Dinuclear μ-Sulfido Complexes of Molybdenum with (Dimethylamino)ethyl-Substituted Cyclopentadienyl Ligands

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The cyclopentadienyl ligand with the (dimethylamino)ethyl substituent has been used in the synthesis of the dinuclear μ-sulfido molybdenum complex $(Me_2NCH_2CH_2CpMo(\mu\text{-}S))_2S_2CH_2$, **4**, and related derivatives. Complex **4** has been isolated and characterized by spectroscopic methods as well as by an X-ray diffraction study. The structure confirms a bis(μ-sulfido) derivative in which the dimethylamino substitutents of the Cp ligands are directed away from the Mo_2S_4 core. Protonation of **4** produces the dicationic complex with dimethylammonium substitutents, which is soluble in water and other polar solvents. Reaction of **4** with $[CuOTf]_2{\cdot}C_6H_6$ leads to the formation of a copper adduct $[(Me_2NCH_2CH_2CpMo(\mu\text{-}S))_2Cu(S_2CH_2)]OTF$, **6a**. NMR studies of **6a** in CD_2Cl_2 suggest that the copper ion is stabilized by two sulfido ligands and by weakly coordinated dimethylamino groups.

Introduction

We have recently reported the synthesis of water soluble dinuclear cyclopentadienylmolybdenum complexes containing bridging sulfide ligands.[1,2] The property of water solubility was achieved by the incorporation of carboxylate groups on cyclopentadienyl and/or sulfido ligands. The new water soluble derivatives were found to be quite similar in reactivity to previous analogues studied in organic solvents. For example, reversible reactions of the sulfido ligands with alkenes were observed to give dithiolate-bridged complexes, and when D_2O solutions of the dimers were placed under hydrogen pressure, the formation of HD and D_2 indicated that the complexes maintained the capability to activate hydrogen and promote HD exchange.

In earlier studies of $(CpMo(\mu\text{-}S))_2S_2CH_2$, we found that protic acid played a role in many of the reactions at the sulfido ligands, which resulted in multiple bond reductions or in carbon−heteroatom bond cleavage.[3−5] It has not been possible to extend this type of chemistry to aqueous solvents because the carboxylate-substituted complexes are not soluble in acidic solution. Rapid protonation of the carboxylate groups leads to neutral dimers, which are soluble only in DMSO or DMF solutions. In order to explore the aqueous chemistry of molybdenum sulfide dimers under acidic conditions, we have synthesized the analogous dinuclear complex in which the Cp ligand is substituted by the (dimethylamino)ethyl group. The product dissolves readily in acidic aqueous solutions with the formation of pendant dimethylammonium cations on each ligand. The synthesis and characterization of sulfido-bridged molybdenum dimers containing this ligand with both the neutral and protonated forms of the amino group are described in this paper.

Another feature of interest for the (dimethylamino)ethyl-substituted Cp ligand is the ability of the molecule to function as a chelating ligand. Many complexes containing this ligand or its permethylated analogue have been reported, and the intramolecular coordination of the dimethylamino group to the metal ion has been promoted by the generation of a vacant coordination site at the metal center.[6−8] Several other metal complexes with related amino-substituted Cp ligands have also been studied.[9−11] A much less common chelating mode for the ligand is the intramolecular coordination of the amino group to a second metal in mixed-metal complexes.[12] The dinuclear molybdenum sulfido complexes containing this ligand permit us to explore the intramolecular coordination of the ligand to an additional metal ion to form new heteronuclear sulfido-bridged complexes. Our initial studies of a trinuclear complex that incorporates a Cu(I) ion are described here.

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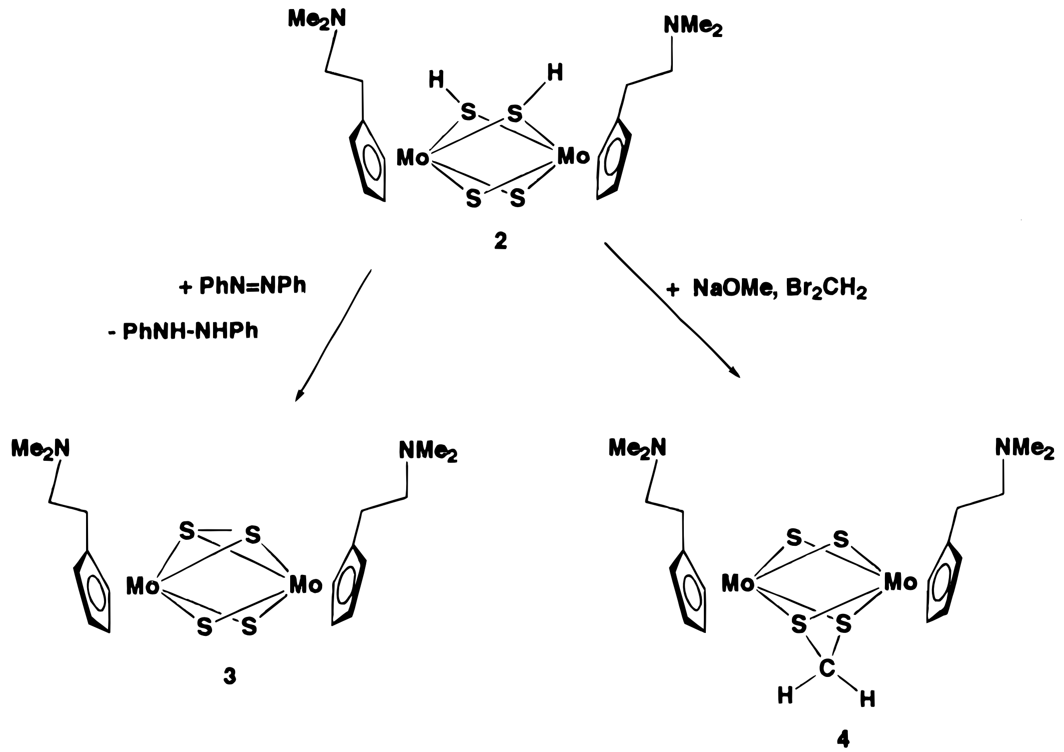
Scheme 1



Results and Discussion

Synthesis of $[Me_2NCH_2CH_2CpMo(\mu\text{-}S)_2(S_2CH_2)]$. ((Dimethylamino)ethyl)cyclopentadiene was synthesized by a slight variation on the reported procedure.[7b] The ligand was deprotonated with butyllithium and was used in the general procedure for the synthesis of $[Cp'Mo(CO)_3]_2$,[13] using an aqueous solution of $Fe(NO_3)_3\cdot 9H_2O$ as the oxidant. This procedure led to the isolation of the dicationic nitrate salt $[Me_2NHCH_2CH_2CpMo(CO)_3]_2(NO_3)_2$, which was deprotonated with triethylamine to give the neutral dimer, **1**. The closely related tricarbonyl dimer of molybdenum with ammoniumethyl substituents on the Cp ligands, $[H_3NCH_2CH_2CpMo(CO)_3]_2(NO_3)_2$, has been reported previously.[10]

Further reaction of **1** with sulfur and then with hydrogen proceeded under conditions similar to those reported for the unsubstituted Cp derivatives[14] to give $[Me_2NCH_2CH_2CpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$, **2**. Spectroscopic data for **2** confirmed the presence of SH ligands. The chemical shifts in the NMR spectrum at -1.54 and -1.61 ppm and the absorbance in the IR spectrum at 2421 cm^{-1} for the SH ligands are similar to those observed for the unsubstituted Cp analogue. No evidence for hydrogen bonding interactions between the S−H groups and the amino nitrogens was observed.

