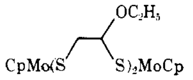
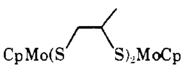
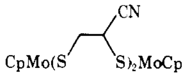
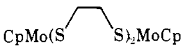
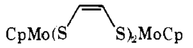
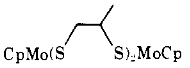
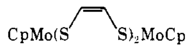
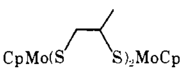
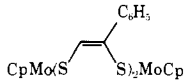
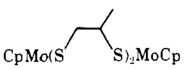
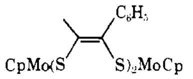


(6)

has been identified by comparison of its spectral and electrochemical characteristics with those of the dimer prepared from ethylene sulfide as described above. Free propene is identified by GC and mass spectral analysis. Reaction 6 can be reversed with excess propene at 65 °C, and the exchange reaction can also be effected with a variety of other alkenes. Terminal olefins with various substituents, e.g., acrylonitrile and ethyl vinyl ether, can be used to form the corresponding dithiolate bridged complexes. We have also observed the exchange reaction with a 1,2-disubstituted olefin, 2-butene. Conditions and yields for these reactions are summarized in Table V. The new dimeric molybdenum complexes have been characterized by elemental analyses and by their NMR spectra, which are consistent with the proposed dithiolate bridged structures. Other data such as IR, mass spectra, and cyclic voltammograms confirm the structural similarity of the products to the 1,2 propanedithiolate bridged complex. Characterization data for the new complexes is included in the Experimental Section and in Tables I and II. Tri- and tetrasubstituted olefins also react with $[C_5H_5MoSC_3H_6S]_2$, but the products do not appear to have the simple 1,2-dithiolate bridged structure. The latter reactions are under further study.

Alkynes react in an analogous exchange reaction with the dithiolate bridged complexes at 25 °C and 1 atm, and this provides a facile general method for the synthesis of new cyclopentadienylmolybdenum dimers with 1,2-*ethene*dithiolate bridges (e.g., reaction 3). Free ethene produced in reaction 3 is identified by gas chromatography. The NMR of the product resulting from the exchange with acetylene, $[C_5H_5MoSC_2H_2S]_2$, shows two singlets at 5.91 and 6.43 ppm (relative intensities 10:4). The chemical shift of the resonance assigned to the hydrogens of the bridging dithiolene ligands is characteristic of vinyl protons and similar to that observed for $Na_2S_2C_2H_2$ ($\delta$ 6.8 ppm).[38] The mass spectrum of the complex has peaks corresponding to parent ion and to the loss

**Table V.** Reaction Conditions for Alkene and Alkyne Exchange Reactions

| starting complex | reactant | conditions | isolated molybdenum product | % yield |
|---|---|---|---|---|
|  | ethene | 2 atm, 25 °C, $C_6H_6$, 60 h |  | 73 |
|  | ethene | 2 atm, 65 °C, $CHCl_3$, 48 h |  | 72 |
|  | propene | 2 atm, 80 °C, $C_6H_6$, 48 h |  | 40 |
|  | *cis*-2-butene | 2 atm, 65 °C, $CHCl_3$, 48 h |  | 35 |
|  | ethyl vinyl ether | 200:1 molar ratio, alkene:complex, 65 °C, $C_6H_6$, 24 h |  | 40 |
|  | acrylonitrile | 200:1 molar ratio, alkene:complex, 65 °C, $CHCl_3$, 48 h |  | 65 |
|  | acetylene | 1 atm, 25 °C, $CHCl_3$, 48 h |  | 54 |
|  | acetylene | 1 atm, 25 °C, $CHCl_3$, 48 h |  | 62 |
|  | phenylacetylene | 100:1 molar ratio, alkyne:complex, 65 °C, $CHCl_3$, 8 h |  | 30 |
|  | 1-phenyl-2-methylacetylene | 100:1 molar ratio, alkyne:complex, 75 °C, $CHCl_3$, 10 h |  | 30 |

of one and two $C_2H_2$ fragments from the parent. The spectrum at *m/e* 450 and below has major envelopes identical with those observed for the other dithiolate bridged complexes and supports the conclusion that the $Cp_2Mo_2S_4$ framework is intact in the complex. Products resulting from the exchange reaction with both mono- and disubstituted alkynes have also been characterized by several spectral methods. These are included in Table V. The complexes with ethenedithiolate bridges are stable in solution, and no reactions are observed with alkenes or with other alkynes.[39]

