Activation of Hydrogen by Cationic Cyclopentadienyl Complexes with Sulfido Ligands. 3. Cationic Complexes Derived from Reactions with Halo Esters, Halo Ketones, and Acyl Halides

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Received April 22, 1987

The dinuclear molybdenum complex $(CpMo(\mu\text{-}S))_2S_2CH_2$ (Cp = C_5H_5; **1**) reacts with methyl bromoacetate and with 1-bromo-2-butanone to form cationic derivatives of the formula $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SR)]Br$, where R = $CH_2CO_2CH_3$ (**2**) or $CH_2C(O)CH_2CH_3$ (**6**). These cations react with hydrogen at room temperature to form methyl acetate and 2-butanone, respectively. In the presence of base, the α-carbon atom of the thiolate ligand in each cation is deprotonated. This process is accompanied by carbon–sulfur bond formation to form the 1,1-dithiolate-bridged complexes of general formula $(CpMo)_2(S_2CH_2)(S_2C(H)R')$, where R' = CO_2CH_3 (**3**) or $C(O)CH_2CH_3$ (**7**). Complexes **3** and **7** also react with hydrogen at room temperature to form **1** and methyl acetate or 2-butanone. The reaction of acyl halides, R''COX, where R'' = CH_3, Ph, or CH_2Ph, with **1** under an atmosphere of hydrogen results in the formation of the corresponding aldehyde. A second reaction pathway reductively cleaves the carbonyl bond in the acyl halide to form water and a new molybdenum complex, $[(CpMo)_2(S_2CH_2)(S_2CR'')]X$ (**9**). Complex **9** (R'' = CH_3; X = Br) has been characterized by an X-ray diffraction study. Crystals form in space group $P2_1/c$ with a = 13.983 (3) Å, b = 8.197 (1) Å, c = 15.971 (3) Å, β = 90.72 (2)°, V = 1830.6 Å^3, and Z = 4. The cation contains a bridging dithioacetate ligand which shows an η^2-bonding mode to one molybdenum ion and a η^3 mode to the second metal ion. Factors that influence the facile hydrogenolysis of carbon–sulfur and carbon–oxygen bonds in these systems are discussed.

Introduction

We have recently reported that $(CpMo(\mu\text{-}S))_2S_2CH_2$ (**1**) reacts with alkyl halides and vinyl halides to form cationic derivatives of the general formula $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SR)]^+$.[1,2] The cations undergo an unusual reaction with molecular hydrogen which appears to involve the heterolytic cleavage of this molecule and the formation of an intermediate complex with a reactive hydrosulfido ligand. Final reaction products in these systems have been found to vary depending on the nature of R, but organic products resulting from C=C hydrogenation and C—S hydrogenolysis have been identified in some systems.[2,3] In order to determine how electronic and structural variations within the organic halide affect the reactivity of the resulting thiolate-bridged molybdenum cations, we have investigated the reactions of **1** with a series of carbonyl-containing organic halides including halo esters, halo ketones, and acyl halides. Dinuclear cationic complexes have been formed in most cases, and their reactions with molecular hydrogen and with nucleophiles have been characterized. The general pattern of reactivity with hydrogen involves the hydrogenolysis of the carbon–sulfur bonds in the cations to form free esters, ketones, and aldehydes. However, the acyl halides display a second, unusual mode of reactivity with **1** and hydrogen which involves the reductive cleavage of the carbonyl group. Investigations have shown that the protons produced in the hydrogen activation process play a role in the hydrogenolysis reactions. Some of these results have been reported in a preliminary communication.[4]

Results and Discussion

Reaction of 1 with Methyl Bromoacetate. Methyl bromoacetate reacts with **1** at room temperature to give $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_2CO_2CH_3)]Br$ (**2**). The thiolate ligand in **2** is the conjugate base of methyl mercaptoacetate. When the formation of **2** is followed by ^1H NMR spectroscopy in $CDCl_3$, two apparent isomers are observed, probably related by inversion at the sulfur atom of the bridging thiolate ligand. When the reaction is complete (ca. 2.5 h), the ratio of products is approximately 1:1, but complete conversion to a single complex occurs over a period of ca. 3 days. The rate of the proposed isomerization is slow due to precipitation of the product (as a mixture of isomers) from chloroform solution. When the reaction is carried out in a mixture of chloroform and ethanol (4:1), no precipitation occurs, and a single complex is isolated after 24 h. The formulation of the product is consistent with ^1H NMR and mass spectroscopic data and with results of elemental analyses.

Reactions of $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_2CO_2CH_3)]Br$ (2). Thermolysis of **2** (80 °C, 20 h) in chloroform solution results in complete decomposition giving no identified products. Complex **2** reacts cleanly with H_2 in chloroform at 25 °C to give methyl acetate and **1**. However, the catalytic conversion of excess methyl bromoacetate is limited to very low turnover numbers (see Experimental Section) because of precipitation of the catalyst **1** as $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]Br$. Other salts of this protonated complex have been reported previously.[4] The hydrogenolysis of the halo esters is proposed to result in the formation of the protonated salt of **1** according to reaction 1. The reaction scheme is based on the previous observation that a cationic derivative related to **2** reacts with hydrogen to form a proton and a neutral hydrosulfido-bridged derivative.[3]

When reaction 1 was carried out in the presence of a base, e.g. triethylamine, competing reactions were observed that inhibited the potential catalytic cycle of eq 1. These competing processes appeared to involve the reaction of the base with the cation **2**. Therefore, a more detailed investigation of the reactions of bases with this complex have been carried out in the absence of hydrogen.