Dehydrogenation of **2** with azobenzene led to the disulfide-bridged dimer $(Me_2NCH_2CH_2CpMo)_2(\mu\text{-}S)_2(\mu\text{-}S_2)$, **3**, while deprotonation of **2** in the presence of dibromomethane produced the methanedithiolate-bridged complex $(Me_2NCH_2CH_2CpMo(\mu\text{-}S))_2S_2CH_2$, **4**, see Scheme 1. Complex **4** was one of the principal target compounds of this study and was characterized by microanalyses, and several spectroscopic techniques. The deep blue complex showed maxima in the visible spectra at 520 and 740 nm, very similar to those recorded for the parent complex with unsubstituted Cp ligands. The ^1H NMR spectrum for **4** indicates that the product contains two planes of symmmetry perpendicular to and coincident with the M−M vector. The Cp protons occur as two sets of pseudotriplets between 6 and 6.5 ppm. Two upfield triplets at 2.81 and 2.63 ppm are assigned to the methylene groups of the aminoethyl substituents, and the singlet for the dimethylamino protons occurs at 2.26 ppm. The latter chemical shift is characteristic of an uncoordinated dimethylamino group.[6−8] Other spectroscopic data are included in the Experimental Section.

The cyclic voltammetry of **4** at a glassy carbon electrode was studied in dichloromethane solution. At scan rates of 100 mV/s, an irreversible reduction was observed at -1.80 V vs Fc; some reversible character for this process was observed only at very fast scan rates, e.g., at 10 000 mV/s, the ratio of peak currents, i_{pc}/i_{pa}, was 1.8. The low stability of the reduced product in dichloromethane probably results from nucleophilic attack of the reduced complex on the solvent. Nucleophilic attack on dichloromethane has been characterized for sulfido ligands in a related electron-rich dimer.[15] The reduction process for the analogous product with unsubstituted Cp ligands occurred at a similar potential in acetonitrile solution. In this solvent the reduction was found to be quasi-reversible at scan rates of 100 mV/s with $i_{pc}/i_{pa} = 2$.

Two irreversible oxidations were observed for **4** at 0.05 and 0.30 V vs Fc. The first process was coupled to a reduction at -0.71 V, observed on the reverse scan. Although the first anodic wave is tentatively attributed

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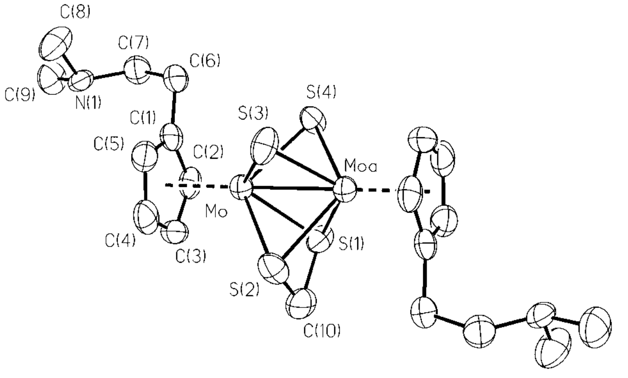

Figure 1. Perspective drawing and numbering scheme for one of two equivalent orientations of **4**.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for 4

Mo−Mo	2.579(2)	Mo−C(1)	2.378(8)
Mo−C(2)	2.293(8)	Mo−C(3)	2.303(9)
Mo−C(4)	2.326(9)	Mo−C(5)	2.368(9)
Mo−S(1)	2.41(3)	Mo−S(2)	2.42(3)
Mo−S(3)	2.35(3)	Mo−S(4)	2.45(3)
S(1)−C(10)	1.78(4)	S(2)−C(10)	1.81(3)
S(3)···S(4)	3.011		
Mo−S(1)−Mo	64.0(7)	Mo−S(2)−Mo	65.2(8)
Mo−S(3)−Mo	65.7(7)	Mo−S(4)−Mo	64.2(7)
S(1)−Mo−S(2)	66.4(9)	S(1)−Mo−S(3)	112.5(10)
S(1)−Mo−S(4)	72.2(9)	S(2)−Mo−S(3)	73.3(9)
S(2)−Mo−S(4)	116.2(11)	S(3)−Mo−S(4)	80.9(8)
S(1)−C(10)−S(2)	95(2)	C(2)−C(6)−C(7)	111.0(7)
C(6)−C(7)−N(1)	113.0(8)		

to oxidation at a metal-centered molecular orbital, the nature of the subsequent reaction has not been established. In contrast, the analogue with the unsubstituted Cp ligand was oxidized quite reversibly ($i_{pa}/i_{pc} = 1$, $\Delta E = 180$ mV) and at a lower potential, −0.18 V vs Fc, in acetonitrile. The second oxidation observed for **4** is unique to the derivative with the aminoethyl−Cp ligands and is assigned to an oxidation of the amino groups.[16]

Single crystals of **4** were isolated from an ether solution, and an X-ray diffraction study was carried out. The molecule crystallized in a centrosymmetric space group, indicating a disorder of the bridging ligands. A model was refined with 50% occupancy of the methanedithiolate ligand in the two available positions. A perspective drawing of one of the two equivalent orientations of the complex is shown in Figure 1, and selected bond distances and angles are give in Table 1. The cyclopentadienyl ligand is coordinated in the conventional η^5-bonding mode with the (dimethylamino)ethyl substituents oriented away from the molybdenum sulfide core of the molecule. The molybdenum−molybdenum distance of 2.579(2) Å is among the shortest to be observed in the quadruply-bridged sulfur dimers.

