Table VIII. Fractional Monoclinic Coordinates for $(Me_2Si)_{16}$ (2)[a]

atom	X	Y	Z
Si(1)	0.18807 (8)	-0.09623 (7)	0.35493 (7)
Si(2)	0.11039 (8)	0.05189 (8)	0.33627 (8)
Si(3)	0.21333 (7)	0.17970 (8)	0.40059 (7)
Si(4)	0.27068 (8)	0.25270 (8)	0.29383 (7)
Si(5)	0.41154 (7)	0.33530 (7)	0.36814 (7)
Si(6)	0.53896 (7)	0.23555 (7)	0.38121 (7)
Si(7)	0.68359 (7)	0.29745 (7)	0.47716 (7)
Si(8)	0.79799 (7)	0.17644 (7)	0.50724 (6)
C(1)	0.3048 (3)	-0.0759 (3)	0.34139 (27)
C(2)	0.1172 (3)	-0.1767 (3)	0.25706 (27)
C(3)	0.0450 (4)	0.0704 (4)	0.2087 (3)
C(4)	0.0203 (3)	0.0497 (3)	0.3936 (4)
C(5)	0.30821 (28)	0.13631 (28)	0.50857 (25)
C(6)	0.1470 (3)	0.2756 (3)	0.4383 (3)
C(7)	0.2847 (3)	0.1666 (3)	0.20548 (26)
C(8)	0.1801 (3)	0.3438 (4)	0.2276 (3)
C(9)	0.4142 (3)	0.38040 (28)	0.48412 (27)
C(10)	0.4167 (3)	0.44150 (28)	0.29405 (28)
C(11)	0.51916 (27)	0.11251 (28)	0.42184 (28)
C(12)	0.5443 (3)	0.2242 (3)	0.26108 (27)
C(13)	0.6809 (3)	0.3487 (3)	0.58890 (28)
C(14)	0.7183 (3)	0.3982 (3)	0.4148 (3)
C(15)	0.77303 (27)	0.09489 (28)	0.40403 (25)
C(16)	0.91396 (28)	0.2352 (3)	0.5245 (3)

[a] The numbers given in parentheses are the estimated standard deviations of the least significant digits.

the E maps, and the carbon atoms were located by subsequent electron density difference maps. The full-matrix least-squares refinements of the structures were based on F_o and by using the relections with $F_o > 3\sigma(F_o)$. Atomic form factors were taken from Cromer and Waber[25] and that for hydrogen was taken from Stewart, Davidson, and Simpson.[26] The structures were refined to convergence by using isotropic thermal parameters for the non-hydrogen atoms, and electron density difference maps were used to locate positions for the hydrogen atoms. It also became apparent at this point that there was one molecule of water of crystallization in the lattice of **1**.

The final cycles of refinement of **1** and **2** assumed that the non-hydrogen atoms vibrate anisotropically and included the hydrogen atoms as idealized isotropic fixed contributors. The water of crystallization in **1** was treated as an idealized group with anisotropic oxygen and isotropic hydrogen atoms. The final values of the discrepancy indices $R_1 = \Sigma ||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$ are given in Table VI. The final difference electron density maps were featureless. Final atomic parameters are reported in Tables VII and VIII for **1** and **2**, respectively.

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Registry No. 1, 72059-96-2; **2**, 72059-99-5.

Supplementary Material Available: Tables of anisotropic thermal parameters and hydrogen atom positions as for **1** and **2** (5 pages); a listing of observed and calculated structure factors (×10) (45 pages). Ordering information is available on any current masthead page.

(24) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1971**, *27*, 368.

(25) Cromer, D. T.; Waber, J. T. *International Tables for X-ray* crystallogrphy; Kynoch Press: Birmingham, England, 1974; Vol. 4, pp 99-101, Table 2.2B.

(26) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

Synthesis and Reactivity of a Dimeric Molybdenum(III) Complex with a Bridging Hydrosulfido Ligand

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Abstract: A (cyclopentadienyl)molybdenum(III) dimer with a bridging hydrosulfido ligand $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SH)$ (**3**) (MeCp = $CH_3C_5H_4$) has been synthesized by an unusual reaction of molecular hydrogen with the paramagnetic species $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}S)$ (**5**). Mechanistic features of this reaction are discussed. Complex **3** has been characterized by spectral methods, and the reactivity of the hydrosulfido ligand has been investigated. The ligand is deprotonated by methoxide ion and alkylated by alkyl halides in the absence of base. Activated alkenes and alkynes insert into the S-H bond of the ligand in the absence of base to form new dimers with alkyl or alkenyl thiolate ligands. The regio- and stereochemistries of the products of these reactions have been characterized and compared to those of reactions of the conjugate base of **3**, which has been synthesized independently. Complex **3** also serves as a hydrogen atom transfer agent to certain unsaturated molecules. The relevance of these systems as models for the hydrodesulfurization catalysts is discussed.

The hydrodesulfurization (HDS) of organosulfur compounds is an important industrial process used in the purification of petroleum feedstocks. The most common catalysts are derived from sulfided molybdenum and cobalt ions supported on alumina.[1] In addition to the hydrogenolysis of carbon-sulfur bonds, hydrogenation of unsaturated compounds and isomerization of olefins also occur over this heterogeneous catalyst.[2] The mechanisms of the reactions are not well understood, although it is generally thought that a MoS_2 phase is the catalytic site for the HDS reaction. Mechanistic proposals for HDS have suggested that

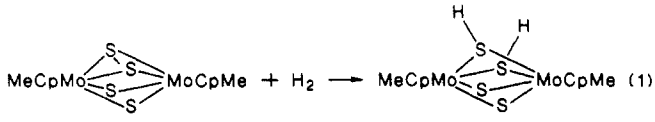
(1) (a) Schuman, S. C.; Shalit, H. *Catal. Rev.* **1970**, *4*, 245. (b) Massoth, F. E. *Adv. Catal.* **1978**, *27*, 265. (c) Grange, P. *Catal. Rev.—Sci. Eng.* **1980**, *21*, 135.

(2) Mitchell, C. P. H. In *Catalysis*; Kemball, C., Ed.; The Chemical Society: London, 1977; Vol. 1, p 223; Vol. 4, p 203 (Special Periodical Report).

0002-7863/86/1508-5482$01.50/0

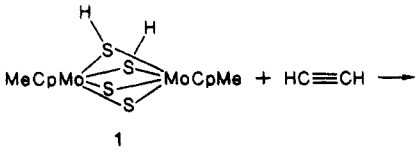
the reaction proceeds through three elementary steps:[3] (1) dissociative chemisorption of H_2 on sulfido ligands to form SH ligands, (2) adsorption of the organosulfur compound at a vacant coordination site of molybdenum, (3) hydrogen atom transfer from SH ligand to the adsorbed organosulfur compound accompanied by carbon–sulfur bond cleavage in this molecule. During the course of the surface studies, questions concerning the acidity, nucleophilicity, and other aspects of the reactivity of hydrosulfido ligands have been raised.[4] The synthesis and characterization of discrete hydrosulfido complexes of molybdenum[5] provides the opportunity to obtain fundamental information on the chemical properties of S–H ligands and, in particular, on their ability to function as a source of hydrogen in substrate reduction.

We have previously reported the reactions of molecular hydrogen with sulfido bridged dimers of (cyclopentadienyl)molybdenum as a novel synthetic route to a dimeric molybdenum(IV) complex[6] with two μ-hydrosulfido ligands, **1**, e.g. reaction 1.[7,8]



1

Several ligand-based reactions of this dimer have been characterized.[8] However, the complex does not effect a stoichiometric or catalytic reduction of molecules with carbon–carbon unsaturation. The interaction of acetylene with the hydrosulfido complex, for example, results in the elimination of molecular hydrogen and the formation of a dimer with two (alkene)dithiolate ligands (reaction 2).[9] The tendency of complex **1** to eliminate molecular



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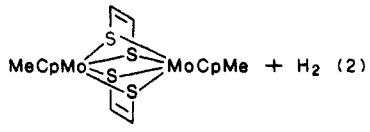


hydrogen in the presence of coordinating substrates has hindered efforts to study the hydrogen transfer properties of the ligands in this complex.