**Reaction of $[C_5H_5MoSC_2H_2S]_2$ with Hydrogen.** When a chloroform solution of $[C_5H_5MoSC_2H_2S]_2$ is stirred under ~2 atm of hydrogen at 55 °C, both 1,2-ethenedithiolate bridges of the compound are hydrogenated to produce $[C_5H_5MoSC_2H_4S]_2$. The reduced complex can be isolated in 50–60% yield and is identified by its NMR spectrum and cyclic voltammogram. The conditions required for hydrogenation are quite specific. No reduction occurs at 25 °C at hydrogen pressures up to 4.5 atm or with sodium borohydride at 65 °C. In addition, a solvent dependence has been observed; e.g., under conditions similar to those cited above, no hydrogenation occurs in benzene or in acetonitrile. The reaction of hydrogen with the complex containing phenyl substituted ethenedithiolate bridges, $[C_5H_5MoSCHC(C_6H_5)S]_2$, does not produce the hydrogenated complex; nor was free styrene detected. The NMR spectrum of the product suggests that decomposition of the basic structure has occurred.

The hydrogenation of $[C_5H_5MoSC_2H_2S]_2$ followed by acetylene exchange enables us to reduce acetylene to ethylene in a cyclic reaction couple (reactions 3 and 4). Ethylene has been produced in several consecutive cycles when acetylene and hydrogen are added in a stepwise sequence to solutions of $[C_5H_5MoSC_3H_6S]_2$ or $[C_5H_5MoSC_2H_2S]_2$. However, simultaneous addition of these reactants to the molybdenum dimers at 65 °C results in the production of only trace amounts of ethylene. Extensive decomposition of the dimeric molybdenum complexes occurs under these conditions. This decomposition may be related to reactions with acetylene at elevated temperatures. We are continuing our efforts to modify conditions for the hydrogenation step of the cycle, since it is expected that room temperature conditions will permit the catalytic reduction of acetylene by this system without external control of sequence.

## Conclusion

Sulfur ligands in many molybdenum-containing catalysts are believed to be important for their electronic and steric influences on the metal ion. The alkene and alkyne exchange reactions of the molybdenum dithiolate complexes, reported in this paper, illustrate that sulfur ligands may also participate in a catalytic cycle by interacting with the substrate. The possible relevance of these reactions to important molybdenum-sulfur catalyst systems should be considered. For example, the carbon-sulfur bond cleavage observed in this system may be related to similar basic processes which occur in hydrodesulfurization catalysts.[42,43] In addition, the application of this system, in which the reduction of acetylene to ethylene is catalyzed by a molybdenum complex with sulfur ligands, bears obvious similarities to basic aspects of nitrogenase chemistry.[8] Further studies (e.g., of the stereospecificity of the hydrogenated product, and of reactions with other substrates) will help to assess the relevance of this system to the mode of action of the enzyme.

## Experimental Section

**Materials.** Reagent grade bis(cyclopentadienylmolybdenum tricarbonyl) and molybdenum hexacarbonyl were purchased from Strem Chemicals. Propylene sulfide (98%) and ethylene sulfide (technical grade) were purchased from Aldrich and used without purification. Chloroform was purified immediately before use by passing it through a column of neutral alumina. Tetrahydrofuran was distilled from $LiAlH_4$. The acetonitrile used in cyclic voltammetric studies was distilled first from $P_4O_{10}$ and a second time from $CaH_2$. The supporting electrolyte, tetra-*n*-butylammonium fluoroborate, was purchased from Southwestern Analytical and dried in vacuo for 48 h.

