Reactivity Studies of Sulfur-Bridged Molybdenum Dimers Containing Electron-Withdrawing Dithiolate Substituents

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Received July 9, 1993®

New complexes of the formula $(Cp'Mo(\mu\text{-}S))_2S_2CHR$, where R = CO_2Me (3) and CO_2Na (4) (Cp′ = C_5H_5, $CH_3C_5H_4$), have been synthesized and characterized spectroscopically. Their reactions have been compared to those of the parent compound, where R = H (1). The synthesis of 3 involved the alkylation of $(MeCpMo)_2(\mu\text{-}S_2)(\mu\text{-}S)_2$ with $BrCH_2CO_2Me$ to form $[(MeCpMo)_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}SCH_2CO_2Me)]Br$ (2(Br)). Complex 2 crystallized in space group $P2_1/c$ with a = 10.379(2) Å, b = 20.820(6) Å, c = 9.597(2) Å, β = 102.56°, V = 2024.3(8) Å^3, and Z = 4. An X-ray diffraction study of 2 confirmed that a μ-sulfido ligand was the site of alkylation and the μ-S_2 ligand remained intact. Complex 2 was deprotonated on an alumina column to form 3. The water-soluble complex 4 was synthesized by the reaction of $[Cp'Mo(\mu\text{-}S)(\mu\text{-}SH)]_2$ with Br_2CHCO_2Na in the presence of base. The reactivities of 3 and 4 are similar to that of 1 in most cases. Unlike 1, complex 3 reacts with triflic acid to cleave a C–S bond of the dithiolate ligand and form the triflate salt of 2. Complex 4 differs from 1 in that it undergoes an observable reaction with hydrogen in neutral or basic aqueous solution. Spectroscopic data for the hydrogen addition product are consistent with the formulation $(CpMo)_2(\mu\text{-}S)_2(\mu\text{-}SH)(\mu\text{-}SCH_2CO_2Na)$ (7). The catalytic activity of 4 and 7 for D_2–H_2O exchange and for the hydrogenation of C=N and N=N bonds in two-phase aqueous/organic solvent systems has been studied.

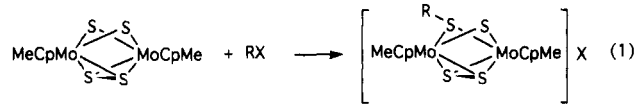
Introduction

An extensive reaction chemistry has been developed for derivatives of the dinuclear sulfido-bridged complex $(CpMo(\mu\text{-}S))_2S_2CH_2$.[1-14] The main thrust of these studies has been the development of new chemistry of coordinated sulfide ligands, but some potential practical applications have also been suggested by this work. These include applications in catalytic hydrogenation and hydrogenolysis reactions[2,4] and in alkene and alkyne separation schemes.[1]

In order to extend the versatility of the reactivity of $(CpMo(\mu\text{-}S))_2S_2CH_2$, we have explored routes to derivatizing the compound to provide solubility in aqueous and other polar solvent systems. It seemed possible to devise synthetic procedures for introducing substituents into the cyclopentadienyl ligands and/or into the methanedithiolate ligand without altering the basic structure of the complex. An important question which we wished to address in this project is what electronic influence the new substituents and the more polar solvents might exert on the reactivity of the sulfido ligands. In this paper we describe the syntheses of complexes of the type $(CpMo(\mu\text{-}S))_2S_2CHR$ with new electron-withdrawing substituents on the methanedithiolate ligands and the characterization of their reaction chemistry. A second paper in this series describes the syntheses of water-soluble molybdenum sulfide complexes with electron-withdrawing substituents on the cyclopentadienyl ligands.[15]

Results and Discussion

Synthesis of Cationic Precursors. The reaction of $(MeCpMo)_2(\mu\text{-}S)_2(\mu\text{-}S_2)$ with alkyl halides led to the formation of alkanethiolate cations of the formula $[(MeCpMo)_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}SR)]^+$ (R = Me, CH_2CO_2Me; eq 1).



(1)

Similar alkylations have been reported for the pentamethylcyclopentadienyl analogue.[16] The reactions are believed to involve nucleophilic attack of a μ-sulfido ligand in the dimer on the organic halide, similar to that reported previously for $(MeCpMo(\mu\text{-}S))_2S_2CH_2$ (1).[3] The bridging sulfide ligand in the reactant dimer should be more nucleophilic than the sulfur atom of the bridging disul-

• Abstract published in *Advance ACS Abstracts*, October 15, 1993.

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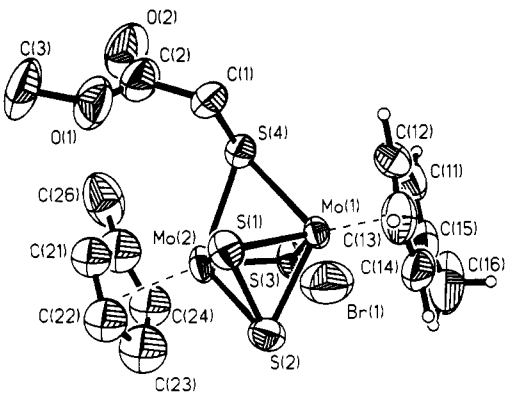

Figure 1. Perspective view of the molecular structure of $[(MeCpMo)_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}SCH_2CO_2Me)]Br$ (**2**(Br)). Thermal ellipsoids are shown at the 50% probability level.

Table I. Selected Bond Distances (Å) and Angles (deg) for $[(MeCpMo)_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}SCH_2CO_2Me)]Br$ (2(Br))

Mo(1)–Mo(2)	2.613(1)	Mo(1)–S(1)	2.388(3)
Mo(1)–S(2)	2.355(4)	Mo(1)–S(1′)	2.366(4)[a]
Mo(1)–S(2′)	2.431(5)	Mo(1)–S(3)	2.295(3)
Mo(1)–S(4)	2.499(3)	Mo(1)–S(3′)	2.347(6)
Mo(1)–S(4′)	2.422(3)	Mo(2)–S(1)	2.355(3)
Mo(2)–S(2)	2.327(4)	Mo(2)–S(1′)	2.285(4)
Mo(2)–S(2′)	2.357(4)	Mo(2)–S(3)	2.335(3)
Mo(2)–S(4)	2.536(3)	Mo(2)–S(3′)	2.393(5)
Mo(2)–S(4′)	2.473(4)	S(1)–S(2)	2.130(4)
S(4)–C(1)	1.708(8)	S(1′)–S(2′)	2.130(6)
S(4′)–C(1)	1.730(8)	S(2)---S(3)	3.071
S(3)---S(4)	2.872	S(1)---S(4)	3.139
Mo(1)–S(1)–Mo(2)	66.8(1)	Mo(1)–S(2)–Mo(2)	67.8(1)
Mo(1)–S(1′)–Mo(2)	68.3(1)	Mo(1)–S(2′)–Mo(2)	66.1(1)
Mo(1)–S(3)–Mo(2)	68.7(1)	Mo(1)–S(4)–Mo(2)	62.5(1)
Mo(1)–S(3′)–Mo(2)	66.9(1)	Mo(1)–S(4′)–Mo(2)	64.5(1)
Mo(1)–S(4)–C(1)	111.6(3)	Mo(2)–S(4)–C(1)	113.3(3)
Mo(1)–S(4′)-C(1)	114.3(3)	Mo(2)–S(4′)–C(1)	114.3(3)

[a] Primed numbers refer to disordered atom orientations with 42% occupancy. See text for a description of the disorder.

fide,[16] and the sulfur–sulfur bond of the latter ligand is proposed to remain intact in the cationic product.