A related sulfido-bridged molybdenum(IV) dimer with a (methane)dithiolate ligand, $(MeCpMo(\mu\text{-}S))_2S_2CH_2$ (**2**), has been found to function as a versatile catalyst for the hydrogenation of unsaturated carbon–carbon and carbon–nitrogen bonds and for the hydrogenolysis of a variety of molecules, including carbon

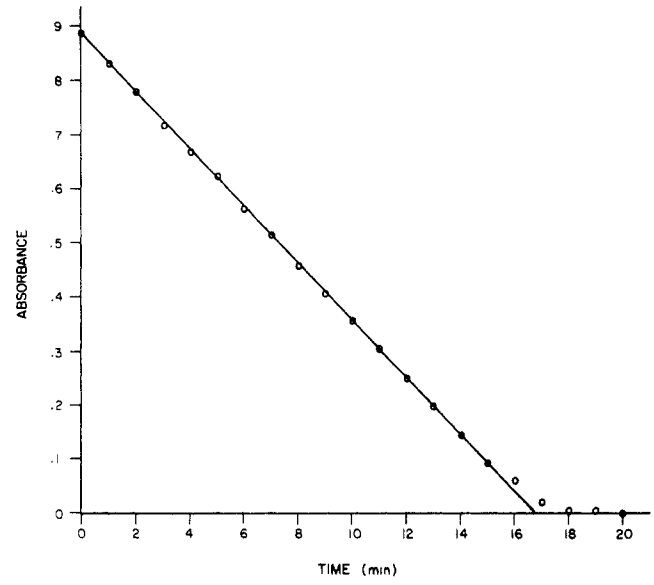
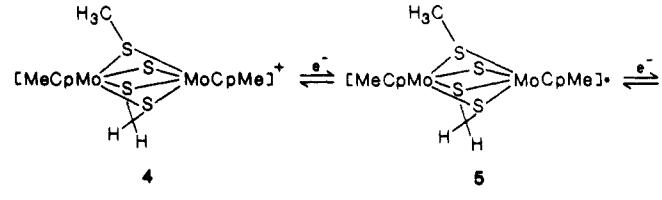


Figure 1. The absorbance of $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}S)$ (**5**) ($\sim 10^{-3}$ M) in THF at 1360 nm during the course of the reaction of **5** with hydrogen.

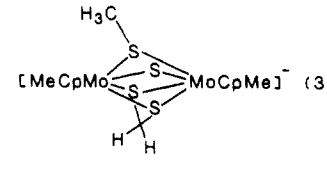
disulfide.[8,10] Although we have been unable to detect spectral evidence for the interaction of **2** with hydrogen, the catalytic reductions may involve a molybdenum(III) hydrosulfido-bridged intermediate as the active catalyst. This speculation has led to the hypothesis that a molybdenum(III) dimer with one or more μ-SH ligands may show interesting reactivity as a hydrogen transfer agent. We report here the synthesis of such a complex $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SH)$ (**3**) and a study of the reactivity of the SH ligand with bases, electrophiles, and a series of unsaturated molecules.

Results and Discussion

Synthesis and Characterization of $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SH)$ (3). The synthesis and characterization of the redox-related series of complexes shown below have been reported recently.[11] The ionic members of this series appeared to be likely



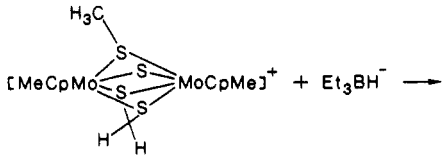
4 **5**



6

precursors to the neutral molybdenum(III) dimer with a hydrosulfido ligand $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SH)$. However, the desired complex proved elusive. Attempts to protonate the anionic derivative, **6**, with trifluoroacetic or other acids proved difficult to follow by NMR, presumably because the acid also acted as an oxidant. The reactions of the cationic derivative, **4**, with hydride sources were complex. For example, reaction with triethylborohydride produced an (ethyl)thiolate bridged derivative (reaction 4) while reaction with sodium hydride yielded the anionic derivative, **6** (reaction 5).[11] The SH complex **3** was detected by NMR in the reaction of the cation with sodium borohydride

(3) Gates, B. C.; Katzer, J. R.; Shuit, G. C. A. *Chemistry of Catalytic Processes*; McGraw-Hill: New York, 1979; p 422.
(4) (a) Tanaka, K.-I.; Okuhara, T. *J. Catal.* **1982**, *78*, 155. (b) Valyon, J.; Schneider, R. L.; Hall, W. K. *J. Catal.* **1984**, *85*, 277. (c) Barbour, J.; Campbell, K. C. *Chem. Commun.* **1982**, 1371. (d) Okamoto, Y.; Tomioka, H.; Imanaka, T.; Teranishi, S. *J. Catal.* **1980**, *66*, 93.
(5) (a) Green, M. L. H.; Lindsell, W. E. *J. Chem. Soc. A* **1967**, 1455. (b) Ruffing, C. J.; Rauchfuss, T. B. *Organometallics* **1985**, *4*, 524. (c) Noble, Mark E.; Huffman, J. C.; Wentworth, R. A. D. *Inorg. Chem.* **1983**, *22*, 1756. (d) Hausmann, H.; Hofler, T.; Kruck, T.; Zimmerman, H. W. *Chem. Ber.* **1981**, *114*, 975. (e) DeSimone, R. E.; Glick, M. D. *Inorg. Chem.* **1978**, *17*, 3574.
(6) In this paper we refer to formal molybdenum ion oxidation states in the complexes with the assumption that none of the dimers involve sulfur–sulfur bonding interactions, unless indicated. As a referee points out, the potential for sulfur–sulfur bond formation in these systems could influence the reactivity of the ligands and alter the assigned metal ion oxidation states. See, for example: Pan, W.-H.; Harmer, M. A.; Halbert, T. R.; Stiefel, E. I. *J. Am. Chem. Soc.* **1984**, *106*, 459.
(7) Rakowski DuBois, M.; DuBois, D. L.; VanDerveer, M. C.; Haltiwanger, R. C. *Inorg. Chem.* **1981**, *20*, 3064.
(8) Casewit, C. J.; Coons, D.; Wright, L. L.; Miller, W. K.; Rakowski DuBois, M. *Organometallics* **1986**, *5*, 951.
(9) Rakowski DuBois, M.; VanDerveer, M. C.; DuBois, D. L.; Haltiwanger, R. C.; Miller, W. K. *J. Am. Chem. Soc.* **1980**, *102*, 7456.
(10) Rakowski DuBois, M. *J. Am. Chem. Soc.* **1983**, *105*, 3710.
(11) Casewit, C. J.; Haltiwanger, R. C.; Noordik, J.; Rakowski DuBois, M. *Organometallics* **1985**, *4*, 119.



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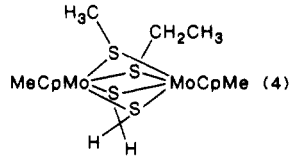

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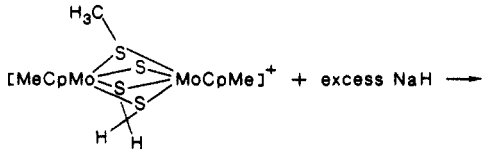

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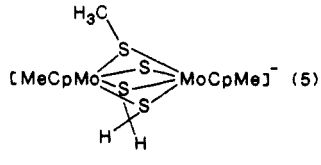
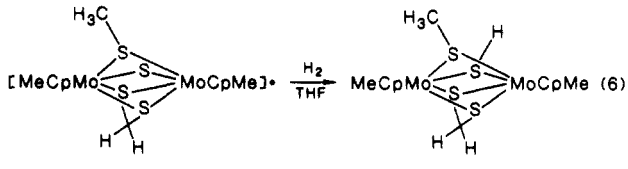


6

supported on alumina, but the mixture of products proved difficult to purify.[11]

During the course of these studies, the electronic and EPR spectra[12] and the reactivity[11] of the neutral mixed valence dimer, **5**, were also investigated. The sulfido ligand in the complex did not react detectably with alkenes or alkynes. Nor was a hydrogen atom abstraction from cyclohexadiene observed. The lack of reactivity contrasted with that of organic thiyl radicals, and we concluded from these studies that little of the unpaired electron density was localized on the sulfido bridge in complex **5**. We were surprised to observe in subsequent studies that the mixed valence dimer, **5**, reacted cleanly under one to two atmospheres of hydrogen at 25 °C to form the hydrosulfido complex **3** (reaction 6). The characterization of this complex is discussed below.