A chloroform solution of **1** and a 4–5-fold excess of methyl bromoacetate was reacted with 4.8 equiv of triethylamine at room temperature. Two products were

(1) Casewit, C. J.; Haltiwanger, R. C.; Noordik, J.; Rakowski DuBois, M. *Organometallics* **1985**, *4*, 119.
(2) Weberg, R. T.; Laurie, J. C. V.; Haltiwanger, R. C.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1986**, *108*, 6242.
(3) Laurie, J. C. V.; Duncan, L.; Weberg, R. T.; Haltiwanger, R. C.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1986**, *108*, 6234.
(4) Coons, D. E.; Laurie, J. C. V.; Haltiwanger, R. C.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1987**, *109*, 283.

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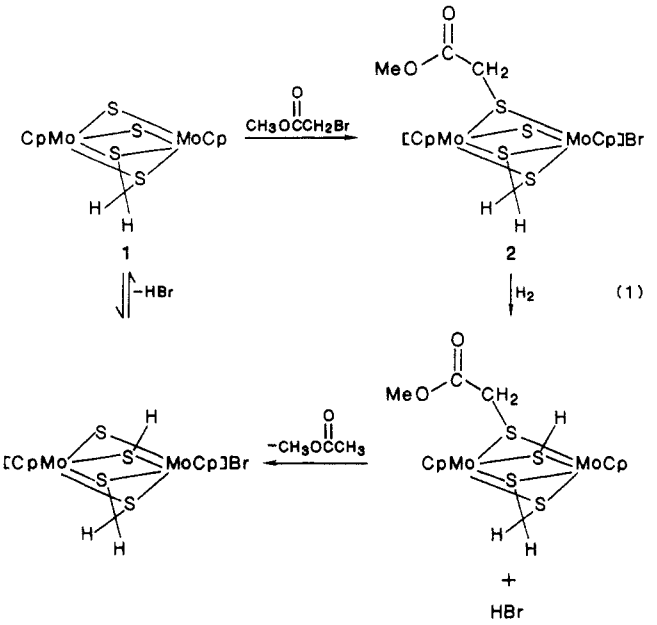
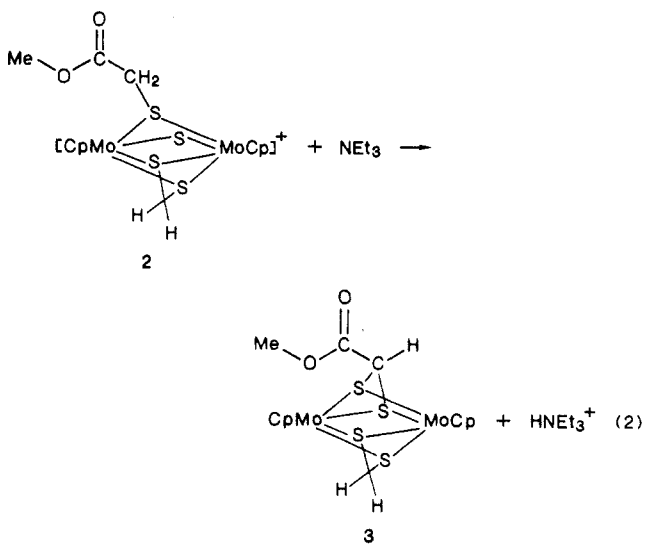
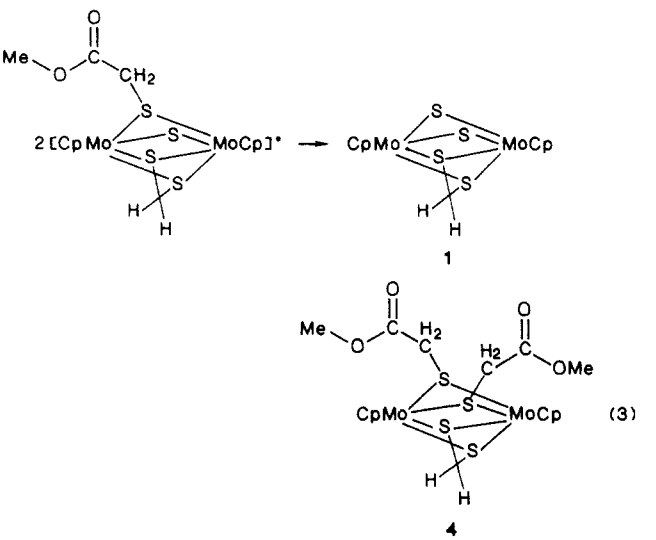


isolated that resulted from the deprotonation and reduction of the cation **2**. Deprotonation at the relatively acidic α-carbon atom in the ligated anion of methyl mercaptoacetate results in the formation of the neutral 1,1-dithiolate-bridged complex **3** in 50% yield (reaction 2). The



^{1}H NMR spectrum of **3** shows two singlets for inequivalent cyclopentadienyl ligands and an AB pattern for the protons of the methanedithiolate ligand. A second, minor product was isolated from this reaction and characterized as a neutral bis(thiolate) complex, $(CpMo)_2(S_2CH_2)(SCH_2CO_2Me)_2$ (**4a**) (see eq 3). The ^{1}H NMR spectrum of **4a** shows four singlets which correspond to the cyclopentadienyl (1), methanedithiolate (1), and equivalent mercaptoacetate (2) anions, respectively. Complex **4** is believed to result from the one electron reduction of **2**[5] followed by disproportionation of the resulting mixed-valence complex, as shown in eq 3. A similar reduction–disproportionation sequence has been characterized previously for a related vinylthiolate-bridged cation,[2] but the mechanism of the R group transfer has not been established.