The proposed structure was confirmed by an X-ray diffraction study of the cationic product where R = CH_2CO_2Me (**2**). The molybdenum ions in the cation are bridged by one sulfido ligand, one thiolate group, and a μ_2-disulfide ligand. The sulfur core of the cation is disordered, with the second orientation of sulfide and thiolate ligands (occupancy 42%) rotated approximately 45° with respect to the first. A perspective drawing of the cation which shows the major orientation of sulfur atoms and the numbering scheme is shown in Figure 1. A listing of selected bond distances and angles for the two cation orientations is given in Table I, and a listing of atomic coordinates for all the atoms is given in Table II. The S–S distance in the disulfide ligand (in both orientation) is 2.130(6) Å, somewhat longer than the bond length of 2.095 Å determined for the μ_2-disulfide in $(Cp^*Mo)_2(\mu\text{-}S)_2(\mu\text{-}S_2)$[17] and the S–S distance of 2.06 Å in elemental sulfur.[18] The distance between the thiolate sulfur S(4) and the adjacent sulfide ligand S(3) is 2.863 Å. This distance is significantly less than the van der Waals distance for sulfur atoms and suggests a weak bonding interaction between S(3) and S(4). Similar short intersulfur distances have been observed in other thiolate–bridged structures.[1,6,7]

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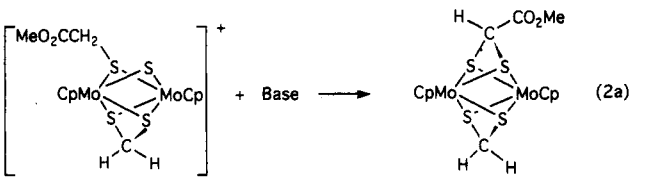
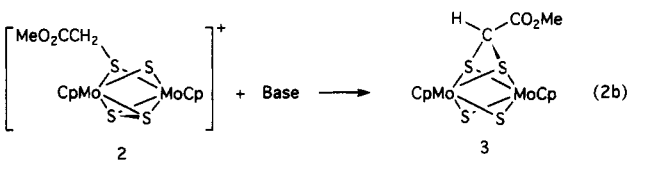
Table II. Atomic Coordinates[a] (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³) for $[(MeCpMo)_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}SCH_2CO_2Me)]Br$ (2(Br))

	x/a	y/b	z/c	U(eq)[b]
Mo(1)	6077(1)	1336(1)	2144(1)	39(1)*
Mo(2)	3731(1)	1171(1)	2666(1)	49(1)*
Br(1)	6477(1)	3712(1)	1679(1)	80(1)*
S(1)†	4408(3)	2146(1)	1805(3)	52(1)*
S(1′)†	4878(4)	361(2)	1879(4)	53(1)*
S(2)†	5286(4)	1879(2)	3942(4)	56(1)*
S(2′)†	5608(4)	655(2)	4031(5)	52(1)*
S(3)†	5479(3)	445(2)	3261(4)	51(1)*
S(3′)†	5097(5)	2088(2)	3413(5)	53(1)*
S(4)†	4302(3)	787(1)	366(3)	50(1)*
S(4′)†	4112(3)	1712(2)	497(4)	51(1)*
O(1)†	1497(9)	1670(5)	−1472(10)	98(2)*
O(1′)†	1820(13)	1720(9)	−2403(18)	100(2)*
O(2)†	1752(9)	679(5)	−2181(11)	113(2)*
O(2′)†	1572(18)	788(12)	−1448(20)	145(2)*
C(1)	3689(7)	1271(4)	−1062(8)	75(2)*
C(2)	2231(8)	1186(5)	−1663(9)	84(2)*
C(3)†	29(12)	1579(9)	−1934(16)	124(2)*
C(3′)†	366(25)	1672(16)	−2875(25)	138(3)
C(11)	7891(6)	942(4)	1409(9)	73(2)*
C(12)	7459(7)	1511(5)	634(8)	87(2)*
C(13)	7668(6)	2011(4)	1633(9)	75(2)*
C(14)	8159(6)	1754(4)	2975(7)	68(2)*
C(15)	8302(6)	1095(4)	2822(8)	64(2)*
C(16)	8877(8)	673(5)	4090(10)	132(2)*
C(21)†	1430(10)	1272(5)	2147(10)	72(3)
C(22)†	1941	1643	3386	82(3)
C(23)†	2608	1220	4466	110(3)
C(24)†	2509	588	3895	88(3)
C(25)†	1782	621	2461	92(3)
C(21′)†	1501(7)	1391(4)	2412(9)	48(2)
C(22′)†	2135	1440	3876	78(2)*
C(23′)†	2596	819	4360	99(2)*
C(24′)†	2247	387	3194	107(2)*
C(25′)†	1570	740	1990	93(2)*
C(26)†	1226(16)	175(10)	1420(19)	118(2)*
C(26′)†	1964(19)	1853(13)	4625(22)	90(2)*
C(26″)†	872(30)	1751(25)	1504(31)	176(3)

[a] Atoms have occupancies of 1.0 except as marked with † above: S(1), 0.58; S(1′), 0.42; S(2), 0.58; S(2′), 0.42; S(3), 0.58; S(3′), 0.42; S(4), 0.58; S(4′), 0.42; O(1), 0.64; O(1′), 0.36; O(2), 0.64; O(2′), 0.36; C(3), 0.64; C(3′), 0.36; C(21), 0.48; C(22), 0.48; C(23), 0.48; C(24), 0.48; C(25), 0.48; C(21′), 0.52; C(22′), 0.52; C(23′), 0.52; C(24′), 0.52; C(25′), 0.52; C(26), 0.48; C(26′), 0.31; C(26″), 0.21. [b] For values marked with an asterisk, the equivalent isotropic U is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Synthesis of $(Cp'Mo(\mu\text{-}S))_2S_2C(H)CO_2Me$ (3). Further reactions of $[(MeCpMo)_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}SCH_2CO_2Me)]$-Br (**2**) were studied. For example, attempts were made to deprotonate the α-carbon of the thiolate ligand by reactions with bases such as pyridine, triethylamine, and lithium diisopropylamide (LDA). In a related system deprotonation of this ligand led to the formation of a neutral dimer with a new 1,1-dithiolate ligand (eq 2a).[8]





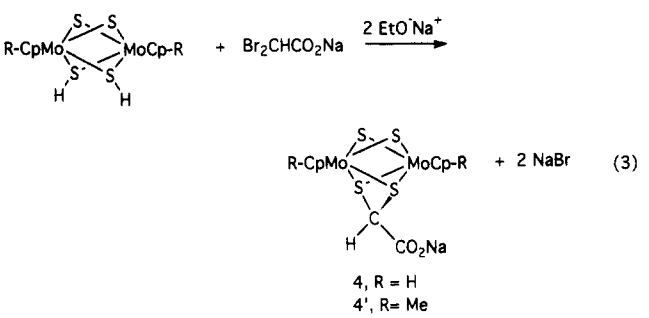
2 3

However, the starting cation **2** was recovered from reactions

with pyridine and triethylamine, while its reaction with LDA led to the formation of insoluble and uncharacterized products.