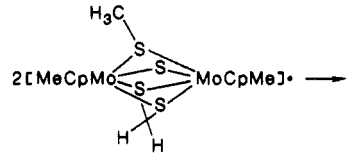


5 3

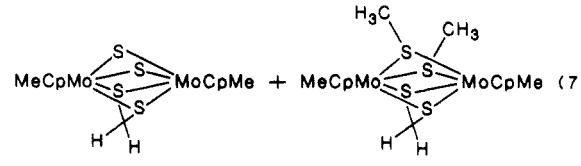
More detailed studies of reaction 6 were carried out by monitoring the disappearance of the near-IR absorbance of complex **5** (1360 nm) when dilute THF solutions were vigorously shaken under excess hydrogen. The studies revealed that the rate of the reaction with hydrogen was markedly dependent on the purity of the starting complex, **5**, and was independent of the concentration of **5** (Figure 1). These results suggest that the rate-determining step of reaction 6 involves the activation of the hydrogen molecule by a minor component in the reaction mixture which then transfers a hydrogen atom to the mixed valence dimer, **5**. Although **5** has been prepared and isolated in analytically pure form, two types of intermolecular reactions have been identified for this complex in solution. The possible roles of the products of these reactions in the hydrogen activation process were therefore considered.

An intermolecular reaction of **5** has been observed to occur at room temperature when the solution is exposed to light. The product of this reaction has been isolated and identified as a diamagnetic tetrameric derivative, $[(MeCpMo)_2(S_2CH_2)(S)(SCH_3)]_2$ (**7**).[13] The structure and reactivity of this product are under further study and will be discussed elsewhere. Since we did not initially realize that **5** was light sensitive, small amounts of **7** were generally present in solutions of the mixed valence derivative. However, the addition of an equivalent of **7** to a solution of **5** did not alter the rate of its reaction with hydrogen.

A second intermolecular reaction of **5**, which proceeds slowly in THF at 25 °C and more rapidly when solutions are refluxed under an inert atmosphere, involves an unusual disproportionation to the molybdenum(III) and molybdenum(IV) complexes shown in reaction 7. One of these products, the (methane)dithiolate-



5



2

bridged dimer, **2**, is known to be an active catalyst in hydrogenation reactions[8,14] and seemed to be a likely candidate as the hydrogen activating agent in reaction 6. In support of this hypothesis, the addition of complex **2** to solutions of the mixed valence dimer **5** under hydrogen resulted in a dramatic catalysis of reaction 6. For example, we found that for a solution of **5** in which **2** was not spectroscopically detectable, the reaction proceeded over a period of 40 min, while in the presence of an equivalent of **2**, the reaction was complete in the time required to place the solution in the spectrometer. In our kinetic studies of reaction 6, discussed above, trace amounts of $(MeCpMoS)_2S_2CH_2$ (**2**) may have been present in **5** either as a trace contaminant from the synthesis of **5** or as a result of reaction 7.

The elemental analyses and spectral data for the product, **3**, are consistent with the proposed formulation. The proton NMR spectrum of **3** generated in situ in THF-d_8 is rather broad at room temperature, but the spectrum sharpens at −60 °C (Figure 2). The chemical shifts of the Cp, *Me*Cp, and S*CH*$_3$ groups of **3** are similar to those observed for the related Mo(III) dimer $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)_2$, for which a structure has been established by X-ray crystallography.[14] The chemical shift of the SH resonance at −1.3 ppm and the vibration frequency of the S–H ligand at 2380 cm^{-1} are similar to those reported for the bridging SH ligands of the Mo(IV) dimer $[MeCpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$ (**1**).[9] The reason(s) for the broadening of the NMR spectrum at room temperature have not been definitely established. Evidence for a hydrogen atom exchange between **5** and **3** is observed in the NMR spectrum during the course of reaction 6,[15] and a similar exchange in the product solution with trace amounts of **5** and/or **2** could account for the observed line widths.

The SH complex **3** is extremely air sensitive and is rapidly oxidized to give the mixed valence dimer **5**. However, we were unable to observe a well-defined oxidation wave in cyclic volt-

(12) Casewit, C. J.; Rakowski DuBois, M. *Inorg. Chem.* **1986**, *25*, 74.

(13) This reaction was discussed briefly in ref 11 and was originally thought to require oxygen.

(14) McKenna, M.; Wright, L. L.; Miller, D. J.; Tanner, L.; Haltiwanger, R. C.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1983**, *105*, 5329.

(15) When reaction 6 is followed by NMR, broad resonances (>300 Hz) attributed to complex **5** are initially observed at chemical shifts greater than 20 ppm. As the reaction proceeds these signals move upfield into the diamagnetic region and sharpen somewhat to give the spectrum shown in Figure 2a. During the course of reaction 6, a sharp SH resonance is observed, because in a hydrogen atom exchange between **3** and **5**, the hydrogen is never part of a paramagnetic molecule. After the reaction is complete this resonance also broadens somewhat, perhaps due to exchange with **2**. Increasing the temperature to 50 °C results only in some additional broadening.

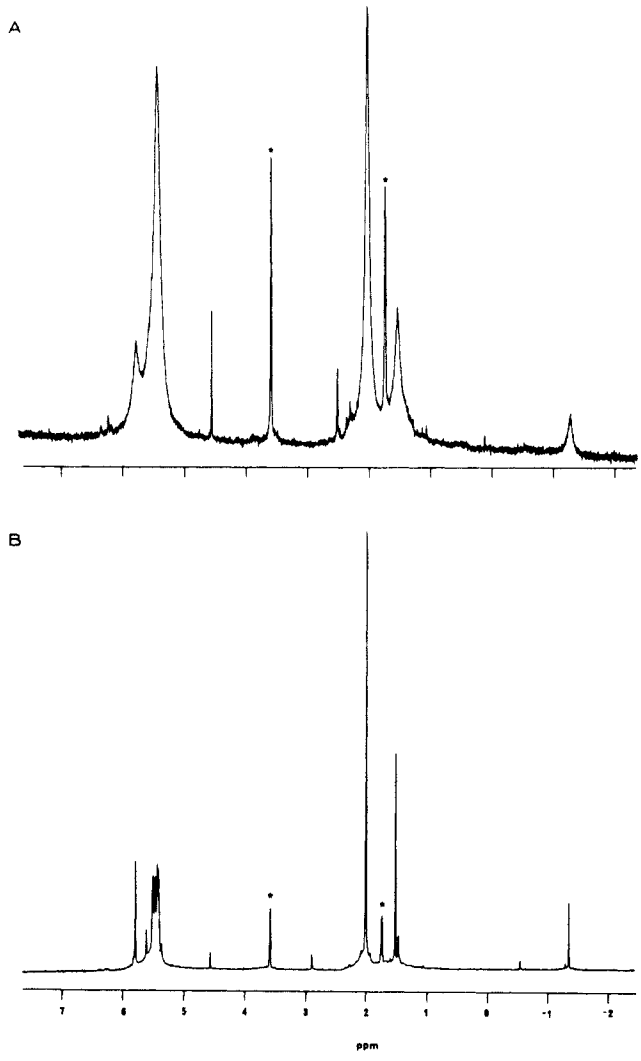
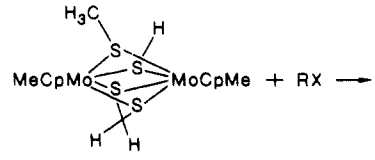


Figure 2. 250-MHz ^1H NMR spectrum of $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SH)$ (**3**) in THF-d_8. (A) At 25 °C. (B) At −60 °C. δ −1.35 (s, 1, SH), 1.52 (s, 3, SCH_3), 2.00 (s, 6, CH_3Cp), 5.46 (m, 8, Cp), 5.79 (s, 2, S_2CH_2), 4.6 (H_2 dissolved in solvent). Resonances marked with an asterisk are from proton impurities in THF-d_8. Weak singlets at 5.6, 1.5, and −1.3 ppm are assigned to the analogous complex $(CpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SH)$. ($[CpMo(CO)_3]_2$ is an impurity in $[MeCpMo(CO)_3]_2$, the original starting material in these syntheses.) The weak resonances at 2.9 and −0.6 ppm are unidentified.

ammetric studies of **3**.[16] In the presence of hydrogen, solutions of complex **3** appear to be quite stable. No sensitivity to light has been observed, and no decomposition occurred when the complex was heated in THF at 60 °C for 24 h. However, when solutions of **3** were evacuated in two separate experiments, we observed by near-IR spectroscopy that approximately 20% of the mixed valence dimer **5** was formed in each case. Its rate of formation was qualitatively observed to be dependent on the amount of complex **2** which was present. It therefore appears that hydrogen atom transfer between the SH complex **3** and complex **2** is a reversible process.[17]

Reactions of $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SH)$ with Electrophiles. The bridging hydrosulfido ligand of $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SH)$ (**3**) exhibits nucleophilic properties. For example, the SH ligand is alkylated at 25 °C with alkyl halides in THF to form the bis((alkyl)thiolate)-bridged complexes[11,14] (reaction 8). No base is required for these reactions.