Although the reactivity of the dinuclear methanedithiolate-bridged derivatives of molybdenum has been extensively studied, a crystal structure of one of these derivatives has not been reported previously. Previous molecular orbital calculations on this complex (unsubstituted Cp ligand) indicated that the extensive sulfur-based reactivity observed for the structure was consistent with the presence of two bridging sulfido atoms rather than a $\mu^2-\eta^2$ disulfido ligand.[17] The calculations also indicated that there was an antibonding interaction between these two bridging ligands. In the structure of **4**, the distance between S(3) and S(4) was found to be 3.01 Å, which is considerably longer than the bond length normally observed for disulfide ligands (2.0−2.1 Å). The observed distance is identical to that reported for the distance between the two sulfido ligands in $(Cp^*Mo)_2(\mu\text{-}S)_2(\mu\text{-}S_2)$[18a] and slightly longer than the sulfur-sulfur distance in the symmetrically arranged quadruply-bridged structure of $[CpMo(SMe)_2]_2$.[18b]

Synthesis of Water-Soluble Derivatives $[(Me_2NHCH_2CH_2CpMo(\mu\text{-}S))_2S_2CH_2]X_2$. Complex **4** was protonated with dilute nitric acid or with HPF_6 to form the dicationic derivatives with dimethylammonium groups, **5a** when X = NO_3, **5b** when X = PF_6, e.g., Scheme 2. The complexes were isolated and characterized spectroscopically. In the ^1H NMR spectrum of **5a** in D_2O, the resonances for the (dimethylammonium)ethyl substituents are significantly shifted downfield relative to those of **4**; the two methylene triplets were observed at 3.36 and 2.99 ppm and the Me_2N singlet occurred at 2.76 ppm. Smaller downfield shifts were observed for the protons of the Cp ligands. The infrared spectrum of **5a** (KBr pellet) showed broad bands in the region from 2300 to 2800 cm^{-1}, characteristic of a tertiary ammonium ion. Although several examples of N−H···S hydrogen bonding interactions have been reported recently for metal complexes with different types of amino/thiolate ligands,[19] the spectroscopic data for **5** do not provide any clear evidence for hydrogen bonding between the ammonium N−H groups and the sulfido ligands.

The solubility of **5a** in neutral water at 25 °C was determined to be 0.16 M, similar to that reported for the carboxylate-substituted derivative $(NaO_2CCpMo(\mu\text{-}S))_2S_2CH_2$.[1] The PF_6 salt was significantly less soluble in water. Both **5a** and **5b** also showed some solubility in other polar solvents, such as MeOH, CH_3CN, and propylene carbonate. A pH titration of an aqueous slurry of **4** was carried out with nitric acid. A single inflection point was observed for the protonation of the independent Cp ligands, and the pK_a for the protonated derivative was determined to be 8.10. This value indicates that the coordinated ligand is more acidic than the trimethylammonium ion which has a pK_a of 9.81.

Reactions with Alkenes. In previous work, we have explored the potential of the dinuclear molybdenum complexes to function as selective olefin binding agents in olefin separation schemes. As a part of that study, we examined how substituents on the Cp ligands altered the rates of reversible olefin binding to the sulfido ligands and the stabilities of the adducts,[20] and the reactions of **4** and **5** with olefins were also investi-

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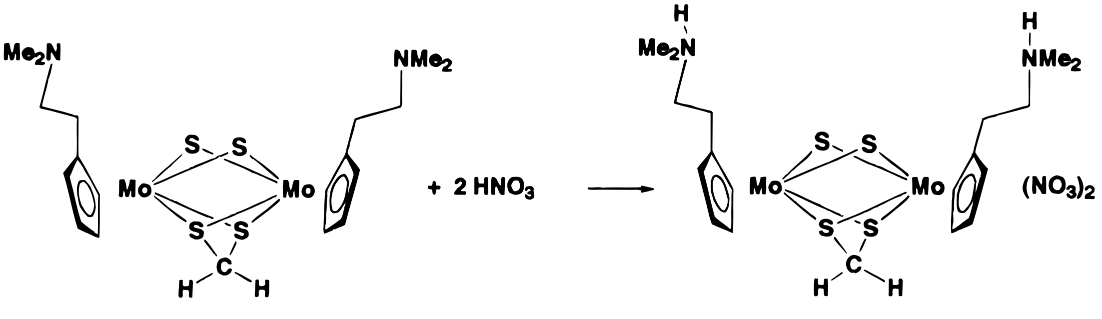
Scheme 2



4

5

gated in this context. In chloroform solution, **4** reacted rapidly with alkenes to form the expected alkanedithiolate-bridged products. These adducts differed from the previously studied analogues with unsubstituted Cp or with MeCp ligands in that they were much more prone to olefin dissociation. For example, attempts to isolate the ethanedithiolate complex $(Me_2NCH_2CH_2CpMo)_2(S_2CH_2)(SC_2H_4S)$ by partial evaporation of the solvent led to ethylene dissociation and recovery of **4**. Olefin adducts of **5** in aqueous solution also showed limited stability; known reactions of the adducts with protic acid[21] contributed to decomposition in these systems. In order to compare the effects of the Cp (dimethylammonium)ethyl substituents on the rates of olefin addition, the kinetics of the addition of *trans*-2-hexene to **5b** in MeOH solution were studied by visible spectroscopy. The value of k_{on} at 24 °C was found to be 0.043 $M^{-1}\ s^{-1}$, about an order of magnitude smaller than the rate constant for the addition of *trans*-2-hexene to $(NaO_2CCpMo(\mu\text{-}S))_2(S_2CH_2)$ under identical conditions. This decrease in rate may be a result of the greater steric requirements of the pendant aminmonium group relative to the carboxylate substitutent, which provides more effective shielding of the μ-sulfido ligands from olefin approach.

Reaction of $(Me_2NCH_2CH_2CpMo(\mu\text{-}S))_2(S_2CH_2)$ with Cu(I) Ion. When the Cp substituents are in an eclipsed conformation, **4** has the appropriate geometry to provide a tetrahedral N_2S_2 ligand donor set for an additional metal ion. Complex **4** reacted with $[Cu(OTf)]_2{\cdot}C_6H_6$ in dichloromethane or with $[Cu(CH_3CN)_4]PF_6$ in acetonitrile to form a new cationic product which incorporates the Cu(I) ion. The resulting products $[(Me_2NCH_2CH_2CpMo(\mu\text{-}S)_2Cu(S_2CH_2)]X$, **6a**, when X = OTF, and **6b**, when X = PF_6, were isolated and characterized spectroscopically. The mass spectrum for **6a** showed an envelope of peaks centered at *m*/*e* = 670, which corresponds to the parent ion of the cation. The intensities of the peaks agree well with the pattern calculated for isotopes of one copper and two molybdenum ions. In the infrared spectrum, a strong band at 1262 cm^{-1} was consistent with the presence of ionic triflate[22] and the conductivity of 150 $\Omega^{-1}\ cm^2\ mol^{-1}$ in acetonitrile was characteristic of a 1:1 electrolyte.[23] The cyclic voltammetry of **6a** was studied under conditions similar to those used for **4**. A quasi-reversible reduction (ΔE = 182 mV) and oxidation (ΔE = 122mV) were observed at −1.09 and −0.04 V, respectively, vs ferrocene. Additional poorly defined waves were observed at more anodic potentials. Addition of the copper ion to the dinuclear complex makes the complex both easier to oxidize and reduce compared to **4**, but since the nature of the frontier orbitals in **6** have not been determined, a more detailed discussion of the electrochemistry is premature. The visible spectrum of **6a** in dichloromethane showed maxima (ϵ = 2000 $M^{-1}\ cm^{-1}$) at 563 and 826 nm, while in acetonitrile, a new band near 750 nm was also observed.