Although reactions with bases in solution were not successful, deprotonation of the ester-substituted thiolate ligand in **2** was achieved by passing a dichloromethane solution of the cation through a neutral alumina column (eq 2b). The color of the solution changed from deep red to blue upon contact with the alumina. It is not clear why alumina promotes this reaction so effectively, but reactions of other organometallic complexes with alumina have been reported.[19] Collection of the major blue band from the column and removal of solvent led to the isolation of the product $(MeCpMo(\mu\text{-}S))_2S_2C(H)CO_2Me$ (**3**), which was characterized by spectroscopic data. Elemental analyses and the NMR spectrum for **3** (see Experimental Section) were consistent with its proposed formulation. The visible spectrum of **3** in chloroform provided evidence that this product is electronically similar to $(MeCpMo(\mu\text{-}S))_2S_2CH_2$[1] (**1**), which is formulated as a Mo(IV) dimer with two μ-sulfido ligands.[20] Strong absorptions of this latter complex at 586 (1086 M^{-1} cm^{-1}) and 732 nm (1080 M^{-1} cm^{-1}) in $CHCl_3$[21] compare closely to those observed for **3** at 580 (2060 M^{-1} cm^{-1}) and 728 nm (2070 M^{-1} cm^{-1}). The cyclic voltammetry of **3** in acetonitrile, which showed a quasi-reversible oxidation at −0.04 V vs Fc and a reversible reduction at −1.64 V vs Fc, was also similar to that reported for **1**.[22] On the basis of the similarities between **3** and **1**, the deprotonation of cation **2** and intramolecular sulfide ligand substitution to form **3** is proposed to be accompanied by the cleavage of the sulfur–sulfur bond of the disulfide ligand.

Synthesis of $(MeCpMo(\mu\text{-}S))_2S_2CHCO_2^-Na^+$ (4). When **3** was hydrolyzed at 70 °C in an aqueous/THF solution of NaOH, the ester substituent was converted to the acid salt. A more convenient synthesis of the carboxylate-substituted derivative was developed using the known hydrosulfido complex with either Cp or MeCp ligands and a salt of dibromoacetic acid, as shown in eq 3. The resulting complex was filtered from THF and



purified by chromatography on alumina. The product was not soluble in chlorinated hydrocarbons but showed moderate solubility in methanol and neutral or basic water. The sodium salt of the Cp derivative $(CpMo(\mu\text{-}S))_2S_2C(H)CO_2Na$ (**4**) proved to have greater water solubility than the MeCp derivative (**4'**), and most of our characterization has been obtained for **4**.

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(22) Redox potentials for **1** were determined to be −0.04 and −1.61 V vs Fc by the addition of −0.31 to the reported potentials vs SCE.[3] Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980.

Table III. Equilibrium Constants (M^{-1}) for Reactions of Molybdenum Complexes with Olefins at Room Temperature

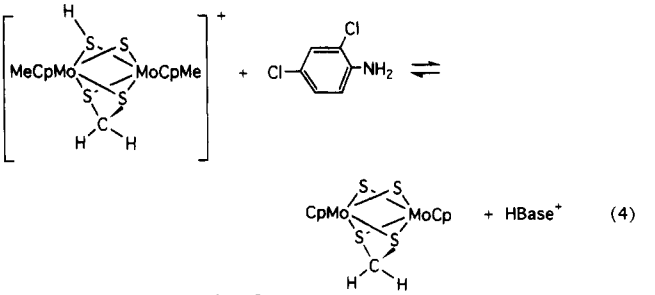
olefin	$(MeCpMo(\mu\text{-}S))_2S_2CH_2$ ($CDCl_3$)	$(MeCpMo(\mu\text{-}S))_2CHCO_2Me$ ($CDCl_3$)	$(CpMo(\mu\text{-}S))_2S_2CHCO_2Na$ (D_2O)
ethene	$>10^4$	$>10^4$	$>10^4$
propene	1200	1500	4200
trans-2-butene	400	220	240
styrene	13		60[a]

[a] Determined in CD_3OD.

The ^1H NMR spectrum of **4** in D_2O showed two Cp singlets at 6.51 and 6.39 ppm, and a resonance at 3.39 ppm was assigned to the CH proton of the dithiolate ligand. The infrared spectrum showed asymmetric and symmetric carboxylate stretches at 1625 and 1371 cm^{-1}, respectively. The complex displayed the characteristic deep blue of methanedithiolate-bridged derivatives. Visible spectroscopy of aqueous solutions established that **4** obeyed Beer's law with absorptions at 510 (sh), 576 (1210 M^{-1} cm^{-1}), and 735 nm (1100 M^{-1} cm^{-1}). These bands are similar to those observed for the related nonaqueous systems (vide supra). Although the NMR spectrum of **4** was clean and sharp with no apparent impurities, elemental analyses of **4** were consistently low (in C, H, and S). These data suggest that the chromatographed product may still be contaminated with a byproduct of eq 4, sodium bromide.

Reactivity of 3 and 4 with Alkenes and Electrophiles. As suggested by the spectroscopic and electrochemical data for **3** and **4**, the reactivities of these complexes were similar to that of $(MeCpMo(\mu\text{-}S))_2S_2CH_2$ (**1**). For example, the sulfido ligands of both **3** and **4** underwent interactions with olefins to form alkanedithiolate complexes. The equilibrium constants for these reversible interactions at room temperature were estimated from ^1H NMR data in solutions of known concentrations in sealed NMR tubes. The equilibrium constants, determined for $CHCl_3$ solutions of **3** and for aqueous solutions of **4**, were found to be similar to those determined for **1**.[23] The data are given in Table III.

A quantitative measure of electron density at the sulfido ligands in some of these dinuclear complexes has been provided by the determination of the equilibrium constant in sulfur protonation reactions. For example, the K_{eq} value for eq 4 was determined in acetonitrile[24] and used to



calculate a K_a of 4×10^{-9} for the protonated dimer at room temperature.[11] In order to obtain a quantitative comparison of the electron-withdrawing effect of the ester substituent on the molybdenum sulfur core of the dimer, we attempted to determine the K_a value for the protonated form of **3**.