Alkenes and alkynes used in the exchange reactions were reagent grade and used without further purification.

**Physical Measurements.** NMR spectra were measured at 90 MHz on a Varian 390 spectrometer. Chemical shifts are reported below with respect to tetramethylsilane. Infrared spectra of Nujol and hexachlorobutadiene mulls were recorded on a Perkin-Elmer 337 spectrophotometer. Mass spectra were obtained at 70-eV electron energies with a Varian MAT CH-5 spectrometer. Characteristic molybdenum isotope patterns were observed; *m/e* values are listed below for $^{96}$Mo. Conductivity measurements were carried out using a Serfass bridge Model RCM15 from Industrial Instruments. Magnetic susceptibilities were obtained using a Faraday balance equipped with a Sartorius Model 4433 electrobalance and a Varian V4005 electromagnet and V2900 power supply. Volatile products from the exchange reactions were identified using a 2-m Porapak N column in a Varian 920 gas chromatograph with thermal conductivity detector. Elemental analyses were provided by Spang Laboratories. Cyclic voltammetric studies were carried out with a Princeton Applied Research 174 A polarographic analyzer. Platinum wires were used as working and auxiliary electrodes. The saturated calomel reference electrode was separated from the test solution by a bridge tube tipped with a Vycor frit.

**X-ray Crystallography.** Examination of the dark green crystals of $[C_5H_5MoSC_3H_6S]_2BF_4$ on a Syntex P1 diffractometer operated at room temperature showed them to be monoclinic in a unit cell of dimensions $a = 18.226$ (1) Å, $b = 9.206$ (4) Å, $c = 12.911$ (5) Å, and $\beta = 100.83$ (3)°. The volume is 2128 Å$^3$. Systematic absences observed on the diffractometer are consistent with space group $C2/c$ ($C_{2n}{}^6$, no. 15). Assuming four molecules of the compound (mol wt 621.29) per unit cell the calculated density is 1.939 g/mL, in good agreement with the measured value of 1.93 g/mL. Intensity data were collected on a crystal (0.15 × 0.16 × 0.21 mm) mounted parallel to the long dimension using standard procedures as programmed by Syntex. Molybdenum K$\alpha$ radiation, monochromatized by a graphite crystal in the incident beam was used throughout the experiment. Some 1100 reflections were surveyed within a single quadrant over the range $2.0° < 2\theta < 40.0°$. Each reflection was measured using $\theta$–$2\theta$ scanning techniques with a scan rate of 4.0°/min and scan ranges calculated to start 1.0° below $2\theta$ for K$\alpha_1$ ($\lambda = 0.709\ 26$ Å) and to end 1.0° above $2\theta$ for K$\alpha_2$ ($\lambda = 0.713\ 54$ Å). Backgrounds were measured at the beginning and end of each scan. The data, monitored every 100 measurement cycles by three standard reflections, showed no significant variation. The data were corrected for Lorentz and polarization effects.[44] No correction was made for absorption, $\mu$(Mo K$\alpha$) = 15.68 cm$^{-1}$, because of the low linear absorption coefficient and the near equality of the dimensions of the crystal.

The position of the molybdenum atom was determined from a three-dimensional Patterson map. The remaining atoms were located in subsequent three-dimensional difference Fourier maps. Upon isotropic refinement,[45] the parameters converged with $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.082$ and $wR = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2 = 0.108$. Additional refinement with all atoms treated anisotropically converged with $R = 0.033$ and $wR = 0.043$. The standard deviation of an observation of unit weight was 1.587. All least-squares refinements were calculated using the 829 reflections which met the criterion of $F_o > 3.0\sigma(F_o)$.[45] Atomic scattering factors used were those for neutral atoms.[46] Anomalous dispersion effects were included in the scattering curves for molybdenum and sulfur.[46]

**Syntheses. $[C_5H_5MoSC_nH_{2n}S]_2$, 1 ($n$ = 2), 2 ($n$ = 3). A.** $C_5H_5MoH(CO)_3$[47] (1.6 g, 6.5 mmol) was dissolved in 20 mL of THF under a nitrogen atmosphere, and the appropriate episulfide (19.5 mmol) was added. After the solution was stirred for 12 h, the resulting red-brown precipitate was filtered. The complex was recrystallized from $CHCl_3$: **1**, yield 50%; **2**, yield 60%.