Products **3** and **4a** have also been isolated from the reaction of **2** with lithium diisopropylamide. Complex **1**



is also observed as a product in this system which differs from the previous one by the use of the isolated cation **2** as a reactant and by the absence of any excess methyl bromoacetate. The observation of **1** is consistent with the proposed disproportionation shown in reaction 3.

Products resulting from deprotonation and reduction of **2** were also isolated when the preceding reaction was carried out in the presence of hydrogen. In this case, a different isomer of **4** was isolated for which the ^{1}H NMR spectrum shows two methoxy and two SCH_2 resonances corresponding to inequivalent μ-SCH_2CO_2Me ligands. This isomer **4b** presumably contains an axial–equatorial[6] arrangement of thiolate substituents.

The reaction of cation **2** with ethylmagnesium bromide proceeds by a different primary pathway that involves alkylation of the sulfido ligand of **2**. Two apparent isomers of the resulting bis(thiolate)-bridged complex $(CpMo)_2(S_2CH_2)(\mu$-$SCH_2CO_2Me)(\mu$-$SEt)$ (**5**) are observed in the ^{1}H NMR spectrum. These are proposed to differ in the orientations of the thiolate substituents. Inversion about the sulfur atoms does not appear to be facile for this complex. The ratio of isomers varied considerably in different synthetic runs.

Reaction of 1 with 1-Bromo-2-butanone. The reaction of this halo ketone with **1** proceeds at room temperature to form two compounds. Although column chromatography was not effective in achieving a separation, recrystallization of the products from chloroform/ether gave a mixture of purple and brown crystals which could be manually separated. A sample of each product in >90% purity was obtained in this manner and characterized by ^{1}H NMR. The purple complex was identified as a cationic derivative of formula $[(CpMo)_2(S_2CH_2)(\mu$-$S)(\mu$-$SCH_2C(O)C_2H_5)]Br$ (**6a**). The ^{1}H NMR spectrum is consistent with this formulation. The chemical shift of the Cp resonance near 7 ppm is particularly characteristic of cations of this structural type.[2,3] The ^{1}H NMR spectrum of the brown product **6b** shows two cyclopentadienyl resonances indicating that the structure is one of lower symmetry than that of **6a**, but crystals suitable for an X-ray diffraction study have not yet been obtained. The FAB mass spectrum of each product shows the same parent ion at m/e 535, suggesting that the two products are isomers. In addition, **6a** and **6b** interconvert in an equilibrium process. The equilibrium ratio of 56:44 **a**/**b** is observed in the NMR spectrum within a few hours at ambient temperature

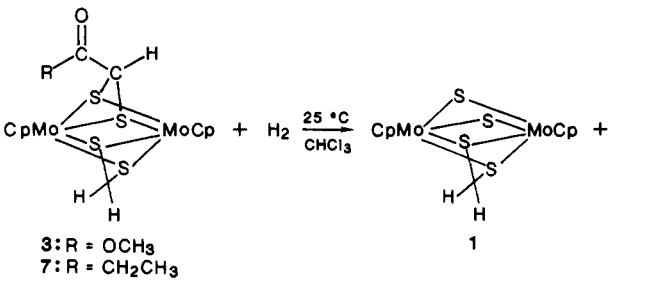
(5) The nature of the reducing agent, e.g. triethylamine or a deprotonated molybdenum complex, has not been established.

(6) Shaver, A.; Fitzpatrick, P. J.; Steliou, K.; Butler, I. S. *J. Am. Chem. Soc.* **1979**, *101*, 1313.

starting with a sample enriched in either isomer.

The reactivity of **6** was generally similar to that observed for previously studied cationic derivatives. Facile hydrogenolysis of the carbon–sulfur bond in **6** occurs under a hydrogen atmosphere at room temperature to form butanone and **1**. The α-carbon in the thiolate ligand of **6** is deprotonated by excess triethylamine. The resulting neutral 1,1-dithiolate-bridged product $(CpMo)_2(S_2CH_2)(S_2CHC(O)C_2H_5)$ (**7**) has been isolated and characterized by spectroscopic data. When **1** is reacted with excess 1-bromobutanone and triethylamine under hydrogen, the ^1H NMR spectrum of the products provides evidence for the reduction–disproportionation product $(CpMo)_2(S_2CH_2)(\mu\text{-}SCH_2C(O)C_2H_5)_2$ as well as for **7**.

Reactivity of Neutral Molybdenum(III) Complexes. Relatively few dinuclear molybdenum(III) complexes with 1,1-dithiolate ligands have been studied previously. The methanedithiolate ligand in these systems has been found to be very unreactive and has generally been useful in maintaining an intact dinuclear structure during the course of reactions which occur at the other sulfur sites in the molecule.[7] We were, therefore, somewhat surprised to observe that the substituted methanedithiolate ligands synthesized in this work are considerably more reactive. The neutral deprotonation products discussed above, **3** and **7**, react cleanly with hydrogen in chloroform solution at room temperature to form **1** plus methyl acetate and 2-butanone, respectively (eq 4). Other neutral Mo(III)



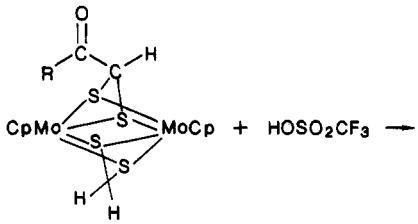
3: R = OCH_3
7: R = CH_2CH_3

1

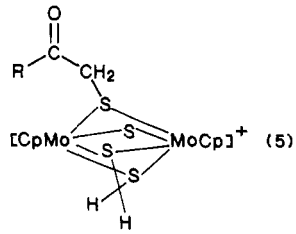
$RCCH_3$ (4)

complexes characterized in this work, such as $(CpMo)_2(S_2CH_2)(SCH_2CO_2CH_3)_2$ (**4**) and $(CpMo)_2(S_2CH_2)(SEt)(SCH_2CO_2CH_3)$ (**5**) are also hydrogenolyzed. For example, when a chloroform solution of **4** is sealed in an NMR tube under hydrogen and heated to 65 °C, complete conversion to **1** and methyl acetate is observed by NMR spectroscopy within 30 min.