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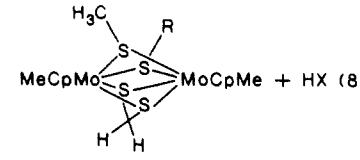
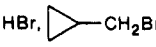


RX = CH_3I, PhCH=CHBr,  CH_2Br

In contrast, the molybdenum(IV) hydrosulfido complex $[MeCpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$ (**1**) is not alkylated by methyl iodide under neutral conditions. The alkylation of bridging and nonbridging SH ligands in other metal complexes has also generally required a catalytic amount of base;[5b,c,18] in the absence of a deprotonating agent, a stronger alkylating agent, such as the triethyloxonium ion, has been used.[5d,19]

In some cases the cationic complex **4** is detected as a secondary product in reaction 8. In separate experiments we have confirmed that this product results from the reaction of the SH complex **3** with the protic acid. Hydrogen is also detected as a product in the reaction with acid. The formation of **4** is slow,[20] and neither the yield of the products nor the mechanistic features of the hydrogen elimination have been established.

Investigations of the Acidity of $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SH)$ (3). We were interested in establishing the relative acidity of the hydrosulfido ligand in **3** because this property is important in understanding the fundamental reactivity of the ligand. In addition, the ability of SH groups on molybdenum sulfide surfaces to play a role in acid catalysis has been the subject of considerable speculation.[4] Studies of synthetic systems may provide a useful contribution toward understanding the acidity of surface SH groups.

The difference in the reactivities of the hydrosulfido derivative, **3**, and its conjugate base, **6**, with acetylene provides a synthetic method for probing the acidity of the S–H ligand in **3**. We have reported previously that the anion reacts with acetylene to form the (vinyl)thiolate-bridged derivative (reaction 9).[11] Deuterium labeling experiments have established that excess acetylene is the proton source in this reaction. In contrast, no reaction is observed with the neutral SH complex under similar conditions (reaction 10). By carrying out reaction 10 in the presence of base and monitoring the products for the presence of the (vinyl)thiolate-bridged derivative, we have established conditions necessary for significant deprotonation of **3**. No reaction is observed in the presence of excess weak nitrogen bases such as triethylamine or 1,8-bis(dimethylamino)naphthalene (proton sponge). However, the acetylene reaction does occur in the presence of an equivalent of sodium methoxide and other more basic alkoxides.

Although detailed comparisons of acidities of other complexes with μ-SH ligands are not possible, strong bases such as alkoxides have been required to deprotonate these ligands in a variety of electronic environments, ranging from $\mu\text{-}SH[W^0(CO)_5]_2$[21] to

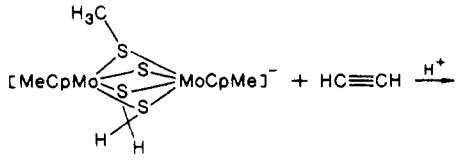
(16) Cyclic voltammetric studies were carried out in THF because NMR spectroscopy confirmed the stability of **3** in this solvent. Solutions of **3** ($\sim 10^{-3}$ M) in THF/0.2 M $(Bu_4N)PF_6$ were analyzed in a conventional 3-compartment cell with platinum wire as working and counter electrodes and a Ag wire as reference. No well-defined waves were observed over a range from +2.0 to −2.0 V vs. Ag wire.

(17) We have not attempted a detailed characterization of the equilibrium constant for this reaction because of the extreme air sensitivity of the hydrosulfido complex. It is difficult to be certain, even under carefully controlled conditions, that at least some of complex **5** is not produced as a result of trace amounts of oxygen.

(18) (a) Seyferth, D.; Henderson, R. S. *J. Organomet. Chem.* **1981**, *218*, C34. (b) Noble, M. E.; Folting, K.; Huffman, J. C.; Wentworth, R. A. D. *Inorg. Chem.* **1984**, *23*, 631.

(19) (a) Kopf, H.; Schmidt, M. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 953. (b) Höfler, M.; Hausmann, H.; Heidelberg, H. A. *J. Organomet. Chem.* **1981**, *213*, C1.

(20) In reactions of millimolar concentrations of **3** with an equivalent of trifluoroacetic acid in THF, formation of the cation **4** is not quantitative even after several days at room temperature.



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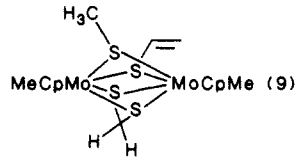
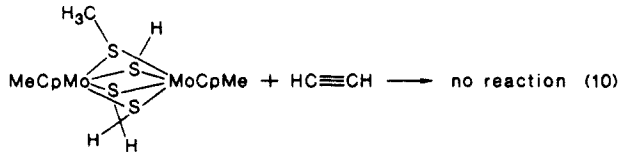


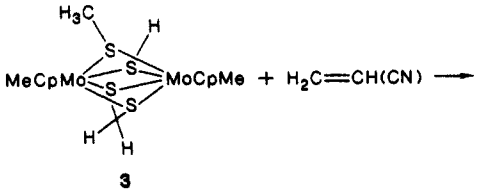


3

$Cp_2Ti(\mu\text{-}SH)_2Mo(CO)_4$[5b] to $[CpMo^{IV}(\mu\text{-}S)(\mu\text{-}SH)]_2$.[9] In contrast, the SH ligands in the Mo(V) dimer $[Mo(NC_6H_4CH_3)(S_2P(OC_2H_5)_2)]_2(\mu\text{-}S)(\mu\text{-}SH)(\mu\text{-}O_2CCF_3)$[5c] and the cationic derivative $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]^+$[11] show considerably stronger acidic properties.

Insertion Reactions of $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SH)$ (3). Complex **3** does not react with acetylene, as mentioned above, nor with ethene or allene. However, several activated alkenes and alkynes have been found to insert into the S–H bond of complex **3** in THF in the absence of base. The products of these reactions are isolated as orange-brown viscous oils. While characterization by X-ray diffraction or by elemental analyses has not been possible, the gross structure and purity of each of the products have been verified by 250-MHz NMR and by high-resolution mass spectroscopy. These insertion reactions may serve as a model for the participation in hydrogenations by surface SH groups in the HDS catalysts. In some cases, the insertion products isolated in these homogeneous systems have been found to undergo a further reaction with hydrogen to form the free reduced alkene or alkane.[22]

Acrylonitrile reacts at room temperature with complex **3** to form the regiospecific product shown in eq 11 in 54% yield. We have



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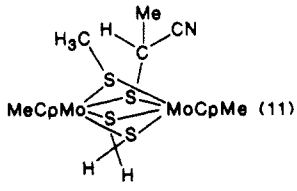


not attempted to maximize the yields of the insertion reactions discussed here.[23] However, we have established that the other regioisomer is not formed in each of the reaction systems. For example, in the acrylonitrile system, the other isomer, resulting from sulfido attack at the β-carbon of acrylonitrile, has been isolated under identical workup conditions from the regiospecific