B. Under a nitrogen atmosphere $[C_5H_5Mo(CO)_3]_2$ (1.40 g, 2.9 mmol) was dissolved in 50 mL of THF and the appropriate episulfide (12.8 mmol) was added. The solution was refluxed for 5–10 h. After cooling, the solution was filtered and the brown precipitate was washed with ether. Slow evaporation of filtrate yielded additional product. The complex was recrystallized from $CHCl_3$. **1**: yield 80%. NMR in $CDCl_3$ (multiplicity, relative intensity, assignment): $\delta$ 1.80 (s, 8, $-SC_2H_4S-$), 5.08 ppm (s, 10, Cp). Highest *m/e* in mass spectrum (rel intensity): P, 506 (~2); P − $C_2H_4$, 478 (2); P − $2C_2H_4$, 450 (100); $Cp_2Mo_2S_3^+$, 418 (10); $Cp_2Mo_2S_2^+$, 386 (40); $Cp_2Mo_2S^+$, 354 (15). **2**: yield 66%. NMR in $CDCl_3$: $\delta$ 1.23 (m, 8, $-SCH(CH_3)$), 2.20 (m, 4, $-SCH_2-$), 5.11, 5.18, 5.24 ppm (3 s, 10, Cp). Highest *m/e* in mass spectrum: P, 534 (2); P − $C_3H_6$, 492 (2); P − $2C_3H_6$, 450 (100); $Cp_2Mo_2S_3^+$, 418, (10); $Cp_2Mo_2S_2^+$, 386, (45); $Cp_2Mo_2S^+$, 354 (16); $Cp_2Mo_2^+$, 322 (16).

**$[C_5H_5Mo(SC_nH_{2n}S]_2BF_4$, 3 ($n$ = 2), 4 ($n$ = 3).** The neutral complex **1** or **2** (1.0 mmol) was dissolved in 40 mL of dichloromethane and an ethanolic solution of $AgBF_4$ (0.195 g, 1.0 mmol) was added. The green solution was stirred for 30 min, then filtered and evaporated slowly to ~3 mL to induce crystallization of the product. The compound was recrystallized from acetonitrile/ethanol and a second time from dichloromethane/ethanol. **3**: yield 90%. $\mu_{eff}$ (25 °C): 1.66 $\mu_B$. $\Lambda_M(CH_3CN$, 28 °C) 139 $\Omega^{-1}cm^2\ mol^{-1}$; typical $\Lambda_M$ for 1:1 electrolyte in $CH_3CN$, 120–160 $\Omega^{-1}cm^2\ mol^{-1}$.[48] **4**: yield 90%. $\mu_{eff}$ (25 °C): 1.68 $\mu_B$. $\Lambda(CH_3CN$, 20 °C): 133 $\Omega^{-1}\ cm^2\ mol^{-1}$.

**$[C_5H_5MoSC_nH_{2n}S]_2(PF_6)_2$, 5 ($n$ = 2), 6 ($n$ = 3).** Complex **3** or **4** (0.40 mmol) was dissolved in 20 mL of EtOH/20 mL of $CH_2Cl_2$, and $(NH_4)_2Ce(NO_3)_6$ (0.22 g, 0.40 mmol) was dissolved in 25 mL of EtOH. The two solutions were combined and stirred for 20 min. The blue-green precipitate was filtered and redissolved in 10 mL of 5–6 M $HNO_3$. Addition of excess $NaPF_6$ induced immediate precipitation of the product. **5**: yield ~54%. $\mu_{eff}$ (25 °C) 2.73 $\mu_B$ (1.7 kOe). Values decrease slightly with increasing field strength: 2.54 (5.6 kOe), 2.47 $\mu_B$ (8.8 kOe). **6**: yield ~90%. $\mu_{eff}$ (25 °C): 2.66 (1.7 kOe), 2.51 (5.6 kOe), 2.46 $\mu_B$ (8.8 kOe). $\Lambda_m$(DMF, 23 °C): 126 $\Omega^{-1}\ cm^2\ mol^{-1}$. Typical $\Lambda_m$ for 2:1 electrolytes in DMF, 130–170 $\Omega^{-1}\ cm^2\ mol^{-1}$.[48]