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However, the reaction of **3** with triflic acid did not proceed to form a sulfur-protonated cation as a stable product. Instead, protonolysis of the alkanedithiolate ligand occurred to form the thiolate cation $[(MeCpMo)_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}SCH_2CO_2Me)]SO_3CF_3$, which was identified by comparison of spectroscopic data with those of the bromide salt **2**. Previous examples have been observed in dinuclear sulfur-bridged molybdenum complexes where electron-withdrawing thiolate substituents have promoted C–S bond protonolysis reactions.[25,26] The sensitivity of the $\mu\text{-}S_2CHCO_2Me$ ligand in **3** to protic acid is in marked contrast to the behavior of the unsubstituted methanedithiolate ligand in **1**. The latter has proven to be quite robust under acidic reaction conditions.

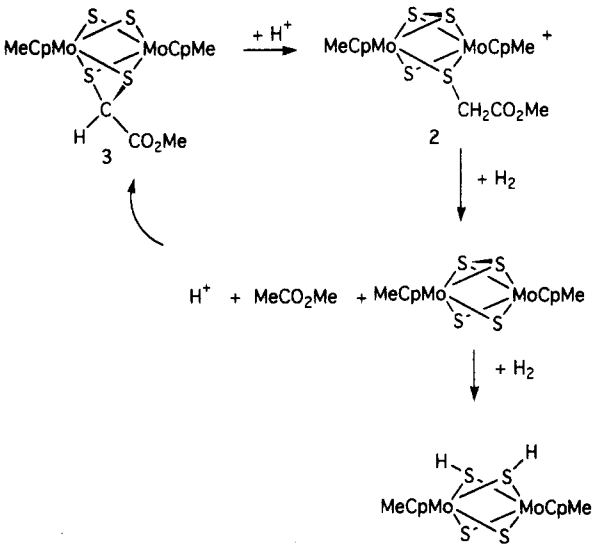
The protonation chemistry of **4** in aqueous solution was also investigated. The addition of HCl to **4** resulted in formation of a blue precipitate, which was filtered and dried. The NMR spectrum of this product in DMSO-d_6 was similar to that of **4** with resonances shifted slightly downfield (see Experimental Section). The data are consistent with the formation of $(CpMo(\mu\text{-}S))_2S_2CHCO_2H$ (**5**). The product could be extracted with basic water to re-form **4**. Further addition of trifluoroacetic or triflic acid to **4** or **5** led to complex product mixtures, and a clean C–S cleavage of the alkanedithiolate ligand was not characterized.

The reactions of **3** and **4** with other electrophiles led to sulfur-substituted products. For example, methyl iodide and methyl bromoacetate each reacted with **3** to form the corresponding methyl and methyl acetate substituted thiolate cations $[(CpMo)_2(S_2CHCO_2Me)(\mu\text{-}S)(\mu\text{-}SR)]^+$. Spectroscopic data for these products are included in the supplementary material.

Complex **4** reacted with methyl iodide in aqueous solution to form an analogous thiolate cation, **6**. The NMR spectrum of the alkylated product included a resonance at 1.66 ppm, which was assigned to a methanethiolate ligand. Cp resonances of **6** were shifted downfield to ~7 ppm, a shift characteristic of alkanethiolate cations. No evidence was observed in the NMR or IR spectra for the formation of the methyl ester complex, which would be the Cp analogue of the MeCp derivative **3**, described above. Complex **6** can be formulated as $[(CpMo)_2(S_2CHCO_2Na)(\mu\text{-}S)(\mu\text{-}SCH_3)]I$. Alternatively, the product could dissociate NaI to form a zwitterionic derivative. We have been unsuccessful in obtaining single crystals of **6** to determine by X-ray diffraction whether sodium and iodide ions are an integral component of the complex in the solid state. The FAB^+ mass spectrum of the product showed a molybdenum isotope pattern at m/e 545 which corresponds to the sodium-containing cation formulated above.

Reactions of 3 and 4 with Hydrogen. As we reported previously, a new product was not detected when $(MeCpMo(\mu\text{-}S))_2S_2CH_2$ (**1**) was reacted with 1-3 atm of H_2.[4] However, evidence that the complex does interact with hydrogen was provided by the catalytic formation of HD from an H_2/D_2 mixture[14] and by the catalytic role of **1** in the hydrogenation of certain organic substrates.[4] For example, the hydrogenation of azobenzene to diphenylhydrazine was proposed to proceed by reversible hydrogen addition to the sulfide ligands of **1**, followed by rapid hydrogen atom transfer from an SH ligand in the active catalyst to azobenzene. A model for the proposed hydrogen atom transfer step in the catalytic cycle was characterized using a structurally related molybdenum(III) dimer with an S–H ligand.[5]

Scheme I



The reactivity of compound **3** toward H_2 was investigated in similar types of experiments. Although no spectroscopic changes were initially observed when **3** was placed under H_2, both HD formation and azobenzene hydrogenation were catalyzed by **3** under conditions similar to those used previously for **1** (see Experimental Section).

In the presence of a protic acid catalyst (e.g., CF_3CO_2H), a net reaction of **3** with hydrogen was observed. Final products were found to be methyl acetate and $[MeCpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$. As discussed above, protic acid produces the thiolate cation $[(MeCpMo)_2(\mu\text{-}S)(\mu\text{-}S_2)(SCH_2CO_2Me)]^+$. Independent studies of this cation showed that it reacts with hydrogen to produce the final observed products. The reaction involves a heterolytic cleavage of H_2 that re-forms the protic catalyst (see Scheme I). A mechanistic study of reactions of related thiolate-bridged cations with H_2 to form products that result from hydrogenolysis of the thiolate ligand has been reported previously.[25]

Unlike complexes **1** and **3**, which did not undergo a detectable reaction with H_2 in the absence of added acid, **4** did react with H_2 to form a new product. When a solution of **4** in neutral D_2O was stirred under ~3 atm of hydrogen, a color change from blue to red was observed over a period of ca. 3 days, and the product, **7**, precipitated as a noncrystalline red solid. The FAB mass spectrum of **7** showed a molybdenum envelope at m/e 532 consistent with the addition of H_2 to the starting complex. The NMR spectrum of **7** in D_2O showed a sharp Cp singlet at 6.03 ppm (10 H) and a broader resonance at ca. 2.0 ppm (2 H). The equivalency of the Cp ligands indicates that the $\mu\text{-}S_2CHCO_2Na$ ligand is no longer intact. A reaction that would result in a dimer with equivalent CpMo sites is suggested in eq 5. The proposed structure of **7** is consistent with additional spectroscopic data. For example, the ^{13}C NMR spectrum of **7** showed resonances for the Cp, carboxylate, and methylene carbons. The assignment of the methylene carbons was confirmed by DEPT experiments. The S–H ligand in the proposed product was not detected in the NMR spectrum, but rapid exchange of this proton with

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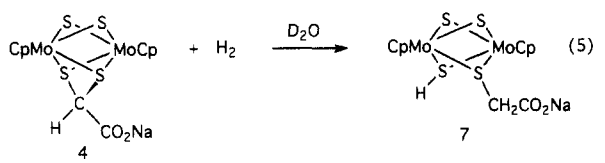

4 7 (5)

D_2O is expected. In the infrared spectrum of 7 isolated from H_2O a weak band at 2420 cm^{-1} was assigned to an S–H stretch. In addition, the visible spectrum of 7 was very similar to those reported for the related structures $[CpMo(\mu\text{-}S)(\mu\text{-}SR)]_2$ in organic solvents.[27]

The mechanism of H_2 addition to 4 has not been established. We speculate that a protonolysis of the alkanedithiolate ligand like that observed for 3 might be promoted by reducing conditions. For example, the addition of H_2 to sulfido ligands of 4 could generate an acidic SH group which may be involved in a (intra- or intermolecular) C–S bond cleavage in the reduced complex.