The reaction of $[Cu(OTf)]_2{\cdot}C_6H_6$ with the analogous dimer with unsubstituted Cp ligands in dichloromethane has also been studied. The product that formed was insoluble in most organic solvents, and mass spectral data showed a strong *m*/*e* for the formula $[(CpMo(\mu\text{-}S))_2S_2CH_2)]_2Cu^+$, as well as a much weaker envelope for $[(CpMo(\mu\text{-}S))_2S_2CH_2]_2Cu_2{}^{+2}$. In this system, the copper appears to serve as a bridging ion between sulfido ligands of two dinuclear units. The bridging interaction was disrupted when a phosphine ligand was added, and the phosphine adduct $[(CpMo(\mu\text{-}S))_2(S_2CH_2)CuPPh_3]OTf$ has been isolated and characterized. In contrast, in the reaction of **4** with copper(I), mass spectral evidence for the interaction of two dinuclear units with the copper ion was not observed.

The NMR spectrum of **6a** in the coordinating solvent CD_3CN showed significant differences compared to the spectrum in chlorinated solvents, such as $CDCl_3$ or CD_2Cl_2. In CD_3CN, the N−Me resonance was observed at 2.26 ppm and two distorted triplets (an A_2B_2 pattern) were observed for the methylene protons of the Cp substitutent at 2.71 and 2.84 ppm. These chemical shifts are very similar to those observed for the aminoethyl group of the ligand in the starting reagent **4** (in $CDCl_3$) at 2.26, 2.63, and 2.81 ppm, respectively. The resonance for the methanedithiolate protons, which is very sensitive to substrate binding at the sulfido ligands in these types of dimers, showed a significant downfield shift to 3.32 ppm, compared to a shift of 2.64 ppm for the same ligand in **4**. The data suggest that the Cu(I) ion is coordinated to the sulfido ligands in the dimer, but does not interact with the dimethylamino groups in this solvent. One or two acetonitrile ligands may complete the coordination sphere of the copper ion in this environment. When the same sample of **6a** was dissolved in $CDCl_3$, the singlet for the dimethylamino protons was shifted downfield to 2.40 ppm and both multiplets for the methylene protons overlapped at 2.81 ppm. A broadened resonance for the methanedithiolate

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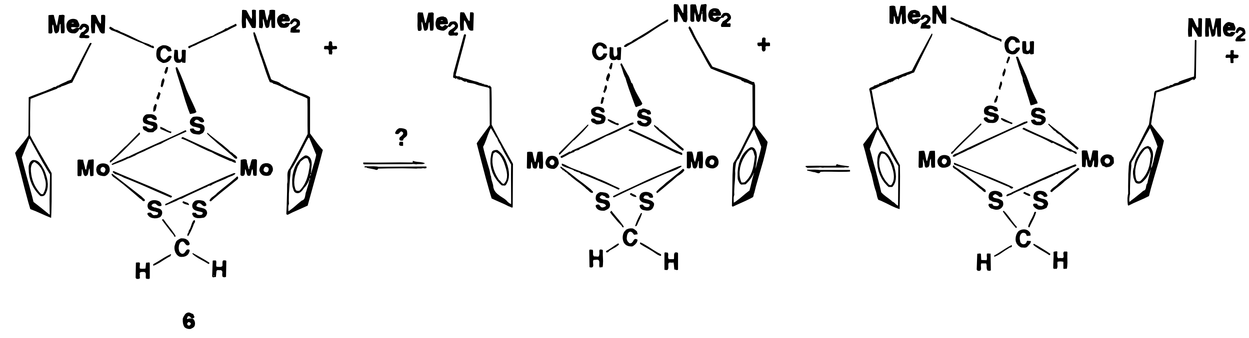
Scheme 3



protons remained near 3.3 ppm. The spectrum of **6a** in CD_2Cl_2 showed very similar chemical shifts over a temperature range from 0 to −80 °C. The resonances recorded at low temperatures broadened, but did not show distinct evidence for inequivalent (dimethylamino)ethyl groups.

In previous NMR studies of mononuclear complexes containing the (dimethylamino)ethyl substitutent on the Cp ligand, downfield shifts of both the dimethylamino and $N-CH_2$ resonances have been observed upon coordination of the ligand arm to the metal ion.[6−8] For the trinuclear complex reported here, coordination of the dimethylamino group to the copper ion involves a different type of chelate ring formation than those observed in the mononuclear derivatives and the NMR chemical shifts are not so diagnostic. Nevertheless the downfield shifts observed for this ligand in chlorinated solvents suggest that the amino groups do interact with the copper ion to some degree. We are unable to distinguish between the possibilities of a tetrahedral geometry about the copper ion, **6**, or a three-coordinate geometry which would arise from a fluxional interaction of (dimethylamino)ethyl groups, as shown in Scheme 3. The latter situation may be favored for the labile Cu(I) ion, as it would result in a 48-electron trinuclear product. However, we were unable to resolve resonances for inequivalent dimethylamino groups in the NMR spectrum over the temperature range studied.

X-ray Diffraction Study of a Cu(I) Adduct of 4. Several attempts to crystallize **6a** from dichloromethane solution have been made, but these efforts have been unsuccessful. Over an extended period of time in this solvent, an uncharacterized decomposition reaction occurs and a dark solid precipitates from solution. A single crystal isolated from such a dichloromethane decomposition reaction was characterized by an X-ray diffraction study and found to be a trinuclear Mo_2Cu complex with a chloride ligand coordinated to the trigonal copper ion, $(Me_2NCH_2CH_2CpMo(\mu\text{-}S))_2(S_2CH_2)$-CuCl, **7**. A closely related complex resulting from the reaction of $(Cp^*Mo)_2(\mu\text{-}S)_2(\mu\text{-}S_2)$ with Cu(I)Cl has been proposed previously.[24] A perspective drawing and numbering scheme for **7** are shown in Figure 2, and selected bond distances and angles are given in Table 2. The (dimethylamino)ethyl substituents are directed away from the Mo_2S_4 core of the molecule in an orientation very similar to that observed for **4**. The bond distances and angles in the dinuclear molybdenum portion of the cation are also very similar to those reported for the starting reagent **4**. In the packing arrangement of **7**, no close intermolecular contacts were observed.