**$[C_5H_5MoS_2]_n$.** Complex **1** or **2** was placed in a tube which was evacuated, sealed, and heated at 150–170 °C for 48 h. The remaining black solid was washed with $CHCl_2$ and THF and dried in vacuo. IR (cm$^{-1}$, HCBD mull): 3080, 3085 (w), 1425 (m), 1190 (m), 1010, 1020 (w) (Cp absorbances obscured by HCBD, 850–750 cm$^{-1}$), 430 (w).

**Alkene and Alkyne Exchange Reactions. Reaction with $C_2H_4$.** Compound **2** (0.20 g, 0.37 mmol) was dissolved in 15 mL of $CHCl_3$ in a 50-mL tube. The solution was evacuated on a vacuum line and 1 atm of $C_2H_4$ was added. The solution was frozen at −196 °C and an additional ~1 atm of $C_2H_4$ was condensed into the tube, which was sealed with a Kontes Teflon high-vacuum stopcock. The solution was stirred at 25 °C for 24–48 h. The gases were sampled, and propene was detected. The gas pressure was released and the solution was filtered to remove a small amount of black solid. The filtrate was slowly evaporated to ~2 mL and the resulting red-brown product was filtered, yield 72%. NMR and CV were identical with that reported for **1**.

**Reaction with $H_2C{=}CH(OC_2H_5)$.** Compound **2** (0.35 g, 0.64 mmol) was slurried in ~6 mL of benzene and 6 mL of ethyl vinyl ether in a sealed tube at 70 °C. After 48 h, the resulting red-brown solid was filtered. Slow evaporation of solvent to ~2 mL yielded more product, which was recrystallized from $CHCl_3$ with a few drops of ethyl vinyl ether added. Yield: ~40%. $^1$H NMR in $CDCl_3$: $\delta$ 1.07 (two t, 6, $-CH_3$), 1.72 (m, 2), 2.19 (m, 2), 3.38 (m, 2, $-OCH_2$),[38] 3.87 (m, 2, $-OCH_2-$),[38] 4.28 (m, 2), 5.05, 5.18, 5.30 ppm (3 singlets, 10, Cp).

**Reaction with $H_2C{=}CH(CN)$.** Compound **2** (0.28 g) was slurried in ~5 mL of $CHCl_3$ and 5 mL of acrylonitrile in a sealed tube at 70 °C. After ~3 days, the resulting yellow-brown product was filtered, washed with $CHCl_3$, DMF, and ether, and dried in vacuo, yield 65%. Product was not soluble enough for NMR characterization. IR: $\nu_{C\equiv N}$ 2212, 2230 cm$^{-1}$ (strong).

**Reaction with *cis*-2-Butene.** Compound **2** (0.5 mmol) was dissolved in ~10 mL of $CHCl_3$ and *cis*-2-butene was added in a procedure analogous to that reported for ethylene exchange. The product was recrystallized from $CHCl_3$, yield ~30%. The complex is more unstable in solution than the derivatives with monosubstituted bridges and difficult to isolate in a pure state. Anal. Calcd: C, 38.48; H, 4.63; S, 22.78. Found: C, 37.31; H, 4.40; S, 22.42. However, the NMR spectrum confirms the nature and gross purity of the product. NMR in $CDCl_3$: $\delta$ 1.18 (multiplet, 12, $-CH_3$), 2.00 (broad, 4, SCH−), 5.14, 5.18, 5.23 ppm (3 singlets, 10, Cp).