The volatile products in the reaction of 4 with H_2 in D_2O have been identified by mass spectroscopy after long reaction periods (ca. 6 weeks). Evidence for H_2–D_2O exchange was observed, and a ratio of 14% H_2, 11% HD, and 75% D_2 was determined. Although 4 was converted to 7 during this time, much of the H_2–D_2O exchange activity was attributed to 4. A similar experiment with an isolated sample of 7 showed only 6% HD and 11% D_2. Further studies on the pH dependence of this exchange may provide an interesting comparison with the same reaction catalyzed by the hydrogenase enzymes, which are believed to contain metal sulfide or selenide complexes or clusters at their active sites.[28]

Catalytic Reductions of Organic Substrates. The advantages of water-soluble catalysts for the transformation and ready separation of organic substrates have been described previously[29] and demonstrated in several cases.[30] Complex 4 served as a catalyst precursor for the hydrogenation of C=N and N=N bonds in organic substrates in two-phase solvent systems. For example, when solutions of 4 in H_2O and 25 equiv of azobenzene in CH_2Cl_2 were stirred or shaken under 1–2 atm of hydrogen, the catalytic conversion of azobenzene to diphenylhydrazine was observed. Yields on repeated runs, determined after 24-h periods, were quite variable (15–80%), perhaps because of variations in mixing efficiency. Partial conversion of 4 to 7 occurred during these reactions. When isolated samples of 7 were used in the same reactions, low yields (2–12%) of diphenylhydrazine were observed. Further efforts were not made to differentiate the catalytic activities of the two complexes. Complexes 4/7 were also used to catalyze the hydrogenation of methyl thiocyanate to the thioamide CH_3NHCHS and to reduce nitrobenzene to aniline at room temperature. Similar catalytic reactions have been characterized for 1 in organic solvents.[4]

Summary and Conclusions. The new complex $(MeCpMo(\mu\text{-}S))_2S_2C(H)CO_2Me$ (3) is similar to the parent methanedithiolate complex 1 in spectroscopic and electrochemical characteristics and in most aspects of reactivity. μ-Sulfido ligands of 3 reacted reversibly with olefins and with electrophilic alkyl halides. However, the reaction of 3 with protic acid resulted in the cleavage of a carbon–sulfur bond of the dithiolate ligand to form $[(MeCpMo)_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}SCH_2CO_2Me)]^+$ (2). In contrast, the unsubstituted methanedithiolate ligand in 1 is stable under acidic conditions, and the reaction of 1 with a strong acid resulted in protonation of a bridging sulfido ligand.

The water-soluble complex $(CpMo(\mu\text{-}S))_2S_2C(H)CO_2Na$ (4) was also electronically similar to 1. The reactivity of 4 with hydrogen in aqueous solution provided an interesting extension to that of 1. While 4 showed catalytic hydrogenation activity similar to that of 1, a net hydrogen addition to 4 was also observed. In contrast, the addition of H_2 to 1 has never been detected spectroscopically. The hydrogen addition product has been isolated; spectroscopic data suggest the formulation $(CpMo(\mu\text{-}S))_2(\mu\text{-}SH)(\mu\text{-}SCH_2CO_2Na)$ (7). The mechanism of the reaction of 4 with hydrogen and the role of intermediate species in H_2–D_2O exchange are topics of continuing interest in our laboratory.

Experimental Section

Reagents. $(MeCpMo)_2(\mu\text{-}S)_2(\mu\text{-}S_2)$ and $[Cp'Mo(\mu\text{-}S)(\mu\text{-}SH)]_2$ were synthesized according to published procedures.[4,27] Br_2CHCO_2Na was synthesized by the reaction of dry Br_2CHCO_2H with sodium hydride in dry THF. ^1H NMR (250 MHz, D_2O): δ 5.77 ppm. Solvents were dried by conventional procedures; reactions were carried out under a nitrogen atmosphere using standard Schlenkware.

Synthesis of $[(MeCpMo)_2(\mu\text{-}S_2)(\mu\text{-}S)(\mu\text{-}SCH_2CO_2CH_3)]Br$ (2(Br)). $(MeCpMo)_2(\mu\text{-}S)_2(\mu\text{-}S_2)$ (0.10 g, 0.21 mmol) was dissolved in ca. 20 mL of CH_2Cl_2 under nitrogen, and $BrCH_2CO_2CH_3$ (100 μL, 1 mmol) was syringed into the solution. The solution was stirred at ambient temperature under a nitrogen atmosphere for 2–2.5 h. The blue solution became brown within 5 min and burgundy within 30 min. The solvent was removed on the vacuum line to give a red-burgundy powder, which could be recrystallized from CH_2Cl_2/hexanes. Yield: 0.097 g, 72%. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.61 (m, 8, C_5H_4), 3.62 (s, 3, CO_2CH_3), 2.46 (s, 6, $C_5H_4CH_3$), 2.29 (s, 2, $CH_2CO_2CH_3$). ^{13}C NMR ($CDCl_3$): δ (ppm) 169.53 (CO_2), 121.86 (C_5H_4), 104.10 (C_5H_4), 103.50 (C_5H_4), 102.04 (C_5H_4), 101.06 (C_5H_4), 52.49 (1, CO_2CH_3), 38.82 (1, CH_2), 16.71 (2, $CH_3C_5H_4$). MS (FAB+): m/e 551 (P of cation), 478 (P – $CH_2CO_2CH_3$), 446 (P – $CH_2CO_2CH_3$, –S). IR (CH_2Cl_2): 1734 cm^{-1} (ν_{CO}).

X-ray Diffraction Study of 2. Dark maroon crystals of 2 were obtained by slow diffusion of hexanes into a CH_2Cl_2 solution at ca. –20 °C. The crystals of 2 were mounted on glass fibers and coated with epoxy. The structure was solved using direct methods and Fourier techniques. The central core of sulfurs, the methyl carboxylate, and one of the methylcyclopentadienyl rings are disordered. Occupancies were determined by least-squares refinements and then were held fixed while displacement parameters were refined. Cyclopentadienyl rings were refined as rigid pentagons. Except for the disordered carbon atoms with lower site occupancies and the C(21), C(21′) pair, which are separated by only 0.35 Å, all atoms were refined anisotropically. Careful examination of the contacts in the molybdenum–sulfur core confirmed the presence of a sulfur–sulfur bond and also the fact that there is no other reasonable model for the disorder. Crystallographic data are given in Table IV.