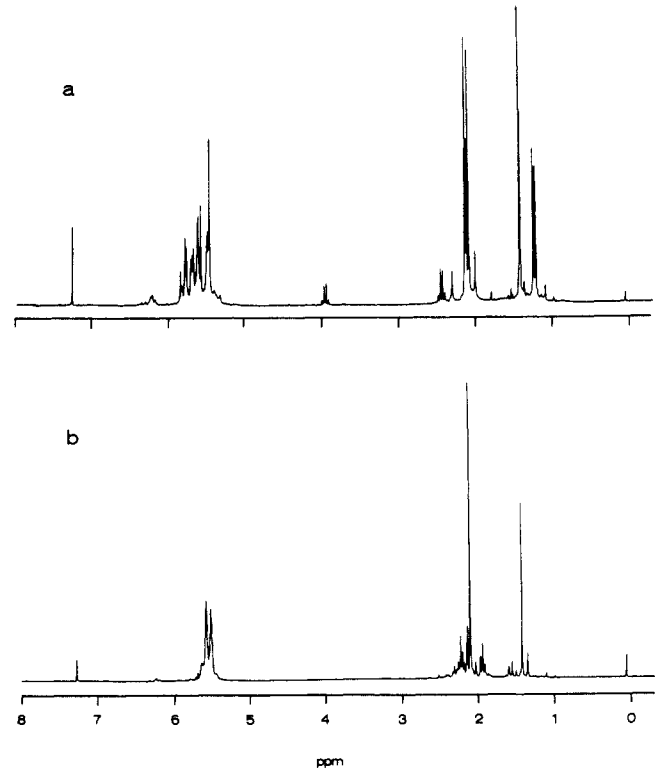
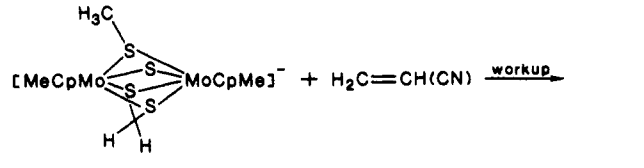


Figure 3. (a) 250-MHz ^1H NMR of $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SCH(CN)(CH_3))$, the product of the reaction of **3** with acrylonitrile. NMR assignments are included in the Experimental Section. (b) 250-MHz ^1H NMR of $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SCH_2CH_2CN)$, the product of the reaction of **6** with acrylonitrile. δ 1.40 (s, 3, SCH_3), 1.92 (t, 2, CH_2, J = 7 Hz), 2.08 (s, 6, CH_3Cp), 2.20 (t, 2, CH_2, J = 7 Hz), 5.55 (m, 10, Cp + S_2CH_2).

reaction of the anionic conjugate base **6** with this substrate (reaction 12).[11] The proton NMR spectrum of each of the products



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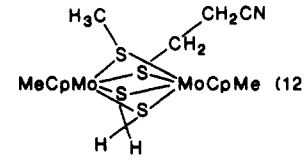


is shown in Figure 3. Conversely, Complex **6** reacts with acrylonitrile in the presence of the protonating agent, excess trimethylamine hydrochloride, to form the product of α attack. These results demonstrate that members of the conjugate acid–base pair, **6** and **3**, are interconvertible. Since the mixed valence dimer **5** is a possible impurity in both the air sensitive neutral hydrosulfido complex **3** and the anionic derivative **6**, it is important to point out that complex **5** does not react with acrylonitrile or with any of the other substrates discussed in this section.[11]

A comparison of the reactivity of organosulfur compounds reveals that both organic thiolate anions and thiyl radicals add to the β-carbon of acrylonitrile.[24] The ligated hydrosulfido group of $(\mu\text{-}SH)_2Fe_2(CO)_6$ also reacts with acrylonitrile to give the product of β-addition.[18a] The regiochemistry of reaction 11 appears to be unique to the SH ligand of **3** and has not been observed previously in either organosulfur or sulfur-ligated metal chemistry.

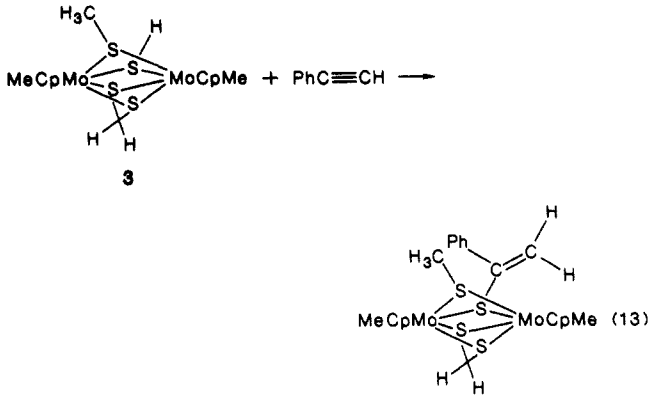
(21) Gingerich, R. G. W.; Angelici, R. J. *J. Am. Chem. Soc.* **1979**, *101*, 5604.

(22) For example, the product of reaction 12 reacts at 60 °C with hydrogen (2–3 atm) over a period of several days to form propionitrile. Further discussion of these reactions with hydrogen will be presented elsewhere.

(23) The other major product of the reaction after workup in air is **7**, which is known to ultimately form through air oxidation of **3**.[11] This suggests that product yields might be improved with longer reaction times.

(24) (a) Hurd, C. D.; Gershbein, L. L. *J. Am. Chem. Soc.* **1947**, *69*, 2328. (b) Griesbaum, K. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 273.

Products of different regio- and/or stereochemistry have also been observed in the reactions of activated alkynes with the neutral hydrosulfido complex, **3**, and its conjugate base, **6**. For example, phenylacetylene inserts into the SH bond of **3** at 25 °C to provide the α-phenyl(alkenyl)thiolate derivative (reaction 13). In contrast



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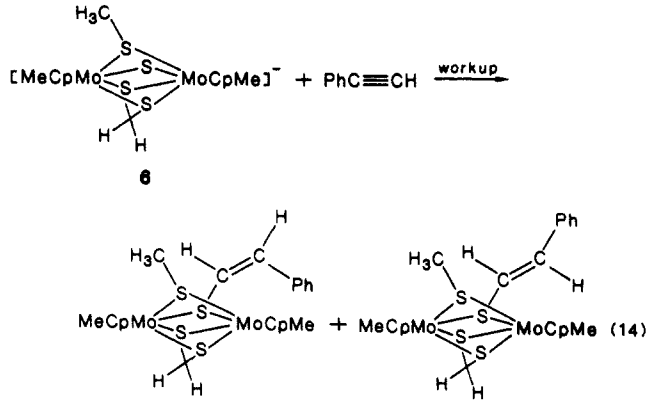
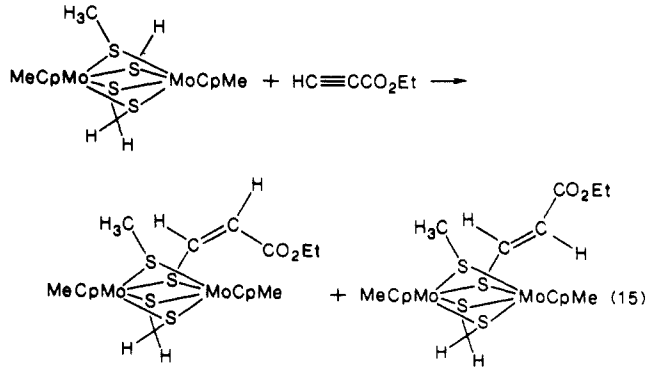
the anion, **6**, adds to the β-carbon of phenylacetylene to give a mixture of dimers with a 2:1 ratio of *cis*- and *trans*-β-phenyl-(alkenyl)thiolate ligands (reaction 14). Organic thiolates add



6

to the β-carbon of phenylacetylene to give the cis isomer.[25] To our knowledge, there has been only one previous example of the insertion of this alkyne into a coordinated SH ligand. The reaction of CpNi(SH)(PBu_3) with phenylacetylene in refluxing benzene reportedly yields the α-phenyl(alkenyl)thiolate derivative.[26]

At 25 °C ethyl propiolate reacts with the hydrosulfido bridged complex **3** to yield both the (*cis*- and *trans*-alkenyl)thiolate bridged dimers shown in reaction 15 in 58% overall yield. The observed