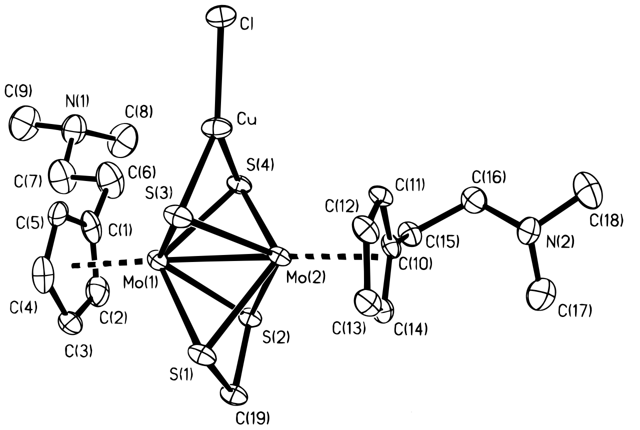


Figure 2. Perspective drawing and numbering scheme for **7**.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 7

Mo−Mo	2.5839(6)	Mo−S(1)	2.4671(14)
Mo−S(2)	2.4589(14)	Mo−S(3)	2.4254(14)
Mo−S(4)	2.3972(14)	S(1)−C(19)	1.838(5)
S(2)−C(19)	1.826(5)	S(3)−Cu	2.194(2)
S(4)−Cu	2.206(2)	Cu−Cl	2.178(2)
Mo(1)−Cu	3.0704(8)	Mo(2)−Cu	2.8076(8)
Mo−S(1)−Mo	63.24(3)	Mo−S(2)−Mo	63.70(3)
Mo−S(3)−Mo	64.21(4)	Mo−S(4)−Mo	65.06(4)
S(3)−Cu−Cl	135.57(6)	S(4)−Cu−Cl	126.89(6)
S(3)−Cu−S(4)	97.16(5)	Mo(1)−Cu−Cl	155.65(5)
Mo(2)−Cu−Cl	151.60(5)	S(3)−Cu−Mo(1)	51.65(4)
S(3)−Cu−Mo(2)	56.71(4)	S(4)−Cu−Mo(1)	50.88(4)
S(4)−Cu−Mo(2)	55.86(4)		

The coordination of the Cu ion in **7** is trigonal planar with a S−Cu−S angle of 97.16° and larger Cu−S−Cl angles of 135.5° and 126.9°. The Cu−S and Cu−Cl bond distances fall within the normal range for these bonds. Some asymmetry is observed in the copper coordination to the dimer. The plane defined by S(3), S(4), Cu, C(l) and that of S(1), S(2), C(19) are not directly aligned and the angle between the normals of these planes is 12.2°. As a result, the copper ion is tilted slightly toward one molybdenum center and the Mo(2)−Cu distance of 2.8076(8) Å is significantly shorter than the Mo(1)−Cu distance of 3.0709(8) Å. Although a M−M′ bonding interaction cannot be assigned solely on the basis of distance, the asymmetry, which does not appear to be a result of packing forces, suggests that there may be a weak bonding interaction between Cu and Mo(2). The distance is similar to previously reported Cu−Mo distances in mixed-metal M_4S_4 cubane and M_3S_3 incom-

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(24) Brunner, H.; Grassl, R.; Wachter, J.; Nuber, B.; Zeigler, M. L. *J. Organomet. Chem.* **1990**, *393*, 119.

plete cubane structures.[24,25] Examples of Mo−M′ bonding interactions have been observed previously for clusters derived from the Mo_2S_4 core,[26] and extended Huckel calculations have provided a bonding description for one such system.[17]

Summary and Conclusions

Cyclopentadienyl ligands with functionalized side chains, such as the (dimethylamino)ethyl substituent, have been shown or proposed in previous work to be useful in several applications, including water solubilization of organometallic complexes, anchoring of cyclopentadienyl species to surfaces, preparation of oligonuclear metal complexes, and light stabilization of coordinatively unsaturated complexes.[6] In this work, we have shown that the ((dimethylamino)ethyl)cyclopentadienyl ligand can be incorporated into dinuclear molybdenum complexes with μ-sulfido ligands in order to provide water solubility in acidic aqueous solution. We have also begun to explore the role of this ligand in the formation of new heteronuclear metal sulfido clusters. Our preliminary results suggest that it may be possible to introduce to the dinuclear complexes a third metal ion that is only lightly stabilized by amino coordination and, therefore, quite reactive with other substrates or ligands. Further work to establish the characteristics of such trinuclear complexes, as well as further applications of this ligand in the modified dinuclear molybdenum systems, are planned.

Experimental Section

Reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and degassed before use. (Dimethylamino)ethyl chloride hydrochloride, molybenum hexacarbonyl, and $[CuOTF]_2 \cdot C_6H_6$ were purchased from Aldrich and used without purification.

Synthesis of $(CH_3)_2NCH_2CH_2C_5H_4$. A procedure reported previously[7b] was slightly modified. A solution of NaCp (0.2 mol in 100 mL THF) was added dropwise over 20 min to a stirred suspension of $(CH_3)_2NCH_2CH_2Cl \cdot HCl$ (11.5 g, 0.08 mol) in 100 mL of THF, cooled to 0 °C. The resulting white suspension was stirred at room temperature for 20 h. The reaction mixture was then treated with 400 mL of water, and the THF layer was collected. The water layer was further extracted with pentane (2 × 200 mL). The combined organic extracts were washed with water (100 mL) and then dried over Na_2SO_4. After filtration, the solvent was removed in vacuo to give a pale brown oil. The oil was distilled into a receiver cooled to 0 °C, and a colorless fraction which distilled between 25−30 °C (0.01 mmHg) was collected; yield, 8.7 g. The ^1H NMR spectrum ($CDCl_3$) showed the product to be a 10:1 mixture of the desired product and dicyclopentadiene. The oil was extracted with three portions of dilute HCl (150 mL of ca. 0.48 M, 72 mmol), and the HCl/H_2O extracts were added directly to a mixture of NaOH (4 g), water (60 mL), and diethyl ether (100 mL). The ether solution of the free amine was separated from the basic (pH 13) aqueous layer. The basic solution was further extracted with 2 × 100 mL of diethyl ether and 100 mL of petroleum ether (35−60 °C). The combined organic extracts were dried over Na_2SO_4, filtered, and the solvent removed under water aspirator pressure to give a light brown oil. This oil was vacuum distilled into a receiver cooled to 0 °C to give a colorless oil (bp 26−27 °C at 0.01 mmHg). Yield: 6.4 g, 59%. The oil is best stored under nitrogen in the freezer. MS(EI$^+$): m/z 137 (P$^+$). ^1H NMR (300 MHz, $CDCl_3$) showed the product to be a 1:1 mixture of 1,2- and 1,3-isomers: δ 6.40 (overlapped m, 3H, Cp), 6.23 (m, 1H, Cp), 6.15 (m, 1H, Cp), 6.01 (m, 1H, Cp), 2.91 (d, 2H, CH_2 of Cp), 2.87 (d, 2H, CH_2 of Cp, isomer 2), 2.47 (overlapped m, 4H, CH_2-CH_2), 2.22 (d, 12H, $N(CH_3)_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.38 (Cp, ipso), 144.94 (Cp, ipso), 134.56 (CH of Cp), 133.74 (CH of Cp), 132.40 (CH of Cp), 130.69 (CH of Cp), 126.90 (CH of Cp), 126.50 (CH of Cp), 59.71 (N−CH_2), 59.02 (N−CH_2), 45.40 (NMe_2), 45.37 (NMe_2), 43.34 (CH_2−Cp), 41.22 (CH_2−Cp), 29.02 (Cp−CH_2), 28.24 (Cp−CH_2).