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Table IV. Crystal Data, Data Collection Conditions, and Solution and Refinement Details for [(MeCpMo)$_2$(μ-S$_2$)(μ-S)(μ-SCH$_2$CO$_2$Me)]Br (2(Br))

	Crystal Data
formula	$C_{15}H_{19}O_2S_4BrMo_2$
color; habit	very dark maroon
cryst dimens	0.23 × 0.25 × 0.55 mm
space group[a]	$P2_1/c$
cryst syst	monoclinic
unit cell dimens[b,c]	a = 10.379(2) Å
	b = 20.820(6) Å
	c = 9.597(2) Å
	β = 102.56(2)°
vol	2024.3(8) Å^3
formula units/cell	Z = 4
fw	619.2
density (calcd)	2.032 g/cm^3
abs coeff	3.568 mm^{-1}
F(000)	1184 e
	Data Collection
diffractometer used	Siemens P3/F
radiation	Mo Kα (λ = 0.710 73 Å)
temperature	22–24 °C
monochromator	highly oriented graphite cryst
mosaic character[d]	0.32°
2θ range	3.0–50.0°
scan type	Wyckoff
scan speed	variable; 2.02–58.59°/min
index ranges	$-12 \le h \le 12, -3 \le k \le 24, -11 \le l \le 11$
no. of rflns collected	8636
no. of unique rflns[e]	3581 (R_{int} = 2.78%)
no. of obsd rflns	2944 ($F > 6.0\sigma(F)$)
	Refinement
weighting scheme	$w = 1.0/[\sigma^2(F) + 0.0001F^2]$
final residuals (obsd data)	R = 4.43%, R_w = 6.31%
goodness of fit	2.74
largest and mean Δ/σ	0.067, 0.004
data-to-param ratio	10.3:1
largest diff peak	0.58 e/Å^3
largest diff hole	−0.79 e/Å^3

[a] *International Tables for X-ray Crystallography*; D. Reidel: Dordrecht, Holland, and Boston, MA, 1983; Vol. A. [b] Cell dimensions were determined by a least-squares fit of the setting angles for 25 reflections with 2θ in the range 28.5–46.2°. Angle tolerances for centering, 2θ, ω, and χ; 0.02, 0.01, and 0.04. [c] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. [d] Crystal mosaic character was determined from the width at half-height of ω scans. [e] $R_{int} = [\sum N(\sum w(F_{mean} - F)^2)/\sum(N-1)\sum wF^2]^{1/2}$. [f] The quantity minimized in the least-squares procedures is $\sum w(|F_o| - |F_c|)^2$. $R = R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, and $R_w = R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

Attempted Reactions of [(MeCpMo)$_2$(μ-S$_2$)(μ-S)(μ-SCH$_2$CO$_2$CH$_3$)]Br (2(Br)) with Bases. (a) Complex **2** (0.075 g, 0.12 mmol) was dissolved in ca. 15 mL of THF under nitrogen in a Schlenk flask. NEt$_3$ (20 μL, 0.14 mmol) was syringed into the solution, and the reaction mixture was stirred at room temperature under nitrogen for 1 week. The solvent was removed, and the ^{1}H NMR spectrum of the brown solid indicated that **2** had not reacted.

(b) Complex **2** (0.07 g, 0.11 mmol) was put in a Schlenk flask in the drybox. Lithium diisopropylamide–mono(tetrahydrofuran) (LDA·THF), 1.5 M in cyclohexane (0.4 mL, 0.6 mmol), was syringed into the Schlenk tube, and distilled THF (30 mL) was vacuum-transferred into the flask. The brown solution was sealed under vacuum and stirred at ambient temperature for 1 day. The solvent was removed on the vacuum line, and a brown-black powder remained. The material was insoluble in common organic solvents, and ^{1}H NMR data were not obtained.

Synthesis of (MeCpMo(μ-S))$_2$S$_2$CHCO$_2$Me (3). Complex **2** was dissolved in distilled CH_2Cl_2 and put on a neutral alumina column. The burgundy starting material turned a rich blue color on the alumina surface. The first yellow fraction was eluted with CH_2Cl_2 and was not characterized. The second blue fraction, eluted with CH_2Cl_2, was collected, and the solvent was removed by rotavaporation to give **3**. Yield: 50%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.37 (m, 8, C_5H_4), 3.66 (s, 3, CO_2CH_3), 3.37 (s, 1, $CHCO_2CH_3$), 2.43 (s, 3, $CH_3C_5H_4$), 2.37 (s, 3, $CH_3C_5H_4$). ^{13}C NMR ($CDCl_3$): δ (ppm) 170.4 (1, CO_2CH_3) 112.1 (2, Cp′), 101.6 (2, Cp′), 100.6 (2, Cp′), 98.94 (1, Cp′), 97.7 (1, Cp′), 52.6 (1, CO_2CH_3), 43.8 (1, $SCHCO_2CH_3$), 16.94 (1, $CH_3C_5H_4$), 16.91 (1, $CH_3C_5H_4$). MS (FAB$^+$): m/e 551 (P), 478 (P − $CHCO_2CH_3$), 446 (P − $CHCO_2CH_3$, −S). IR (CH_2Cl_2): 1732 cm^{-1} (ν_{CO}). Anal. Calcd for $C_{15}H_{18}Mo_2S_4O_2$: C, 32.65; H, 3.52; S, 23.24. Found: C, 32.55; H, 3.20; S, 23.43. CV (CH_3CN/Et_4NBF_4; E, V vs Fc)): −1.64, ΔE = 68 mV; −2.24, irreversible; +0.04, ΔE = 214 mV at 100 mV/s, 191 mV at 50 mV/s.

Reaction of (MeCpMo(μ-S))$_2$S$_2$CH(CO$_2$CH$_3$) (3) with Trifluoromethanesulfonic Acid. Complex **3** (0.057 g, 0.044 mmol) was combined with distilled CH_2Cl_2 (6 mL) and trifluoromethanesulfonic acid (10 μL, 1.08 mmol) under nitrogen. The blue solution turned red immediately, and after 30 min the solvent was removed under vacuum. The remaining red oily material was dried under a dynamic vacuum for several hours and then recrystallized from distilled CH_3CN/Et_2O under nitrogen to give [(MeCpMo)$_2$(μ-S$_2$)(μ-S)(μ-SCH$_2$CO$_2$Me)]CF$_3$SO$_3$. Yield: 0.040, 68%. Spectroscopic data for the triflate salt differ slightly from those of the bromide salt of **2**. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.82–6.71 (m, 8, C_5H_4), 3.66 (s, 3, $CH_2CO_2CH_3$), 2.67 (s, 2, $CH_2CO_2CH_3$), 2.46 (s, 6, $CH_3C_5H_4$). ^{13}C NMR ($CDCl_3$): δ (ppm) 169.2 (1, CO_2CH_3), 123.7 (2, Cp′), 105.0 (2, Cp′), 103.7 (2, Cp′), 103.1 (2, Cp′), 53.4 (1, $CH_2CO_2CH_3$), 26.2 (1, $CH_2CO_2CH_3$), 16.9 (2, $CH_2C_5H_4$).