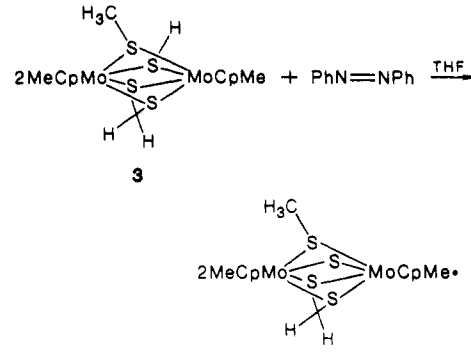
cis to trans ratio is 4:1. In contrast, the addition of the conjugate base of **3** to ethyl propiolate yields primarily the (*trans*-alkenyl)thiolate derivative with only a trace of the cis isomer observed by ^1H NMR.[11] The reaction of an organic thiolate with ethyl propiolate has been reported to form the *cis*-alkenyl sulfide.[27]

Dimethylacetylene dicarboxylate also reacts with **3** to give a bridging (alkenyl)thiolate derivative of unknown stereochemistry in 18% yield. In this case the ^1H NMR of the product is identical with that of the product obtained from the reaction of the anionic dimer, **6**, with the same alkyne.[11]

The regioselectivity of the reactions of the anionic dimer, **6**, with this series of alkenes and alkynes parallels that of organic thiolate anions; the products are consistent with attack by a strongly nucleophilic sulfur on the unsaturated molecules. Differences in the stereochemistries of the products derived from the anionic complex as compared to those of the organic systems may be a result of steric repulsions between the dimer and alkyne substituents.

Our characterization of the insertion products of the hydrosulfido complex establish that these reactions proceed by a different mechanism from those of the anionic derivative. An interesting parallel to these reactivity studies has been reported for a metal–hydride complex and its conjugate base, hydridocobaloxime, $HCo(DMG)_2B$ (DMG = dimethylglyoxime and B = pyridine or phosphine), and cobaloxime I, $[Co(DMG)_2B]^-$, respectively.[28] For example, the reaction of $[Co(DMG)_2B]^-$ with acrylonitrile yields $CNCH_2CH_2Co(DMG)_2B$, whereas $HCo(DMG)_2B$ adds to acrylonitrile to produce the other regioisomer $CH_3CH(CN)Co(DMG)_2B$. Elementary steps involved in the mechanism of metal–hydride addition have not been investigated in detail. However, it seems likely that there are mechanistic similarities between the addition reactions of hydridocobaloxime and those of the hydrosulfido complex **3**, in view of the fact that the metal hydride complex has been found to be weakly acidic, $H^{\delta+}$–$Co^{\delta-}$.[28,29]

Hydrogen Atom Transfer by $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SH)$ (3). The hydrosulfido complex **3** also has been found to react with molecules with carbon–nitrogen and nitrogen–nitrogen unsaturation. For example, azobenzene and other azo compounds are reduced by hydrogen atom transfer from **3** (reaction 16).[8]



3 **5**

Similar reductions of the imines $C_6H_5CH{=}NR$ (R = C_6H_5, CH_3) to the corresponding amines are also observed. The reactions proceed rapidly, and no intermediates resulting from insertion into the S–H bond have been observed. Two equivalents of the hydrosulfido complex **3** are required for the reduction of azobenzene even in the presence of an excess of the potential hydrogen atom donor cyclohexadiene. As discussed elsewhere,[8] the stoichiometry of reaction 16 suggests that the bond dissociation energy of the S–H ligand in **3** is significantly lower than those of organic thiols which average ~90 kcal/mol.[30]

The abilities of the two known dimeric molybdenum hydrosulfido complexes, $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SH)$ (**3**) and $[MeCpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$[9] (**1**), to function as hydrogen transfer agents have been compared. We have also included comparisons with the undetected intermediate derived from the reaction of $(MeCpMoS)_2S_2CH_2$ (**2**) with hydrogen, since this reactive species is also likely to involve SH ligands. In comparing reactions

(25) Truce, W. E.; Simms, J. A. *J. Am. Chem. Soc.* **1956**, *78*, 2756.
(26) Sato, M.; Sato, F.; Takemoto, N.; Iida, K. *J. Organomet. Chem.* **1972**, *34*, 205.
(27) Truce, W. E.; Heine, R. F. *J. Am. Chem. Soc.* **1957**, *79*, 5311.
(28) (a) Shrauzer, G. N.; Windgassen, R. J. *J. Am. Chem. Soc.* **1967**, *89*, 1999. (b) Naumberg, M.; N.-V.-Duong, K.; Gaudemer, A. *J. Organomet. Chem.* **1970**, 231.
(29) Chao, T.-H.; Espenson, J. H. *J. Am. Chem. Soc.* **1978**, *100*, 129.
(30) Oae, S., Ed. *Organic Chemistry of Sulfur*; Plenum Press: New York, 1977; p 119.

between these dimeric systems, we observe that, unlike the intermediate derived from the (methane)dithiolate-bridged dimer and hydrogen, the molybdenum(IV) complex $[MeCpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$ (**1**) does not transfer hydrogen to the mixed valence dimer **5**. Assuming that the lack of reaction is thermodynamically rather than kinetically controlled, we can present the following order of hydrogen transfer ability:

$$[(MeCpMoS)_2S_2CH_2 + H_2] > (MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SH) > [MeCpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$$

Summary. The first example of a molybdenum(III) dimer with a bridging hydrosulfido ligand has been synthesized and characterized. The SH ligand has been found to be deprotonated by methoxide ion and to be alkylated by alkyl halides in the absence of base. Alkenes and alkynes with electron-withdrawing substituents insert into the SH bond of the molybdenum(III) complex. These reactions proceed in the absence of base and, in fact, often proceed with a different regioselectivity than those of the analogous deprotonated complex. The S–H bond dissociation energy of the molybdenum(III) complex appears to be significantly lower than those of organic thiols, and the hydrosulfido complex functions as an effective hydrogen atom donor to azo compounds and imines.

Experimental Section

Materials. The synthesis and characterization of $[(MeCpMo)_2(\mu\text{-}S)(\mu\text{-}SCH_3)S_2CH_2]^+$ (**4**), $(MeCpMo)_2(\mu\text{-}S)(\mu\text{-}SCH_3)S_2CH_2$ (**5**), and $[(MeCpMo)_2(\mu\text{-}S)(\mu\text{-}SCH_3)S_2CH_2]K$ (**6**) have been reported previously.[11,12] Potassium graphite, KC_8, was purchased from Alfa. Reagent grade organic halides, azo compounds, imines, alkenes, alkynes, and hydrogen were purchased from commercial suppliers and used without purification. Tetrahydrofuran was distilled from calcium hydride prior to use. All reactions were carried out under an inert atmosphere with use of standard glove box or Schlenk line techniques. Products were isolated in air unless otherwise noted.

Instrumentation. Electronic spectra were recorded on Cary 14 and Cary 219 spectrophotometers. Routine ^1H NMR spectra were measured at 90 MHz on a Varian 390 spectrometer, and high-field ^1H NMR spectra were recorded on a Bruker WM250 spectrometer. Mass spectra were obtained on a Varian MAT CH-5 spectrometer or a VG 7070 EQ-HF tandem mass spectrometer. High-resolution mass spectra were obtained with the latter instrument. Elemental analyses were provided by Spang Laboratories.

Rate Studies of the Reaction of $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}S)$ (5) with Hydrogen. For the rate studies, THF solutions of **5** ($\sim 10^{-3}$ M) were prepared under a nitrogen atmosphere in a Vacuum Atmospheres glove box. In some cases **2** or **7** was added to the solution. About 3 mL of this solution was filtered through a glass wool plug into a 10 mm spectrometer cell equipped with a high-vacuum valve and a glass gas reservoir 35 mL in volume. The solution was degassed in 1 or 2 freeze–pump–thaw cycles, and 1 atm of hydrogen was added at −196 °C. After the solution was warmed to ambient temperature, it was shaken vigorously and the near-IR absorbance at 1360 nm was monitored. Vigorous shaking was continued and the absorbance measured at periodic intervals until the reaction was complete. Prior to the rate studies, the applicability of Beer's law to solutions of **5** was confirmed. Plots of A_{1360} vs. concentration of **5** in THF were linear over the concentration range of 2×10^{-3} to 1×10^{-5} M with correlation coefficients of 0.999.