**Reaction with $HC{\equiv}CH$.** Compound **1** or **2** (1.0 mmol) was dissolved in 30 mL of $CHCl_3$ in a 1-L flask, the solution was evacuated, and 1 atm of $HC{\equiv}CH$ was added. The solution was stirred at 25 °C for 48 h. GC sampling of the gases established that ethylene (or propylene) and acetylene were present. The solution was filtered to remove a small amount of brown solid. The filtrate was slowly evaporated to ~5 mL to crystallize the yellow-brown product. The complex was recrystallized from $CHCl_3$ or benzene, yield 60%. NMR in $CDCl_3$: $\delta$ 5.91 (s, 10, Cp), 6.43 ppm (s, 4, $SC_2H_4S$). IR (Nujol mull): $\nu_{C=C}$ 1545 (strong), $\delta_{HC=}$ 685 cm$^{-1}$ (strong). Highest *m/e* in mass spectrum:

P, 502 (78); P − $C_2H_2$, 476 (18); P − $2C_2H_2$, 450 (100); $Cp_2Mo_2S_3^+$, 418 (31); $Cp_2Mo_2S_2^+$, 386 (41).

**Reaction with $C_6H_5C{\equiv}CH$.** Compound **2** (0.36 g, 0.67 mmol) was dissolved in ~10 mL of $CHCl_3$ and 5 mL of $C_6H_5C{\equiv}CH$ was added. The solution was stirred at 20 °C for 20 h, then filtered and evaporated to dryness. The green residue was washed with ether, leaving a yellow solid. This solid was recrystallized from $CHCl_3$ two times, washed with ether, and dried in vacuo, yield ~30%. NMR in $CDCl_3$: $\delta$ 5.92 (s, 10, Cp), 6.69 (broad m, 2, SCH=), 7.21 ppm (m, 10, $C_6H_5$–). IR (Nujol mull): $\nu_{C=C}$ 1480 (strong), $\delta_{HC=}$ 690 $cm^{-1}$ (strong). Highest *m/e* in mass spectrum: P, 654 (42); P − $CHC(C_6H_5)$, 552 (12); P − $2CHC(C_6H_5)$, 450 (100); $Cp_2Mo_2S_3^+$, 418 (10); $Cp_2Mo_2S_2^+$, 386 (27).

**Reaction with $C_6H_5C{\equiv}CCH_3$.** Compound **2** (0.26 g, 0.49 mmol) was dissolved in 20 mL of $CHCl_3$ and 5 mL of $CH_3C{\equiv}CC_6H_5$ was added. The solution was refluxed for 9 h. After the solution was cooled, it was filtered to remove a small amount of insoluble material. The filtrate was evaporated to ~3 mL to form yellow-green crystals. These were recrystallized from $CHCl_3$, yield ~30%. NMR in $CDCl_3$: $\delta$ 1.56 (broad, ~6, $-CH_3$), 5.90 (s, 10 Cp), 7.11 ppm (m, 10, $C_6H_5$–). IR (Nujol mull): $\nu_{C=C}$ 1490 (strong), $\delta_{HC=}$ 700 $cm^{-1}$ (strong). Highest *m/e* in mass spectrum: P, 682 (44); P − $(CH_3)CC(C_6H_5)$, 566 (10); P − 2 $CH_3CC(C_6H_5)$, 450 (100); $Cp_2Mo_2S_3^+$, 418 (6); $Cp_2Mo_2S_2^+$, 386 (23).

**Attempted Exchange Reactions with $[C_5H_5MoSC_2H_2S]_2$. A.** $[C_5H_5MoSC_2H_2S]_2$ (0.10 g, 0.2 mmol) was dissolved in 20 mL of benzene in a 500-mL flask, the solution was evacuated, and ~2 atm of ethylene was added. The solution was stirred at 25 °C for 48 h and at 65 °C for 24 h. No reaction occurred, and $[C_5H_5MoSC_2H_2S]_2$ was recovered and checked by NMR.

**B.** The procedure described above was repeated with methylacetylene, using 1 atm and stirring at 25 °C for 24 h. No reaction occurred and $[C_5H_2MoSC_2H_2S]_2$ was recovered and checked by NMR.