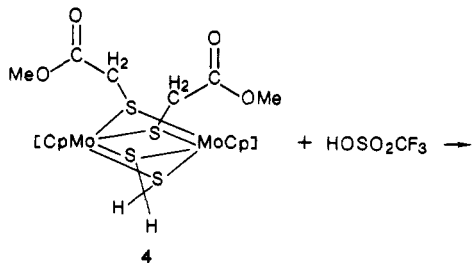
Information on the reaction mechanism of these hydrogenolysis reactions is provided by the results of a study of the reactivity of the same complexes with protic acid. Complexes **3**, **4**, and **7** each react rapidly with 1–2 equiv of triflic acid to form the previously characterized cations **2** and **6** (eq 5 and 6). These results suggest that the reactions of the neutral derivatives with molecular hydrogen are initiated by trace amounts of acid in the chloroform solutions. Once a carbon–sulfur bond in **3** or **4** is cleaved by acid, the resulting cation can undergo reaction with hydrogen as described above to generate additional acid as well as the reduced organic products. In order to test this hypothesis, the reaction of **7** with hydrogen in the presence of ca. 0.5 equiv of proton sponge was carried out in C_6D_6 and monitored by NMR spectroscopy. No hydrogenolysis products were observed at room temperature over a period of 3 days. However, when



3: R = OCH_3
7: R = CH_2CH_3



2: R = OCH_3
6: R = CH_2CH_3



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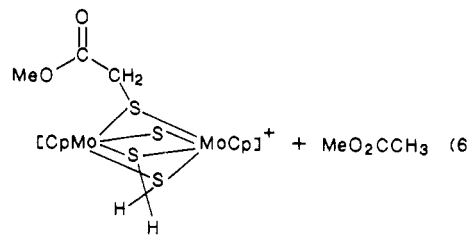

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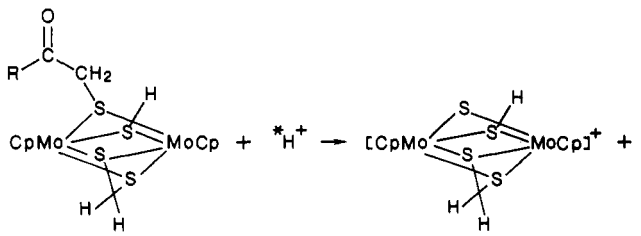
the solution was heated at 70 °C for 2 days, butanone and **1** were observed in ca. 80% yield. Although the acid-catalyzed pathway appears to predominate at room temperature, the data suggest that a second pathway for ligand hydrogenolysis is available at higher temperatures.

The protonation studies also suggest that in the reaction cycle for halo ester or halo ketone hydrogenolysis, the actual elimination of free ester or ketone may occur as a result of proton attack on the thiolate ligand of the neutral intermediate, e.g. eq 7, rather than by an unusual elimination of the adjacent thiolate substituents, R and H. Further studies of such protonation processes are underway in our laboratory.



$RCCH_2{}^*H$ (7)

Reaction of 1 with Acyl Halides. The cationic complexes of the formula $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC(O)R)]^+$ are detected by NMR spectroscopy when >3 equiv. of an

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

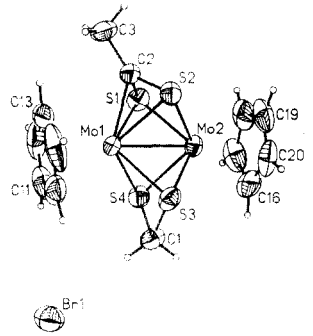


Figure 1. Perspective drawing of $(CpMo)_2(S_2CH_2)(S_2CCH_3)Br$ (**9**). Thermal ellipsoids are shown at the 50% probability level.

acyl halide are added to a solution of **1**. However, the acylation is readily reversible, and cationic derivatives of the above formula have not been isolated. The reversible nature of the interaction has been verified by reacting an equimolar mixture of CD_3COCl and CH_3COBr with **1** in $CDCl_3$ under nitrogen. A 1:1 ratio of CH_3COBr and the exchanged product CH_3COCl was observed by NMR spectroscopy within 5 min. In the absence of **1**, halide exchange under these conditions took place in ~6 h.

Under an atmosphere of hydrogen, a mixture of **1** and acetyl chloride (~2 equiv) reacts at room temperature to form a cationic complex with the formula $[(CpMo)_2(S_2CH_2)(S_2CCH_3)]Cl$ (**9**) which has been isolated in 84% yield. The second product from this reaction is expected to be water. When the reaction is followed by NMR spectroscopy, indirect evidence for the formation of water is provided by the methyl resonance of acetic acid which increases in area as the reaction proceeds. The NMR spectrum also indicates that a second competing reaction occurs in this system which effects the hydrogenolysis of ca. 40% of the acetyl chloride to acetaldehyde.