$(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SH)$ (3). A THF solution of **5** (0.08 g, 0.16 mol) was prepared in situ under N_2 by the reduction of $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_3)]^+$ (**4**) with potassium graphite, KC_8. The filtered solution was degassed in 1 free–pump–thaw cycle, and 1 atm of hydrogen was added at −196 °C. The pink solution was stirred at 25 °C until an orange-brown color was observed (2–12 h). The product was isolated under an inert atmosphere by removal of the solvent. The resulting solid was further purified by dissolving it in diethyl ether, filtering it through a glass wool plug, and evaporating the solvent. Yield: 0.076 g, 94%. This procedure was repeated to give a brown microcrystalline powder which was washed with pentane and dried in vacuo. 250-MHz ^1H NMR at −60 °C (THF-d_8): −1.35 (s, 1, SH), 1.52 (s, 3, SCH_3), 2.00 (s, 6, CH_3Cp), 5.46 (m, 8, Cp), 5.79 (s, 2, S_2CH_2). Mass spectrum, m/e 508 (P), 507 (P − H), 493 (P − CH_3), 492 (P − CH_3 − H), 461 (P − H − S_2CH_2), 446 ($Cp'_2Mo_2S_3$). IR (Nujol): 2380 (ν_{S-H}). Anal. Calcd for $Mo_2S_4C_{14}H_{20}$: C, 33.07; H, 3.96; S, 25.22. Found: C, 33.14; H, 4.07; S, 25.11.

Oxidation and Evacuation of $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SH)$ (3). A 1.6×10^{-3} M solution of $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}S)$ (**5**) in THF was placed in the spectrometer cell described above. The solution was freeze–thaw degassed, 1 atm of hydrogen was added, and the cell was sealed. When the conversion of **5** to **3** was complete, as indicated by visible spectroscopy, the solution was exposed to air. The visible spectrum indicated that 95% of complex **5** was regenerated.

In a second set of experiments, a THF solution of complex **3** was formed in the spectrometer cell as described above. The solution was frozen at −196 °C and evacuated on a vacuum line two times. The cell was sealed with a Teflon stopcock, and the evacuated solution was warmed to room temperature. Near-IR spectroscopy indicated that 24% of complex **5** was present after 15 and 40 min. Addition of hydrogen to the same solution to reform **3** followed by a second evacuation produced 19% of complex **5**.

$(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SCH(CN)CH_3)$. (A). A THF solution of **3** (0.16 mmol), generated in situ, was added to 42 μL (0.64 mmol) acrylonitrile in 2 mL of THF. The solution was stirred at 25 °C under vacuum. After 4 days the solvent was removed and the crude product chromatographed on an alumina column. Elution with CH_2Cl_2 produced an orange band containing the pure product. Removal of solvent gave 48 mg of an orange-brown oil (54% yield). Two isomers, presumably differing only in the equatorial or axial configuration of the α-cyanoethyl group on sulfur, are observed by ^1H NMR. The other possible regioisomer was not detected. 250-MHz ^1H NMR ($CDCl_3$) isomer A: 1.22 (d, 3, $SC(CN)CH_3$, J = 7 Hz), 1.41 (s, 3, SCH_3), 2.07, 2.11 (2 s, 6, CH_3Cp), 2.43 (q, 1, SCH(CN), J = 7 Hz), 5.6 (m, 10, Cp + S_2CH_2). 250-MHz ^1H NMR ($CDCl_3$) isomer B: 1.21 (d, 3, $SCH(CN)CH_3$, J = 7 Hz), 1.40 (s, 3, SCH_3), 2.10, 2.12 (2 s, 6, CH_3Cp), 3.94 (q, 1, SCH(CN), J = 7 Hz), 5.6 (m, 10, Cp + S_2CH_2). The A:B ratio is 60:40. Mass spectrum, m/e 561 (P), 507 (P − $CH(CN)CH_3$), 461 (P − $CH(CN)CH_3$ − SCH_2), 446 ($Cp'_2Mo_2S_3$). Exact mass calcd for $Mo_2S_4C_{17}H_{23}N$ (^{98}Mo) 564.8822, found 564.8855.

(B). A THF solution of **6** (0.16 mmol) was added to 60 mg (0.63 mmol) of trimethylamine hydrochloride in 1 mL of methanol. This solution was stirred for 1 min and then added to a solution of 42 μL (0.64 mmol) of acrylonitrile in 5 mL of THF. The solution was protected from light and stirred at 25 °C for 4 days. Workup according to the procedure described above provided 60 mg of $(MeCpMo)_2(\mu\text{-}S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SCH(CN)CH_3)$ (67% yield). The other regioisomer was not observed in the ^1H NMR of the crude or purified product. For comparison, reaction of **6**, with acrylonitrile in the absence of acid, provided a 32% yield of $(MeCpMo)_2(\mu\text{-}S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SCH_2CH_2CN)$.[11]

$(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SC(C_6H_5)CH_2)$. A THF solution of **3** (0.16 mmol), generated in situ, was added to 50 μL (0.45 mmol) of phenylacetylene in 2 mL of THF. The solution was stirred at 25 °C for 3 days. The solvent was removed, and the crude product was eluted on an alumina column with CH_2Cl_2. Yield: 23 mg (24%) of orange-brown oil. The other possible regioisomer was not detected. 250-MHz ^1H NMR ($CDCl_3$): 1.43 (s, 3, SCH_3), 2.01 (s, 6, CH_3Cp), 4.72 (s, 1, CH), 5.30 (m, 11, Cp + S_2CH_2 + CH), 7.16 (m, 5, C_6H_5); mass spectrum, m/e 610 (P), 595 (P − CH_3), 549 (P − CH_3 − SCH_2), 507 (P − $C(C_6H_5)CH_2$), 461 (P − $C(C_6H_5)CH_2$ − SCH_2), 446 ($Cp'_2Mo_2S_3$). Exact mass calcd for $Mo_2S_4C_{22}H_{26}$ (^{98}Mo) 613.9026, found 613.9029.

$(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SCHCH(C_6H_5))$. A THF solution of **6** (0.16 mmol) was added to 50 μL (0.45 mmol) of phenylacetylene in 5 mL of THF. The solution was protected from light and stirred at 25 °C under vacuum. After 3 days the solvent was removed and the products were chromatographed on an alumina column. Elution with CH_2Cl_2 provided a yellow band which was chromatographed again on an alumina column and eluted with diethyl ether. Removal of solvent provided 22 mg of the pure product as a brown oil (23% yield). A 2:1 mixture of the cis and trans isomers is observed by NMR. The other possible regioisomer was not detected. 250-MHz ^1H NMR ($CDCl_3$) cis: 1.49 (s, 3, SCH_3), 2.02 (s, 6, CH_3Cp), 5.45 (m, 10, Cp + S_2CH_2), 5.60 (d, 1, CH, J = 11 Hz), 6.21 (d, 1, CH, J = 11 Hz), 7.1–7.7 (m, 5, C_6H_5). 250-MHz ^1H NMR ($CDCl_3$) trans: 1.49 (s, 3, SCH_3), 2.05 (s, 6, CH_3Cp), 5.45 (m, 10, Cp + S_2CH_2), 5.95 (d, 1, CH, J = 15 Hz), 6.51 (d, 1, CH, J = 15 Hz), 7.09 (m, 5, C_6H_5); mass spectrum, m/e 610 (P) 595 (P − CH_3), 549 (P − CH_3 − SCH_2), 446 ($Cp'_2Mo_2S_3$).

$(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SCHCH(CO_2CH_2CH_3))$. A THF solution of **3** (0.16 mmol) was added to 50 μL of ethyl propiolate (0.5 mmol) in 5 mL of THF. The solution was stirred at 25 °C for 4 days. The solvent was removed and the brown oil extracted with CH_2Cl_2–diethyl ether and filtered. Removal of solvent provided 56 mg of brown oil (yield = 58%). The major isomer is the dimer with the (*cis*-alkenyl)thiolate ligand: 250 MHz ^1H NMR ($CDCl_3$) 1.20 (t, 3, CCH_3, J = 7 Hz), 1.48 (s, 3, SCH_3), 2.03 (s, 6, CH_3Cp), 4.07 (q, 2, OCH_2, J = 7 Hz), 5.47 (m, 10, Cp + S_2CH_2), 5.61 (d, 1, CH, J = 10 Hz), 6.06 (d, 1, CH, J = 10 Hz). Minor components of the mixture include the (*trans*-alkenyl)thiolate derivative characterized previously (~20%)[11] and a trace of an unidentified material characterized by vinyl protons at 6.65 and 7.24 ppm (J = 11 Hz). Mass spectrum, m/e 606 (P), 591 (P −

CH_3), 542 (P − CH_3 − SCH_2), 446 ($Cp'_2Mo_2S_3$). Exact mass calcd for $Mo_2S_4C_{19}H_{26}O_2$ (^{98}Mo) 609.8924, found 609.8939.