Synthesis of $[(CH_3)_2NHCH_2CH_2C_5H_4Mo(CO)_3]_2(NO_3)_2$. n-BuLi (14 mL, 1.6 M in hexane, 23 mmol) was added to a stirred solution of the free ligand (3 g, 22 mmol) in 50 mL of THF at 0 °C over 5 min. After the mixture was stirred for another 15 min at 0 °C, the pale yellow solution was added via a cannula to a stirred suspension of $Mo(CO)_6$ (6 g, 22 mmol) in 100 mL of THF. The resulting mixture was refluxed for 62 h. At this stage the solution was clear and showed a dark yellow color. The solution was concentrated to ca. 50 mL in vacuo, and a deoxygenated solution of $Fe(NO)_3 \cdot 9H_2O$ (8.8 g, 22 mmol) in 50 mL of water was added dropwise over 30 min. The color of the solution turned deep red, and a fine crystalline red solid precipitated. The mixture was stirred for another 30 min and the red solid was filtered off in air, washed with cold water, and dried in vacuo. The red solid was contaminated with unreacted $Mo(CO)_6$, which was removed by sublimation at room temperature. The remaining product was extracted with methanol and filtered to remove some insoluble yellow-brown solid, and the filtrate was evaporated to give a red solid. Yield: 7.3 g, 44%. ^1H NMR (300 MHz, D_2O): δ 5.36 (br s, 4H, Cp), 5.20 (br s, 4H, Cp), 3.15 (t, 4H, CH_2−N), 2.75 (m, 16H, CH_2−Cp and $N(CH_3)_2$). MS (FAB$^+$): m/z 634 (P−2(NO_3)).

Synthesis of $[(CH_3)_2NCH_2CH_2C_5H_4Mo(CO)_3]_2$, 1. $[(CH_3)_2NHCH_2CH_2C_5H_4Mo(CO)_3]_2(NO_3)_2$ (7.3 g, 9.7 mmol) was dissolved in MeOH and titrated with dilute triethylamine (50% v/v in methanol) until the pH of the solution was ∼9. The deep red solution was concentrated to ca. 50 mL on a rotoevaporator. Water, 400 mL, was added slowly to precipitate a pink-red solid, which was filtered in air, washed with water, and dried in vacuo for 48 h. In some cases, the product was recrystallized from benzene. Yield: 5.14 g (37%, based on $Mo(CO)_6$). IR (KBr): ν_{CO} 1944, 1922, 1906, 1885 cm^{-1}. MS (FAB$^+$): m/z 633 (P$^+$). ^1H NMR (300 MHz, C_6D_6): δ 4.93 (pseudo t, 4H, Cp), 4.81 (pseudo t, 4H, Cp), 2.30 (t, 4H, CH_2−N), 2.17 (t, 4H, CH_2−Cp), 2.00 (s, 12H, $N(CH_3)_2$). ^{13}C NMR (75 MHz, C_6D_6): δ 93.80 (Cp), 91.44 (Cp), 60.97 (N−CH_2), 45.13 ($N(CH_3)_2$), 27.04 (Cp−CH_2). Anal. Calcd for $C_{24}H_{28}N_2O_6Mo_2 \cdot 0.5C_6H_6$: C, 48.29; H, 4.65. Found: C, 48.50; H, 5.42.

Synthesis of $[(CH_3)_2NCH_2CH_2C_5H_4Mo(\mu\text{-}S)(\mu\text{-}SH)]_2$, 2. A solution of **1** (1.8 g, 2.85 mmol) and sulfur (0.74 g, 2.88 mmol) in 120 mL of dry, N_2-saturated benzene was heated at ∼80 °C (oil bath) under N_2 for 3 days. The reaction mixture has a deep red-brown color at this stage and a small amount of solid. The solvent was removed in vacuo to leave a dark red solid. This red solid was dissolved in 150 mL of dry THF. The solution was degassed by three freeze−pump−thaw cycles, and H_2 (ca. 3 atm) was added to the Schlenk tube. The mixture was stirred at room temperature for 3 days; H_2 and H_2S (caution) were vented in a hood, fresh H_2 was added, and the mixture was stirred for two more days. The deep purple-red solution was filtered through Celite (1 in. thick), and the Celite bed was washed with 2 × 20 mL of THF. The solvent was removed from the filtrate in vacuo to give a dark purple solid. Yield: 1.5 g, 88.5%. The crude product was satisfac-

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torily used in further syntheses without further purification. MS (FAB$^+$): m/z = 595 (P$^+$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.23 (s, 8H, Cp), 2.68 (t, 4H, CH_2−N), 2.62 (t, 4H, CH_2−Cp), 2.24 (s, 12H, $N(CH_3)_2$), −1.54 and −1.61 (2s, 2H, SH). IR (KBr): 2421 cm^{-1} (ν_{S-H}).

$[((CH_3)_2NCH_2CH_2C_5H_4Mo)_2(\mu\text{-}S))_2(\mu\text{-}S_2)]$, 3. To a solution of **2** (0.4 g, 0.67 mmol) in 20 mL of CH_2Cl_2 was added a solution of azobenzene (0.39 g, 2.14 mmol) in 20 mL of CH_2Cl_2 with stirring. The mixture was stirred for 4 h, during which the initial purple color changed to deep green. The solvent was removed in vacuo to give a brown solid, which was washed with ether until the washings were colorless and dried in vacuo. Yield: 0.37 g, 92%. MS (FAB$^+$): m/z = 593 (P$^+$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.23 (pseudo t, 4H, Cp), 6.15 (pseudo t, 4H, Cp), 2.71 (t, 4H, CH_2−N), 2.55 (t, 4H, CH_2−Cp), 2.25 (s, 12H, $N(CH_3)_2$). Anal. Calcd for $C_{18}H_{28}N_2S_4Mo_2$: C, 36.48; H, 4.76. Found: C, 36.59; H, 4.62.