Other acyl halides appear to react in an analogous manner. The reactions of 1–2 equiv of benzoyl chloride and of phenylacetyl chloride with **1** under hydrogen produce primarily benzaldehyde and phenylacetaldehyde, respectively. When a large excess of the acyl chloride (20–25 equiv) is used, the cationic complexes $[(CpMo)_2(S_2CH_2)(S_2CR)]Cl$ (R = Ph and CH_2Ph) are isolated in yields of 71 and 35%, respectively.

In a preliminary communication,[4] one possible mechanism for the formation of **9** was presented in which the sulfur-acylated cation undergoes a further reaction with hydrogen. Since complex **1** also is known to react with hydrogen,[8] further work will be necessary to determine the relative importance of each hydrogen-activating agent in the formation of final products.

Characterization of $[(CpMo)_2(S_2CH_2)(S_2CCH_3)]Br$ (9). The bromide salt of **9** was crystallized by addition of pentane to an ethanol solution. Crystals of $[(CpMo)_2(S_2CH_2)(S_2CCH_3)]Br \cdot {}^1/_2EtOH$ formed in space group $P2_1/c$ with four molecules per unit cell. A perspective drawing of the molecule is shown in Figure 1, and selected bond distances and angles are presented in Table I. Positional and thermal parameters are included in Table II. The two molybdenum ions in the cation are bridged by a methanedithiolate ligand and by a dithioacetate ligand. The dithioacetate acts as a planar bidentate chelating agent for Mo_2. The ligand bonds to Mo_1 in a η^3 fashion through both sulfur atoms and the adjacent carbon atom. The Mo(1)–C(2) distance of 2.224 (4) Å is within the normal range for a single bond between these atoms.[9] The structure provides an example of an unusual bonding mode for a dithio acid anion. However, previous studies of the reactions of dithio esters with dinuclear complexes of molybdenum and iron have established the ability of these related sulfur chelates to coordinate through carbon as well as sulfur atoms.[10,11]

Table I. Selected Bond Distances and Angles for $[(CpMo)_2(S_2CH_2)(S_2CCH_3)]Br$ (9)

Distances, Å			
Mo(1)–Mo(2)	2.635 (1)	Mo(1)–S(1)	2.436 (1)
Mo(1)–S(2)	2.442 (1)	Mo(1)–S(3)	2.456 (1)
Mo(1)–S(4)	2.444 (1)	Mo(1)–C(2)	2.224 (4)
Mo(1)–C(11)	2.329 (6)	Mo(1)–C(12)	2.305 (6)
Mo(1)–C(13)	2.294 (7)	Mo(1)–C(14)	2.315 (7)
Mo(1)–C(15)	2.327 (7)	Mo(2)–S(1)	2.426 (1)
Mo(2)–S(2)	2.429 (1)	Mo(2)–S(3)	2.441 (1)
Mo(2)–S(4)	2.430 (1)	Mo(2)–C(16)	2.228 (6)
Mo(2)–C(17)	2.253 (5)	Mo(2)–C(18)	2.317 (6)
Mo(2)–C(19)	2.323 (6)	Mo(2)–C(20)	2.285 (6)
S(1)–C(2)	1.735 (5)	S(2)–C(2)	1.733 (4)
S(3)–C(1)	1.826 (6)	S(4)–C(1)	1.819 (5)
C(2)–C(3)	1.502 (6)		
Angles, deg			
Mo(2)–Mo(1)–S(1)	57.0 (1)	Mo(2)–Mo(1)–S(2)	57.0 (1)
S(1)–Mo(1)–S(2)	70.7 (1)	Mo(2)–Mo(1)–S(3)	57.2 (1)
S(1)–Mo(1)–S(3)	114.1 (1)	S(2)–Mo(1)–S(3)	76.5 (1)
Mo(2)–Mo(1)–S(4)	57.0 (1)	S(1)–Mo(1)–S(4)	76.8 (1)
S(2)–Mo(1)–S(4)	114.0 (1)	S(3)–Mo(1)–S(4)	67.0 (1)
Mo(2)–Mo(1)–C(2)	75.1 (1)	S(1)–Mo(1)–C(2)	43.4 (1)
S(2)–Mo(1)–C(2)	43.3 (1)	S(3)–Mo(1)–C(2)	118.0 (1)
S(4)–Mo(1)–C(2)	118.3 (1)	Mo(1)–Mo(2)–S(1)	57.4 (1)
Mo(1)–Mo(2)–S(2)	57.5 (1)	S(1)–Mo(2)–S(2)	71.1 (1)
Mo(1)–Mo(2)–S(3)	57.7 (1)	S(1)–Mo(2)–S(3)	115.0 (1)
S(2)–Mo(2)–S(3)	77.0 (1)	Mo(1)–Mo(2)–S(4)	57.5 (1)
S(1)–Mo(2)–S(4)	77.3 (1)	S(2)–Mo(2)–S(4)	115.0 (1)
S(3)–Mo(2)–S(4)	67.4 (1)		