$(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SC(CO_2CH_3)CH(CO_2CH_3))$. A THF solution of **3** (0.16 mmol) was added to 40 μL of dimethylacetylene dicarboxylate (0.32 mmol) in 5 mL of THF. The solution was stirred at 25 °C for 1 day. The solvent was removed and the products were chromatographed on an alumina column. Elution with CH_2Cl_2 provided a greenish-brown band that was collected and evaporated in vacuo to give 18 mg (18% yield) of brown oil. The 250-MHz ^1H NMR and mass spectral data for the product have been previously reported.[11] Exact mass calcd for $Mo_2S_4C_{20}H_{26}O_4$ (^{98}Mo) 653.8822, found 653.8839.

Alkylation Reactions of $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SH)$ (3). A THF solution of **3** (0.16 mmol) was added to 50 μL of methyl iodide (0.80 mol). The solution was stirred under vacuum at 25 °C for 2 days. The solvent was removed in vacuo, and the crude brown product was chromatographed on an alumina column. Elution with CH_2Cl_2 produced an orange-brown band. The solvent was removed to give 40 mg (48%) of $[MeCpMo(\mu\text{-}SCH_3)]_2S_2CH_2$.[11]

A similar reaction of **3** with *trans*-β-bromostyrene gave a 42% yield of an orange-brown oil identified as *trans*-$(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SCH{=}CHC_6H_5)$ (see above for spectral data) and a 36% yield of the purple salt $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_3)]Br^-$. A similar procedure was also used to prepare $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SCH_2CH(CH_2)_2)$ as an orange-brown oil from the reaction of **3** with (bromomethyl)cyclopropane: ^1H NMR in $CDCl_3$ −0.10 (m, 2, cyclopropyl $(CH)_2$), 0.40 (m, 3, cyclopropyl $(CH)_3$), 1.42 (s, 3, SCH_3), 1.63 (d, 2, SCH_2, J = 6 Hz), 2.06 (s, 3, CH_3Cp), 5.46 (m, 10, Cp + S_2CH_2). Mass spectrum, *m/e* 562 (P), 507 (P − $CH_2CH(CH_2)_2$), 461 (P − $CH_2CH(CH_2)_2$ − SCH_2), 446 ($Cp'Mo_2S_3$).

Reaction of $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SH)$ (3) with Trifluoroacetic Acid. A THF solution of **3** (0.18 mmol) was added to 14 μL of CF_3COOH (0.18 mmol). The solution was stirred under vacuum for 10 min at 25 °C. At this time some H_2 was identified in the evolved gases by mass spectroscopy, but the reaction of **3** was not complete. Continued stirring for several days resulted in the formation of a purple precipitate which was filtered and identified as complex **4** by visible spectroscopy.[12,20]

Deprotonation of $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SH)$ (3). A THF solution of **3** (0.16 mmol) was added to 4.8 mg of solid sodium methoxide (0.09 mmol). The solution was degassed in 1 freeze–pump–thaw cycle and 1 atm of acetylene was added at 25 °C. The solution was protected from light and stirred for 3 days at 60 °C. Workup according to a procedure reported previously[11] provided 25 mg of $(MeCpMo)_2(\mu\text{-}SCH{=}CH_2)(\mu\text{-}SCH_2)S_2CH_2$ (29% yield). A somewhat larger yield was obtained when the reaction was carried out with 4 equiv of potassium *tert*-butoxide (yield = 45%), and no product was observed when the reaction was attempted with excess triethylamine, 1 equiv of *N*-phenylbenzylamine, or 0.5 equiv of proton sponge as base. For comparison, reaction of the conjugate base of **3** (**6**) with acetylene under the conditions described above provided a 64% yield of the (alkenyl)thiolate derivative.[11]

Reaction of 3 with *N*-Benzylideneaniline. A THF solution of **3** (0.22 mmol) was added to 96.3 mg (0.53 mmol) imine in the dry box. A color change to the characteristic pink of **5** appeared to be complete in 10 min. In related experiments the identity of **5** was confirmed by EPR spectroscopy.[11] The solution was stirred for 2 h and removed from the dry box, and the solvent was removed in vacuo. The products were dissolved in $CDCl_3$ and an NMR spectrum was taken. The relative ratio of *N*-phenylbenzylamine to *N*-benzylideneaniline was determined by the relative integrations of the methylene protons to the imino proton. A conversion of 0.4 mole of imine to amine per mol of **3** was found.

Disproportionation of $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}S)$ (5). A THF solution of **5** (0.08 mmol) was heated at 60 °C under N_2. After 3 days the solvent was removed and the products were redissolved in $CDCl_3$. ^1H NMR identified the products as a 2:1:1 mixture of the tetramer **7**, the Mo(IV) complex **2**, and a Mo(III) complex of formulation $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)_2$. The latter appears to be an isomer not previously observed.[11] ^1H NMR in $CDCl_3$: 1.34 (s, SCH_3, 6), 1.92 (s, 6, CH_3Cp), 5.45 (s, 10, Cp + S_2CH_2). Mass spectrum, *m/e* 522 (P). The mass balance was essentially quantitative. Control experiments demonstrated that the disproportionation products are not formed when **7** is heated under an inert atmosphere. (When **5** is refluxed in THF under vacuum (T < 60 °C) only the tetramer **7** is formed.)

$[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_3)]_2$ (7). A THF solution of **5** (~ 10^{-3} M) in a Pyrex flask was degassed in 2 freeze–pump–thaw cycles and irradiated with a commercial sun lamp for 30 min. A second solution was stirred in the dark for the same time period. The electronic spectrum of the irradiated solution indicated that **7** had formed in ~30% yield. No evidence for reaction was observed in the solution protected from light. Isolation procedures and NMR data for **7** have been reported elsewhere.[11] FAB mass spectrum in thioglycerol: *m/e* 1014, parent. Electronic spectrum in THF: 688 ($\epsilon = 2.6 \times 10^3$), 510 ($\epsilon = 4.1 \times 10^3$), 390 (sh). Cyclic voltammetry was carried out in acetonitrile/0.1 M n-Bu_4NBF_4 with a platinum wire electrode in a conventional three-compartment cell: $E_{1/2}$ = +0.06V vs. SCE, ΔE = 90 mV; E_a = +0.64 V (irreversible); $E_{1/2}$ = −1.42 V, ΔE = 130 mV. Anal. Calcd for $Mo_4S_8C_{28}H_{38}$: C, 33.14; H, 3.77; S, 25.27. Found: C, 33.21; H, 3.89; S, 25.39.

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Registry No. 3, 100791-16-0; **4**, 103202-43-3; **5**, 93111-42-3; **6**, 93111-51-4; $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SCH(CN)CH_3)$, 103202-41-1; $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SC(C_6H_5)CH_2)$, 103202-42-2; *cis*-$(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SCHCH(C_6H_5))$, 103202-44-4; *trans*-$(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SCHCH(C_6H_5))$, 103301-95-7; $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SCHCH(CO_2CH_2CH_3))$, 103202-45-5; $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SC(CO_2CH_3)CH(CO_2CH_3))$, 103202-46-6; $[MeCpMo(\mu\text{-}SCH_3)]_2S_2CH_2$, 103202-47-7; $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_3)S_2CH_2]Br$, 103202-48-8; $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SCH_2CH(CH_2)_2)$, 103202-49-9; $(MeCpMo)_2(\mu\text{-}SCH{=}CH_2)(\mu\text{-}SCH_2)S_2CH_2$, 103202-50-2; *N*-benzylideneaniline, 538-51-2; *N*-phenylbenzylamine, 103-32-2.