Synthesis of $[((CH_3)_2NCH_2CH_2C_5H_4Mo(\mu\text{-}S))_2(S_2CH_2)$, 4. To a solution of **2** (0.5 g, 8.4 × 10^{-5} mol) in 50 mL of THF was added CH_2Br_2 (0.146 g, 8.40 × 10^{-5} mol) followed by dropwise addition of a freshly prepared solution of NaOMe (0.04 g Na, 1.70 × 10^{-4} mol) in 3 mL of MeOH over 10 min. During this addition, the purple solution started turning blue. The blue solution was stirred for 45 min at room temperature and filtered through a Celite bed (1 in. thick), and the Celite was washed with 2 × 20 mL of THF. The solvent was removed from the filtrate to leave a blue sticky residue, which was extracted with 30 mL of CH_2Cl_2 and loaded onto a basic alumina column. A deep blue band was eluted with CH_2Cl_2/MeOH (50:1). The solvent was removed from the deep blue fraction to give a sticky solid, which solidified on prolonged pumping (5 days). The complex could be recrystallized from Et_2O. Yield: 0.36 g, 71%. MS (FAB$^+$): m/z = 607 (P$^+$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.40 (pseudo t, 4H, Cp), 6.37 (pseudo t, 4H, Cp), 2.81 (t, 4H, CH_2−N), 2.64 (s, 2H, S_2CH_2), 2.63 (t, 4H, CH_2−Cp), 2.26 (s, 12H, $N(CH_3)_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 120.93 (Cp), 99.81 (Cp), 98.08 (Cp), 60.54 (N−CH_2), 45.46 ($N(CH_3)_2$), 33.52 (S_2CH_2), 29.68 (Cp−CH_2). Vis (propylene carbonate): 729 (ϵ = 2590 M^{-1} cm^{-1}) 588 (2000 M^{-1} cm^{-1}) 505 nm (sh). Anal. Calcd for $C_{19}H_{30}N_2S_4Mo_2$: C, 37.62; H, 4.98; N, 4.61; S, 21.14. Found: C, 38.00; H, 5.06; N,4.61; S, 20.54.

X-ray Diffraction Study of $[((CH_3)_2NCH_2CH_2C_5H_4Mo(\mu\text{-}S))_2(S_2CH_2)$, 4. The complex crystallized in the triclinic space group $P\bar{1}$. The asymmetric unit is comprised of half of the molecule, with the remainder generated by inversion. As a result, the bridging atoms must be disordered. Refinement in non-centrosymmetric P1 was unsatisfactory. The refined model assigns 50% site occupancy to each of the bridging atoms, S(1), S(2), S(3), S(4), C(10), H(10a), H(10b). All non-hydrogen atoms were refined with parameters for anisotropic thermal motion. Hydrogen atoms were refined using a riding model for both the geometry and the isotropic hydrogen thermal parameter. Hydrogen thermal parameters were modeled at 1.2 times the value of the thermal parameter for the host atom. The largest residual peak in the final difference map, 0.990 e Å^3, is located 1.12 Å from Mo and is likely an absorption artifact. No unusual features are present in the final map.

$[((CH_3)_2NHCH_2CH_2C_5H_4Mo(\mu\text{-}S))_2(S_2CH_2)](NO_3)_2$, 5. Complex **4** (0.1 g) was dissolved in 20 mL of CH_2Cl_2. Dilute HNO_3 (5% v/v in H_2O) was added dropwise with stirring until the solution was colorless, precipitating an oily residue. The solvent was decanted, and the residue was washed with 3 × 20 mL of ether, which solidified the oil. The solid was dried in vacuo. Yield: 0.12 g (100%). ^{1}H NMR (300 MHz, D_2O) δ 6.52 (pseudo t, 4H, C_5H_4) 6.50 (pseudo t, 4H, C_5H_4) 3.36 (t, 4H, CH_2−N), 2.99 (t, 4H, CH_2−Cp), 2.82 (s, 2H, SCH_2S), 2.76 (s, 12H, $N(CH_3)_2$). IR (KBr): 2650 cm^{-1} (br, tertiary amine salt). Anal. Calcd for $C_{19}H_{32}N_4O_6S_4Mo_2$: C, 31.12; H, 4.30; N, 7.64; S, 17.50. Found: C, 30.86; H, 4.21; N, 7.26; S, 17.26.

Protonation of **4** with dilute HPF_6 (30% in H_2O) resulted in $[(CH_3)_2NHCH_2CH_2C_5H_4Mo(\mu\text{-}S)_2(S_2CH_2)](PF_6)_2$. ^{1}H NMR (300 MHz, D_2O): δ 6.52 (pseudo t, 4H, C_5H_4) 6.49 (pseudo t, 4H, C_5H_4) 3.33 (t, 4H, CH_2−N) 2.97 (t, 4H, CH_2−Cp) 2.78 (s, 2H, SCH_2S) 2.73 (s, 12H, $N(CH_3)_2$). Vis (H_2O): 574 (ϵ = 2500 M^{-1} cm^{-1}), 743 (ϵ = 2460 M^{-1} cm^{-1}) 530, 389 nm (sh).

Reactions with Olefins. The gaseous olefin, propene or ethene, was bubbled through the deep blue solution of **4** (10 mg) in $CDCl_3$ in a NMR tube until the solution turned light brown (ca. 2 min). The complex was identified by ^{1}H NMR spectroscopy in the presence of excess olefin. Propene adduct, $[(CH_3)_2NCH_2CH_2C_5H_4Mo)_2(S_2CH_2)(S_2CH_2CHCH_3)]$ ^{1}H NMR (300 MHz, $CDCl_3$: δ 5.87 (AB, 2H, S_2CH_2), 5.37 (m, 1H, C_5H_4), 5.31 (m, 1H, C_5H_4), 5.23 (m, 4H, C_5H_4), 5.18 (m, 2H, C_5H_4), 2.47 (m, CH_2−N), 2.30 (m, CH_2−Cp), 2.14 (s, 12H, $N(CH_3)_2$), 1.86 (m, 1H, CH), 1.06 (d, 3H, CH_3), 0.947 (dd, 1H, CH_2). In measurements carried out in sealed tubes, the K_{eq} for adduct formation was found to be 1300 M^{-1} at room temperature. Attempts to isolate this complex resulted in a product which was a mixture of **4** and the propylene adduct. The adduct lost propylene even in solid state. Ethene adduct, $[((CH_3)_2NCH_2CH_2C_5H_4Mo)_2(S_2CH_2)(SCH_2CH_2S)]$. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.87 (s, 2H, S_2CH_2), 5.22 (pseudo t, 4H, C_5H_4), 5.17 (pseudo t, 4H, C_5H_4), 2.47 (t, 4H, CH_2−N), 2.21 (t, 4H, CH_2−Cp), 2.14 (s, 12H, $N(CH_3)_2$), 1.62 (s, 4H, SCH_2CH_2S).

Synthesis of $[((CH_3)_2NCH_2CH_2C_5H_4Mo(\mu\text{-}S))_2Cu(S_2CH_2)]X$. $[Cu(CH_3CN)_4](PF_6)$ (37 mg, 9.9 × 10^{-5} mol) was added to a solution of **4** (60 mg, 9.9 × 10^{-5} mol) in 10 mL of CH_3CN. Immediately the color of the solution changed from blue to wine-red. The mixture was stirred at room temperature for 4 h. The solvent was removed from the solution to give a dark solid. MS (FAB$^+$): m/z = 670, (P$^+$ for cation). ^{1}H NMR (300 MHz, CD_3CN): δ 6.49 (pseudo t, 4H, C_5H_4), 6.41 (pseudo t, 4H, C_5H_4), 3.32 (s, 2H, S_2CH_2), 2.83 (t, 4H, CH_2-N), 2.66 (t, 4H, CH_2−Cp); 2.22 (s, 12H, $N(CH_3)_2$). Despite consistent spectroscopic data, elemental analyses were low in nitrogen. Anal. Calcd for $C_{19}H_{30}N_2S_4CuMo_2PF_6$: C, 28.00; H, 3.71; N, 3.43. Found: C, 27.94; H, 3.72; N, 2.65.