**Hydrogenation of $[C_5H_5MoSC_2H_2S]_2$.** $[C_5H_5MoSC_2H_2S]_2$ (0.15 g, 0.30 mmol) was dissolved in 5 mL of $CH_2Cl_2$ or $CHCl_3$ in a 50-mL vessel, and the solution was evacuated in freeze–pump–thaw cycles. One atmosphere of hydrogen was added to the solution, which was cooled to 196 °C. The reaction tube was sealed with a Kontes high vacuum Teflon stopcock, warmed to 60 °C, and stirred for 24 h. The yellow solution slowly turned red-brown. The excess hydrogen was released and the solution was filtered to remove a small amount of insoluble material. Slow evaporation of the filtrate resulted in crystallization of $[C_5H_5MoSC_2H_4S]_2$, yield ~50%, NMR and CV identical with those reported for **1.** When $CH_2Cl_2$ is the solvent, some product with only one reduced ligand, $(C_5H_5)_2Mo_2(SC_2H_2S)(SC_2H_4S)$, is also formed. NMR in $CDCl_3$: $\delta$ 1.77 (s, 4, $-SCH_2CH_2S-$), 5.41 (s, 10, Cp), 6.52 ppm (s, 2, –SCHCHS ).

**Attempted Hydrogenation Reactions. A.** The procedure described above was repeated using benzene and acetonitrile/THF (10 mL/3 mL) as solvents. Solutions were heated to 80–90 °C for periods of 1–3 days. $[C_5H_5MoSC_2H_2S]_2$ was recovered and checked by NMR.

**B.** $[C_5H_5MoSC_2H_2S]_2$ (0.05 g, 0.10 mmol) was dissolved in 25 mL of $CHCl_3$ and the solution was placed in a Parr Model 3911 hydrogenation apparatus. The solution was shaken under 52 psi of hydrogen for 3 days. No hydrogenation product was observed.

**C.** Under a nitrogen atmosphere, $[C_5H_5MoSC_2H_2S]_2$ (0.10 g, 0.20 mmol) was dissolved in 20 mL of THF/10 mL of MeOH and excess $NaBH_4$ (~2 mmol) was added. The solution was refluxed for 24 h. No reaction occurred and $[C_5H_5MoSC_2H_2S]_2$ was recovered and checked by NMR.

**D.** $[C_5H_5MoSCHC(C_6H_5)S]_2$ (0.03 g, 0.05 mmol) was dissolved in 10 mL of $CHCl_3$ in a 50-mL tube, the solution was evacuated, and 1 atm of $H_2$ was added to the tube cooled at −196 °C. The tube was sealed and stirred at 70 °C for 24 h. The color of the solution changed from yellow to purple. No hydrogenation product was detected by NMR. Decomposition products were not characterized.

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**Supplementary Material Available:** Table of observed and calculated structure amplitudes (3 pages). Ordering information is given on any current masthead page.

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# Low-Temperature Electronic Spectra of Solid Tetrakis(dimethyldimethylenephosphonium)dimolybdenum and -dichromium

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**Abstract:** The electronic absorption spectra of the title compounds, which contain quadruple Mo–Mo and Cr–Cr bonds, have been measured on crystalline powders pressed in KBr pellets at 5 K. The molybdenum compound has an absorption band at ca. 2000 cm$^{-1}$ and the low-temperature spectra reveal no less than five resolved vibrational progressions, each of which has a spacing (345 cm$^{-1}$) associated with that totally symmetric vibration in the electronic excited state that is approximately describable as $\nu_{\mathrm{Mo-Mo}}$. The Franck–Condon factors are of two different kinds, one associated with three of the progressions and the other with the two remaining ones. It is shown that this curious spectrum can be explained in detail using theory first discussed by Craig and Small for a transition where both orbitally allowed and vibronic contributions to intensity are of comparable magnitude. The analysis is much the same as that recently employed for the $Mo_2(O_2CCH_3)_4$ spectrum and adds valuable support to the assignment of the electronic transition occurring at ca. 20 000 cm$^{-1}$ in both $Mo_2(O_2CCH_3)_4$ and $Mo_2[(CH_2)P(CH_3)_2]_4$ as the $^1A_{2u} \leftarrow {}^1A_{1g}$ ($\delta^* \leftarrow \delta$) transition. The spectrum of the chromium analogue is blemished by decomposition products and could not be analyzed.