Table II. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³) for $[(CpMo)_2(S_2CH_2)(S_2CCH_3)]Br$ (9)

	x	*y*	*z*	*U*
Mo(1)	1703 (1)	1801 (1)	1678 (1)	32 (1)[a]
Mo(2)	3088 (1)	3979 (1)	1712 (1)	38 (1)[a]
S(1)	2642 (1)	2489 (2)	454 (1)	48 (1)[a]
S(2)	1451 (1)	4669 (1)	1325 (1)	44 (1)[a]
S(3)	2196 (1)	3244 (2)	2960 (1)	48 (1)[a]
S(4)	3338 (1)	1156 (2)	2125 (1)	48 (1)[a]
Br(1)	2084 (1)	−2247 (1)	4315 (1)	75 (1)[a]
C(1)	3044 (4)	1614 (7)	3205 (3)	59 (2)[a]
C(2)	1489 (3)	3261 (6)	517 (3)	44 (1)[a]
C(3)	756 (4)	3144 (8)	−175 (3)	62 (2)[a]
C(4)	4527 (11)	−329 (24)	−43 (10)	92 (5)
C(5)	4250 (15)	−1410 (28)	−642 (14)	103 (6)
C(6)	4820 (29)	−924 (47)	25 (22)	75 (9)
C(7)	5912 (19)	307 (34)	700 (16)	93 (7)
C(9)	5200 (26)	−150 (48)	369 (20)	90 (10)
C(11)	1339 (4)	−898 (7)	2001 (5)	82 (3)[a]
C(12)	1070 (5)	−642 (8)	1219 (4)	89 (3)[a]
C(13)	331 (5)	512 (9)	1234 (5)	102 (3)[a]
C(14)	190 (4)	953 (7)	2058 (7)	95 (3)[a]
C(15)	805 (5)	73 (9)	2517 (4)	83 (3)[a]
C(16)	4391 (4)	4972 (8)	2347 (4)	81 (2)[a]
C(17)	4647 (4)	4542 (8)	1519 (5)	79 (3)[a]
C(18)	4164 (4)	5568 (8)	980 (4)	77 (2)[a]
C(19)	3616 (4)	6618 (7)	1456 (5)	78 (2)[a]
C(20)	3733 (4)	6296 (7)	2280 (4)	80 (2)[a]

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

(8) Casewit, C. J.; Coons, D. E.; Wright, L. L.; Miller, W. K.; Rakowski DuBois, M. *Organometallics* **1986**, *5*, 951.

(9) Schrauzer, G. N.; Hughes, L. A.; Strampach, N.; Robinson, P. R.; Schlemper, E. O. *Organometallics* **1982**, *1*, 44 and references therein.

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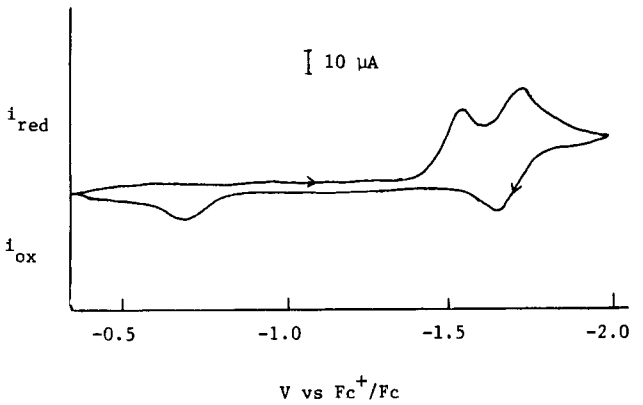
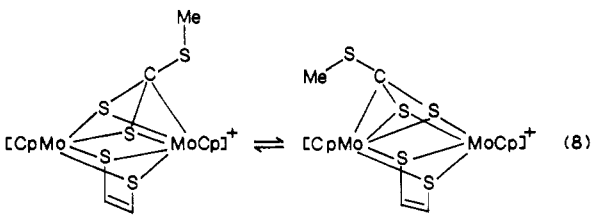


Figure 2. Cyclic voltammogram of $(CpMo)_2(S_2CH_2)(S_2CCH_3)Br$ (**9**) (10^{-3} M in 0.1 M $(n\text{-}Bu)_4NBF_4/CH_3CN$) at a scan speed of 50 mV/s. Ferrocene, $(C_5H_5)_2Fe$ (Fc), was used as an internal reference.

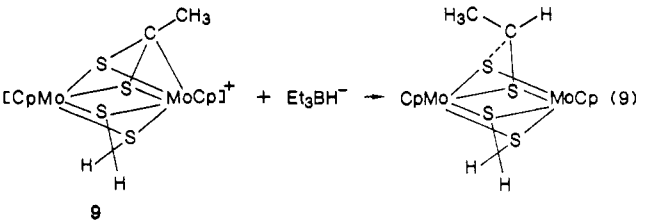
The structure of **9** is related to that of the recently reported cation $[(CpMo)_2(SC_2H_2S)(S_2CSMe)]I$ which contains a thioxanthate ligand in an η^2,η^3-bridging mode.[12] Both structures illustrate the stabilization of a potential positive charge on the dithio ligand by molybdenum–carbon bond formation. The structural parameters of the $Cp_2Mo_2S_4$ core of these cations are generally similar within experimental error. However, the metal–metal distance in **9**, 2.635 (1) Å, is longer than that observed in the thioxanthate-bridged complex, 2.623 (1) Å, and markedly longer than the metal–metal distances in other $Cp_2Mo_2S_4$ derivatives which normally occur in the range of 2.59–2.61 Å.[13]

The ^1H NMR spectra of **9** and related derivatives are characterized by large chemical shift differences between the two cyclopentadienyl resonances and between the two proton resonances of the methanedithiolate ligand (see Experimental Section). The NMR resonances of **9** are sharp at ambient temperature. At temperatures above 85 °C in CD_3OD (under hydrogen pressure), some broadening is observed, but coalescence of the cyclopentadienyl resonances is not observed in a temperature range up to 125 °C. The resonances sharpen again when the solution is cooled to room temperature. These studies establish an exceptional thermal stability for **9**. The lack of fluxional behavior contrasts sharply with that of the related thioxanthate-bridged cation discussed above. Variable-temperature NMR data for this system are consistent with the fluxional process shown in eq 8 with a relatively low free energy of activation of 56 kJ/mol.[12]