$[CuOTf]_2\cdot C_6H_6$ (0.049 g, 0.10 mmol) was added to a solution of **4** (0.12 g, 0.19 mmol) in 10 mL of CH_2Cl_2. The solution, which was initially blue, changed to a purple color as it was stirred for 8 h at room temperature. The solution was filtered, and the filtrate was evaporated to give the triflate salt of the title complex. The product could be further purified by dissolving in CH_2Cl_2, filtering the solution, and reducing the volume of the filtrate. MS (FAB$^+$): m/z 670 (P$^+$ of cation), 623 (P−CH_2). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 6.43 (pseudo t, 4H, C_5H_4), 6.38 (pseudo t, 4H, C_5H_4), 3.21 (s, 2H, S_2CH_2), 2.88 (m, 8H, Cp−H_2CH_2), 2.41 (s, 12H, $N(CH_3)_2$). IR (KBr): 1266 cm^{-1}, OTf. Λ_M (CH_3CN): 150 Ω^{-1} cm^2 mol^{-1}.

Reaction of $(CpMo(\mu\text{-}S))_2S_2CH_2$ with $[Cu(OTf)]_2\cdot C_6H_6$. $(CpMo(\mu\text{-}S))_2S_2CH_2$[14] (0.080 g, 0.17 mmol) was dissolved in dry dichloromethane, and $[Cu(OTf)]_2\cdot C_6H_6$ (0.043 g, 0.086 mmol) was added with a solid addition tube. The reaction mixture was stirred at room temperature for 15 h to give a purple-black precipitate, which was insoluble in $CHCl_3$, CH_3CN, and Me_2CO and very slightly soluble in MeOH. The product gave a deep purple solution in DMSO, which after a short time turned to a deep blue color. ^{1}H NMR (DMSO-d_6): 6.71 (s, 10H, Cp), 3.34 (s, 2H, S_2CH_2). Mass spec (FAB$^+$): m/z 992 ($[CpMo(\mu\text{-}S))_2S_2CH_2]_2Cu$ (relative intensity, 100), 1054 ($[CpMo(\mu\text{-}S))_2S_2CH_2]_2Cu_2$ (relative intensity, 20).

The same reaction was set up and stirred for 2 h. At this time, trimethylphosphine (1 M in hexanes, 0.24 mL) was added via gas tight syringe and the reaction was stirred at room temperature overnight. The solvent was removed, and the product was recrystallized by diffusion of diethyl ether into dichlormethane solution at room temperature. Yield: 0.080 g, 47%. ^{1}H NMR ($CDCl_3$): δ 6.39 (s, 8H, Cp), 3.93 (br s, 2H, S_2CH_2), 1.36 (d, J = 8.8 Hz, 9H, PMe_3). ^{31}P NMR ($CDCl_3$): −30.11 (br s). MS (FAB$^+$): m/z 603 (P$^+$ of cation), 524 (P−

Table 3. Crystal Data for Compounds 4 and 7

	4	**7**
formula	$C_{19}H_{30}Mo_2N_2S_4$	$C_{19}H_{30}ClCuMo_2N_2S_4$
fw	606.57	705.56
crystal syst	triclinic	monoclinic
unit cell dimensions		
a (Å)	7.745(2)	13.9718(3)
b (Å)	8.147(2)	12.8172(2)
c (Å)	10.119(2)	14.33270(10)
α (deg)	112.79(3)	90
β (deg)	101.90(3)	104.3050(10)
γ (deg)	90.95(3)	90
volume, Å^3	572.7(2)	2487.11(7)
space group	$P\bar{1}$	$P2_1/c$
Z	1	4
D_{calcd} (Mg/m^3)	1.759	1.884
λ(Mo Kα) (Å)	0.710 73	0.710 73
temp (K)	298(2)	123(2)
scan type	modified ω scan	ω scans
θ range (deg)	2.73−24.99	1.50−23.25
independent reflections	1990	3560
no. of reflns observed	1515	2965
abs corr	XABS2[a]	semiempirical from ψ−scans
R[b]	0.0635	0.0332
Rw[c]	0.1521	0.0665
GOF	1.008	1.143
largest peak in final diff map (e$^-$/Å^3)	0.990 and −1.084	0.617 and −0.612

[a] XABS2 (Parkin, S. R.; Moezzi, B.; Hope, H. *J. Appl. Crystallogr.* **1995**, *28*, 53) calculates 24 coefficients from a least-squares fit of (1/A vs $\sin^2(q)$) to a cubic equation in $\sin^2(q)$ by minimization of F_o^2 and F_c^2 differences. [b] $R = R_1 = \sum| |F_o| - |F_c| |/\sum|F_o|$. [c] $R_w = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

Me_3), 460 (P−$CuPMe_3$). Vis (CH_2Cl_2): 758 (ϵ = 3357 M^{-1} cm^{-1}), 540 (ϵ = 4540 M^{-1} cm^{-1}), 408 (ϵ = 4540 M^{-1} cm^{-1}). Elemental analyses for these compounds were consistently found to be low in sulfur. Anal. Calcd for $C_{15}H_{21}S_5O_3F_3Mo_2CuP$: C, 23.93; H, 2.81; S, 21.29. Found: C, 24.01; H, 2.51; S, 18.41.

X-ray Diffraction Study of ($Me_2NCH_2CH_2CpMo(\mu$-S$))_2(S_2CH_2)CuCl$, 7. The crystal was mounted in the 123 K N_2 coldstream of a Siemens LT-2A low-temperature apparatus attached to a Siemens SMART CCD diffractometer. Initial cell parameters were determined from an analysis of three sets of 20 0.3° ω scans. Least-squares calculations performed with 5262 strong reflections, $I > 10\sigma(I)$, harvested from the data collection returned the final cell dimensions. Data were corrected for Lorentz and polarization effects, as well as for absorption.

Structure solution via direct methods revealed all non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic parameters for thermal motion. Hydrogens were placed at calculated positions and allowed to ride on the position of the parent atom. Isotropic hydrogen thermal parameters were modeled at 1.2 times the equivalent isotropic thermal parameter of the parent atom. The largest peaks in the final difference map, approximately 0.62 e Å^{-3}, were located near metal positions. Selected details of the data collection and structure solution are given in Table 3.

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Supporting Information Available: Complete tables of crystal data and refinement details, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates for **4** and **7** (17 pages). Ordering information is given on any current masthead page.

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