## Introduction

There is today a general, qualitative understanding of the nature of triple and quadruple bonds between transition-metal atoms, and to a certain degree even a quantitative understanding.[1] However, many points remain obscure and the interpretation of electronic absorption and photoelectron spectra still poses some challenging problems. This is especially true for the quadruply bonded dichromium compounds in general[2] and for certain of the quadruply bonded dimolybdenum compounds.

With regard to the latter, the tetracarboxylates, $Mo_2(O_2CR)_4$, have been particularly enigmatic. The first study[3] of their spectra using oriented crystals at low temperature was made by Cotton, Martin, Webb, and Peters, using $Mo_2(O_2CCHNH_3)_4(SO_4)_4 \cdot 4H_2O$; the lowest energy band, at ca. 20 000 cm$^{-1}$, was examined in detail. This band was shown to consist of vibrational progressions in *both z and xy polarizations,* with different origins in each, thus indicating an important role for vibronic (Herzberg–Teller) excitation in giving intensity to the band. Indeed, the observations were quite consistent with the assumption that the transition is purely vibronic and led, therefore, to the suggestion that the band should *not* be assigned to the $\delta^* \leftarrow \delta$ ($^1A_{2u} \leftarrow {}^1A_{1g}$) transition, since selection rules show that transition is electric dipole allowed with nonzero intensity for *z*-polarized light but no intensity in the *xy* plane.

This study was followed by the work of Trogler, Solomon, Trajberg, Ballhausen, and Gray,[4] who studied $Mo_2(O_2CCH_3)_4$. They also considered the transition to be purely vibronic in nature and proposed a specific assignment, viz., $\pi^* \leftarrow \delta$. Their spectra were much more complex and, hence, potentially informative because of the low symmetry of the crystal; but they did not fully account for all the details. This prompted Martin, Newman, and Fanwick[5] to reinvestigate the $Mo_2(O_2CCH_3)_4$ crystal spectrum.

Martin et al. showed that a correct analysis of the acetate crystal spectrum is possible only when it is recognized that one is dealing with a very unusual, though not entirely unprecedented, situation in which the orbital electric dipole and vibronic intensities are of comparable magnitude. This has a number of ramifications, including the appearance of overlapping progressions having different Franck–Condon factors. Unfortunately, the glycinate crystals first studied were so symmetrical and the spectra so simple that it was impossible to discover the true nature of the transition and the conclusion drawn in that study, though incorrect, was entirely justified by the meager data.

On the basis of their analysis, Martin et al. were led to the conclusion that the $\delta^* \leftarrow \delta$ transition in $Mo_2(O_2CR)_4$ compounds does, indeed, give rise to the lowest energy band in the visible spectrum at ca. 20 000 cm$^{-1}$. This conclusion is in accord with the general picture that has emerged for $\delta^* \leftarrow \delta$ transitions in M–M quadruple bonds and, in particular, fits nicely with the assignments for other species containing Mo–Mo quadruple bonds, viz., $[Mo_2Cl_8]^{4-}$,[6,7] $[Mo_2(SO_4)_4]^{4-}$,[8] and $[Mo_2(CH_3)_8]^{4-}$,[9] and with the results of SCF-X$\alpha$-SW calculations.[10]

Even though the spectral analysis and the assignment made by Martin et al. are reasonable, internally consistent, and satisfying, the fact that they hinge on a phenomenon so unusual as to be justifiably called anomalous might have the undesirable effect of allowing some lingering doubt to survive. It is, therefore, of importance that we can report another example of the same "anomalous" spectroscopic behavior, but one which is so straightforward and clear that it should serve both to erase any doubt about the aptness of the analysis of Martin

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