(8)

The redox behavior of **9** has been investigated by cyclic voltammetry. Two reductions are observed with E_{p_c} = −1.55 and $E_{p/2}$ = −1.69 V vs. the ferrocene/ferrocinium couple. The first cathodic wave shows a coupled weak anodic peak at a widely separated potential (E_{p_a} = −0.67 V), while the second reduction is a reversible process (ΔE_p = 63 mV) (Figure 2). We have speculated that the irreversibility of the first reduction wave is associated with cleavage of the molybdenum–carbon bond of **9**. The cleavage of this bond has been demonstrated by the reaction of **9** with excess lithium triethylborohydride, which forms the neutral 1,1-dithiolate-bridged complex shown in eq 9, as well as other unidentified products.



9 (9)

Reaction of 1 with Methyl Chloroformate and Dimethylcarbamoyl Chloride. Although the reductive cleavage of the carbonyl group was observed for several acyl halides, we have not observed similar reactivity for related halide-substituted carbonyl compounds. For example, no reaction is detected by NMR spectroscopy between methyl chloroformate and **1**. In the presence of hydrogen, the catalytic formation of methyl formate is observed, but the dithio ester analogue of **9** has not been identified in this reaction. *N,N*-Dimethylcarbamoyl chloride was much less reactive with **1** and hydrogen than the other organic halides studied here. After this reaction was heated at 70 °C for 6 days, less than 10% of the substrate had reacted. The sequence of reactions that result in the hydrogenolysis of the carbon oxygen bond not only depends on the presence of a halide substituted carbonyl group but also appears to be quite sensitive to the electronic effects provided by other substituents on the carbonyl.

Summary and Conclusions. The hydrogenolyses of α-halo esters and α-halo ketones and of acyl halides to the corresponding esters, ketones, and aldehydes by hydrogen occur under mild homogeneous conditions in the presence of the dinuclear molybdenum complex **1**. Many other routes are available for the hydrogenolysis of organic halides, particularly for those which are activated by the electron-withdrawing carbonyl group.[14] The present systems have been studied because of their unique reaction mechanisms that involve the stepwise formation and hydrogenolysis of carbon–sulfur bonds in the molybdenum complexes. The hydrogen molecule is heterolytically activated in these hydrogenolysis reactions by cationic molybdenum complexes. In general, the hydrogenolyses of the carbonyl-containing halides appear to follow reaction pathways similar to those characterized for reactions of hydrogen with vinyl and certain alkyl halides in the presence of **1**;[2] the reductive C–X cleavage reactions of the halo esters, halo ketones, and acyl halides are generally characterized by milder reaction conditions, in accord with an activating electron-withdrawing effect of the carbonyl substituents. A second reaction pathway with **1** and hydrogen has been identified for acyl halides in which the carbon–oxygen bond is hydrogenolyzed. Although we have been unable to extend this hydrodeoxygenation reactivity to other carbonyl-containing molecules, the acyl halide reductions provide an interesting specific example of how reductive carbon–chalcogen bond cleavage can be achieved at molybdenum sulfide sites. These reaction systems may

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(14) Pinder, A. R. *Synthesis* **1980**, 425.

provide relevant information on how heterogeneous molybdenum sulfide surfaces function as hydrotreating catalysts.[15]

Experimental Section

Materials. Organic halides and reagent grade hydrogen were purchased from commercial suppliers and used without purification. $(CpMo\mu\text{-}S)_2S_2CH_2$ (1) was synthesized according to a reported procedure.[7] Lithium diisopropylamide–bis(tetrahydrofuran) (1.5 M in cyclohexane), 1,8-bis(dimethylamino)-naphthalene (Proton Sponge), and trifluoromethanesulfonic acid were purchased from Aldrich. Tetrahydrofuran was distilled from calcium hydride and dichloromethane from P_2O_5. Chloroform was dried over 4-Å molecular sieves. Reactions were generally carried out under nitrogen by using standard Schlenk techniques. Products were isolated in air unless noted.

Instrumentation. ^1H NMR spectra were obtained at 90 MHz on a JEOL FX-90Q spectrometer, and the ^{13}C spectra were recorded at 62.9 MHz on a Bruker WM250 spectrometer. Chemical shifts are reported relative to tetramethylsilane. Mass spectra (EI and FAB) were recorded on a VG 7070EQ-HF tandem mass spectrometer. Thioglycerol was used as the matrix for the FAB spectra. Cyclic voltammetry was carried out in 0.10 M n-Bu_4NBF_4/CH_3CN with platinum wires as working and counter electrodes and a $Ag/AgNO_3/CH_3CN$ reference electrode. Potentials were determined by using a Bioanalytical Systems, Inc., BAS-100 electrochemical analyzer at scan rates of 50 and 500 mV/s. Potentials are reported relative to the internal standard ferrocene with a potential of 0.42 V vs. SCE. Elemental analyses were determined by Spang Laboratories, Eagle Harbor, MI.

X-ray Diffraction Study of $[(CpMo)_2(S_2CH_2)(S_2CCH_3)]Br\cdot{}^1/_2EtOH$. Crystals were obtained by addition of pentane to an ethanol solution. Details of the crystal data, experimental conditions, and a summary of solution and refinement details are given in Table III.