(Cp′Mo(μ-S))$_2$S$_2$CH(CO$_2$CH$_3$) (3) in the Presence of Hydrogen and Deuterium. Complex **3** (0.042 g, 0.076 mmol) was dissolved in ca. 20 mL of purified $CDCl_3$ in a Schlenk flask. The solution was degassed in three freeze–pump–thaw cycles. Approximately 0.5 atm of hydrogen and 0.5 atm of deuterium were added at −196 °C. After 30 min an aliquot was removed and the volatiles were analyzed in a mass spectrometer. The relative concentrations of H_2 and D_2 were found to be ca. 3:1. No HD was detected. The solution remained at ambient temperature, and after 5 days the volatiles were analyzed by mass spectrometry. HD (ca. 18%) was detected.

Determination of Equilibrium Constants for Reactions of 3 and 4 with Olefins. In a typical procedure a known weight of **3** or **4** (ca. 0.01 g) was dissolved in 0.8 mL of $CDCl_3$ or D_2O, respectively, in an NMR tube and the solution was degassed in three freeze–pump–thaw cycles. The appropriate equivalents of the olefin were added, and the NMR tube was flame-sealed at −196 °C. The reactions were monitored by ^{1}H NMR spectroscopy at ambient temperature over several days. For the chloroform solutions, equilibrium was established in less than 1 day. Most of the reactions in D_2O showed no further change after ca. 3 days. Concentrations were determined by using integration values for the olefin, the olefin adduct, and the known initial concentration of **3** or **4**. Equilibrium constants were calculated from several ^{1}H NMR spectra, and average values are reported in Table III.

Reaction of 3 with Hydrogen in the Presence and Absence of Trace Acid. A stock solution of **3** (0.019 g, 3.6 × 10^{-5} mol) in C_6D_6 (2.4 mL) was prepared, and the solution was degassed in three freeze–pump–thaw cycles. An aliquot (0.8 mL) was injected into a NMR tube, and approximately 0.76 atm of H_2 was added at −196 °C to the tube, which was then flame-sealed. Trifluoroacetic acid (CF_3CO_2H, 0.5 μL, 1 × 10^{-5} mol) was injected into a second NMR tube, and the above procedure was repeated. Initial ^{1}H NMR spectra indicated the presence of starting materials. The NMR tubes were heated at ca. 55 °C, and after 4 h the ^{1}H NMR spectra of the two samples were recorded. The reaction with trace acid indicated the presence of (Cp′Mo)$_2$(μ-S)$_2$(μ-SH)$_2$ (**26**) and methyl acetate ($CH_3CO_2CH_3$). ^{1}H NMR (300 MHz, C_6D_6): δ (ppm) 6.1–5.8 (m, 8, Cp′), 2.3 (s, 6, CH_3Cp), −1.4, −1.5, −1.7, −1.8 (s, 2, SH). ^{1}H NMR for $CH_3CO_2CH_3$ (C_6D_6): δ (ppm) 3.2 (s, 3, $CH_3CO_2CH_3$), 2.2 (s, 3, $CH_3CO_2CH_3$). There was no reaction detected in the absence of acid. The ^{1}H NMR spectra of the two reaction mixtures were also recorded after 6 days, and the same results were observed.

Catalytic Hydrogenation Reactions of Azobenzene with 3 and $(Cp'Mo(\mu\text{-}S))_2S_2CH_2$ (1). In a typical procedure 0.010 g of either $(Cp'Mo(\mu\text{-}S))_2S_2C(H)CO_2CH_3$ (3) or $(Cp'Mo(\mu\text{-}S))_2S_2CH_2$ (1) was dissolved in 4 mL of $CHCl_3$ in a Schlenk flask, and 0.10 g (5.5×10^{-4} mol) of azobenzene ($C_6H_5N{=}NC_6H_5$) was added. The solution was degassed in three freeze–pump–thaw cycles, and H_2 (1.1×10^{-3} mol) was added at −196 °C. After the flask was sealed, the solution was warmed to ambient temperature and stirred for 30 min. The reaction mixture was frozen, and H_2 was removed. After thawing, the solution was evaporated and the reaction mixture was redissolved in $CDCl_3$. The contents were analyzed by ^1H NMR spectroscopy. The percent conversion of $C_6H_5N{=}NC_6H_5$ to diphenylhydrazine ($C_6H_5NHNHC_6H_5$), determined from the average of integrations of the two compounds in ^1H NMR spectra, was 4.6 ± 0.3% for 3 and 6.7 ± 0.3% for 1.

Synthesis of $(CpMo(\mu\text{-}S))_2S_2C(H)CO_2Na$ (4). $(CpMo(\mu\text{-}S))_2(\mu\text{-}SH)_2$ (0.938 g, 2.07 mmol) and Br_2CHCO_2Na (0.302 g, 1.26 mmol) were dissolved in 60 mL of freshly distilled THF in a Schlenk flask. A freshly prepared solution of NaOEt (4.13 mmol) in ethanol (3 mL) was added dropwise over a 10-min period against a flow of nitrogen. The resulting blue-green solution was stirred for 45 min at 25 °C. The crude product was filtered through Celite, the solvent was evaporated, and the remaining solid was extracted with H_2O. The aqueous solution was filtered and quickly chromatographed under nitrogen on an alumina column using H_2O as eluent. A single blue band was collected in low yield (4.2%). In an alternate isolation procedure, the crude solid was extracted first with diethyl ether (5 × 15 mL). The yellow rinses were discarded, and the remaining solid was extracted with water. The aqueous solvent was removed from the product by rotary evaporation. The yield was 20%, but the product was still contaminated with Br_2CHCO_2Na. When NaOMe in MeOH is used in the place of NaOEt/EtOH, the final product retained MeOH, which we were unable to remove by drying procedures. ^1H NMR (300 MHz, D_2O): δ (ppm) 3.36 (s, 1H, $S_2C(H)CO_2Na$), 6.36 (s, 5H, Cp), 6.49 (s, 5H, Cp). ^{13}C NMR (D_2O): δ (ppm) 49.9 ($S_2C(H)CO_2Na$), 101.9 (Cp), 175.9 ($S_2C(H)CO_2Na$). IR (KBr): 1612 ($\nu_{C=O}$ asym), 1384 cm^{-1} ($\nu_{C=O}$ sym). MS (FAB^+): *m/e* 530 (P^+), 507 (P − Na), 419 (P − $SC(H)CO_2Na$). UV–vis (H_2O): λ_{max} 510 nm (sh), λ_{max} 576 nm (ε 1211 M^{-1} cm^{-1}), λ_{max} 735 nm (ε 1102 M^{-1} cm^{-1}). Anal. Calcd for $C_{12}H_{11}Mo_2O_2S_4Na$ + 1 NaBr: C, 22.76; H, 1.75; S, 20.25. Found: C, 22.77; H, 1.94; S, 18.75.

A similar synthetic procedure was used for the preparation of $(MeCpMo(\mu\text{-}S))_2S_2CHCO_2Na$ (4′). THF was evaporated, and the crude solid was extracted with MeOH. Yield: 40–70% (product retains MeOH). ^1H NMR (250 MHz, D_2O): δ (ppm) 6.38, 6.26 (Cp), 3.38 (S_2CH), 2.23, 2.16 (MeCp). IR (KBr): 1605 (ν_{CO} asym), 1379 (ν_{CO} sym).

Formation of $(CpMo(\mu\text{-}S))_2S_2CHCO_2H$ (5). Diluted HCl (1:1 HCl/H_2O) was added dropwise to a stirred solution of 4 (0.020 g, 3.6×10^{-5} mol) in water (2 mL), until no more solid precipitated. The resulting blue-green solid was filtered, washed with deionized water, and dried *in vacuo*. Yield: 20%. ^1H NMR (250 MHz, DMSO-d_6): δ (ppm) 6.60 (s, 5H, Cp), 6.46 (s, 5H, Cp), 3.75 (s, 1H, $CHCO_2Na$). MS (EI): *m/e* 532 (P). IR (KBr): 3600–3000 (ν_{OH}), 1680 (ν_{CO}), 1620, 1422, 1348, 1289 cm^{-1}.

Formation of $[(CpMo)_2(S_2CHCO_2Na)(\mu\text{-}S)(\mu\text{-}SMe)]I$ (6). Methyl iodide (22 μL, 3.4×10^{-4} mol) was added to a solution of 4 (0.17 g, 3.1×10^{-4} mol) in water (20 mL). The solution was stirred at room temperature for 3 days. The color changed from blue-purple to red-purple. The solvent was removed by rotary evaporation, and the product was recrystallized from H_2O/THF as a red powder. ^1H NMR (300 MHz, D_2O): δ (ppm) 6.91 (s, 5H, Cp), 6.73 (s, 5H, Cp), 5.56 (s, 1H, $S_2CHCO_2^-$), 1.66 (s, 3H, SMe). MS (FAB^+): *m/e* 545 (P of cation).

Formation of $(CpMo(\mu\text{-}S))_2(\mu\text{-}SH)(\mu\text{-}SCH_2CO_2Na)$ (7). Complex 4, $(CpMo(\mu\text{-}S))_2S_2C(H)CO_2Na$ (16 mg, 0.029 mmol), was dissolved in 5–10 mL of D_2O in an Schlenk flask fitted with a high-vacuum valve and Teflon stopcock. The solution was degassed with three freeze–pump–thaw cycles, 600 Torr of hydrogen was admitted at −196 °C, and the tube was flame-sealed. After the mixture was stirred or shaken for 3–5 days at ambient temperature, a color change from blue to red was observed, and a fine red solid precipitated from solution. ^1H NMR (300 MHz, D_2O): δ (ppm) 2.0 (b, 2H, $S_2CH_2CO_2Na$), 6.33 (s, 10H, Cp). ^1H NMR (300 MHz, CD_3OD): δ (ppm) 1.84, 1.90 (2 s, 2H, CH_2CO_2Na), 6.11, 6.12 (2 s, 10H, Cp). ^{13}C NMR (300 MHz, CD_3OD): δ (ppm) 45.69, 46.86 (SCH_2CO_2Na) (CH_2 assignment confirmed by DEPT), 99.22, 99.19 (Cp), 178.3 (SCH_2CO_2Na). IR (KBr): 2420 (ν_{SH}), 1570 ($\nu_{C=O}$ asym), 1370 ($\nu_{C=O}$ sym) cm^{-1}. MS (FAB^+): *m/e* 532 (P^+), 509 (P − Na), 459 (P − CH_2CO_2Na), 419 (P − SCH_2CO_2Na). UV–vis (H_2O): λ_{max} 373 (sh), λ_{max} 511 (ε 1289 M^{-1} cm^{-1}), λ_{max} 710 (ε 869 M^{-1} cm^{-1}). The product appeared to be more soluble in NaOD/D_2O (pH 11). In some cases broad NMR spectra were observed in neutral D_2O; these became sharper in D_2O/NaOD (pH 11).

Reactions of 4 and 7 with H_2/D_2O. Complex 4, $(CpMo(\mu\text{-}S))_2S_2C(H)CO_2Na$ (7.7 mg, 0.015 mmol), was dissolved in D_2O (1 mL) in an NMR tube fitted with a high-vacuum valve and Teflon stopcock. The solution was degassed with three freeze–pump–thaw cycles, and 570 Torr of H_2 was admitted at −196 °C. The solution was shaken at room temperature for ca. 6 weeks. A color change from blue to red was observed, and a red solid was present in the tube. Mass spectral analysis of the volatile products showed 14% H_2, 11% HD, and 75% D_2. The mass spectrum of the blank, in which no complex was present, showed only H_2.

$(CpMo(\mu\text{-}S))_2(\mu\text{-}SH)(\mu\text{-}SCH_2CO_2Na)$ (7; 5.5 mg, 0.01 mmol) in 1 mL of D_2O was reacted with hydrogen in a similar procedure. After 6 weeks at room temperature, no color change was observed, and a red solid was present in the tube. Mass spectral analysis of the volatile products showed 83% H_2, 6% HD, and 11% D_2. No HD was detected in a blank run in the absence of molybdenum complex.

Hydrogenation Reactions Catalyzed by 4. In a typical procedure, 60 mg (0.1 mmol) of $(CpMo(\mu\text{-}S))_2S_2C(H)CO_2Na$ (4) was dissolved in 5 mL of H_2O and 25 equiv of substrate (azobenzene, nitrobenzene, or methyl thiocyanate) was dissolved in 5 mL of CH_2Cl_2 in a 100-mL Schlenk flask. The solution was degassed with two or three freeze–pump–thaw cycles, and 600 Torr of hydrogen was admitted at −196 °C. After it was warmed to room temperature, the two-phase solvent mixture was either shaken or stirred vigorously. Solutions were analyzed at periodic time intervals by withdrawing a $^1/_2$-mL aliquot of the nonaqueous phase, evaporating the solvent, and redissolving the solid in 1 mL of $CDCl_3$. The following yields were determined by ^1H NMR spectroscopy from the integrated areas of the substrate and product resonances: diphenylhydrazine, 79% after 24 h; $PhNH_2$, 6% after 24 h, 36% after 1 week; MeNHCHS, 32% after 42 h.

Acknowledgment. This work was supported by the National Science Foundation and the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy. L.L.L. was supported by a grant from the Chevron Research and Technology Co.

Supplementary Material Available: Complete tables of bond lengths and angles, anisotropic thermal parameters, and hydrogen atom parameters for 2 and text detailing the syntheses and characterization data for $[(MeCpMo)_2(S_2CHCO_2Me)(\mu\text{-}S)(\mu\text{-}SR)]X$ (R = CH_3, CH_2CO_2Me) (9 pages). Ordering information is given on any current masthead page.

OM930463W