For the final refinement, non-hydrogen atoms except those in the disordered solvent molecule were refined anisotropically. Hydrogen atoms were included in fixed idealized positions with thermal parameters equal to 1.2 times the equivalent isotropic U of the atom to which they were attached. The disordered solvent that is located about an inversion center at $^1/_2$, 0, 0 was refined with individual isotropic thermal parameters. All solvent atoms were treated as carbons with partial occupancy factors. No attempt was made to identify the oxygen of the EtOH, or to include hydrogen atoms.

Preparation of $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_2CO_2CH_3)]Br$ (2). $(CpMoS)_2S_2CH_2$ (1) (0.598 g, 1.29 mmol) was dissolved in 40 mL of $CHCl_3$ and 10 mL of ethanol in a 100-mL Schlenk flask. After addition of $BrCH_2CO_2CH_3$ (135 μL, 1.50 mmol), the solution was degassed and stirred at ambient temperature for 24 h. Volatiles were removed by vacuum distillation, and the remaining solid was extracted with methanol and ethanol and filtered. Addition of pentane to the filtrate gave a dark purple solid that was filtered, washed with pentane, and vacuum dried. Yield: 0.510 g, 0.826 mmol, 64%. ^1H NMR ($CDCl_3$): δ 7.05 (s, Cp), 4.75 (s, S_2CH_2), 3.65 (s, OCH_3), 2.65 (s, $SCH_2CO_2CH_3$). FAB-MS: m/e 537 (P of cation), 465 (P – $CHCO_2CH_3$), 418 (P – $CH_2CO_2CH_3$ – SCH_2). Anal. Calcd for $C_{14}H_{17}BrMo_2O_2S_4$: C, 27.24; H, 2.78; Br, 12.94; S, 20.78. Found: C, 27.23; H, 2.70; Br, 12.97; S, 20.69.

Reaction of 2 with H_2. A thin-wall 5-mm o.d. NMR tube containing a solution of 2 in $CDCl_3$ was evacuated at −196 °C. H_2 was admitted to 500 torr, and the tube was flame-sealed. After 18 h at ambient temperature, the solution was blue. The ^1H NMR spectrum of this solution showed clean formation of $(CpMoS)_2S_2CH_2$ (1) (δ 6.56, 2.85) and $CH_3CO_2CH_3$ (δ 3.63, 2.03).

Attempted Catalytic Hydrogenolysis of Methyl Bromoacetate. Typically, 1 (0.030 g, 0.065 mmol) was dissolved in 7 mL of $CDCl_3$ in a 500-mL reaction vessel equipped with a 10-mm Kontes O-ring stopcock. After addition of 20 equiv of methyl bromoacetate, the solution was degassed in three freeze–pump–thaw cycles. Hydrogen (600 torr) was admitted at −196 °C, and the vessel was sealed. The reaction solution was warmed to room temperature and stirred. Progress of the reaction was monitored by opening the flask and removing a sample by syringe followed by recharging the system with H_2. The samples were analyzed by ^1H NMR spectroscopy. Under these conditions, conversion of methyl bromoacetate to methyl acetate is observed until a ratio of ca. 7:1, respectively, is reached (2.5 turnovers). This ratio is

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Table III. Crystal Data and Details of the Structure Determination for $[(CpMo)_2(S_2CH_2)(S_2CCH_3)]Br\cdot{}^1/_2EtOH$

Crystal Data	
formula	$C_{14}H_{18}O_{0.5}S_4Mo_2Br$
mol wt	594.35
space group[a]	$P2_1/c$
cryst system	monoclinic
a,[b] Å	13.983 (3)
b, Å	8.197 (1)
c, Å	15.971 (3)
β, deg	90.72 (2)
V, Å^3	1830.6
Z	4
D(calcd), g/cm^3	2.13
F(000)	1140
μ, cm^{-1}	40.8
Data Collection and Reduction	
diffractometer	Syntex P3/F
radiatn (λ, Å)	Mo Kα (0.710 69)
takeoff angle for graphite monochromator (deg)	4.0
T, K	295–298
cryst habit (needles, plates, etc.)	parallelepiped
cryst color	brown
cryst dimens, mm	0.27 × 0.38 × 0.50
scan technique	θ–2θ
2θ (min–max), deg	4.0–60.0
hkl values scanned	$\pm h,+k,\pm l$
scan speed, deg/min	5.0–60.0
scan range, deg below $K\alpha_1$ and above $K\alpha_2$	0.8, 0.8
bkgd	stationary crystal–stationary counter background time = 0.5 scan time
check reflctns	(−12,−2,−1); (4,6,−2); (4,1,11); (5,−6,6)
freq	every 96 measurements
variatn	random, no decline
no. of reflctns measd	11 139
no. of unique reflctns	5379
agreement factor during averaging[c]	0.016
no. of obsd reflctns	3522
σ criterion	$F > 6\sigma(F)$
abs correctn	empirical
transmisn factors	0.96, 0.62
Structure Determination and Refinement	
method of phase determination	direct methods
programs	SHELXTL[d]
scattering factors	neutral atoms[e]
R and wR[f] for obsd data	0.033, 0.041
R and wR[f] for all data	0.064, 0.051
wt for all data	$1.0/(\sigma^2(F) + 0.0004F^2)$
no. of parameters	204
no. of observns per parameter	17.5/1
esd of observn of unit wt	1.256
av shift/error	0.024
max shift/error	0.122
obsd for	disordered EtOH
residual electron density, e/Å	0.84 near bromine

[a] *International Tables for X-ray Crystallography*, Kynoch: Birmingham, England, 1965; Vol. 1. [b] Cell dimensions were determined by least-squares fit of the setting angles of 25 reflections with 2θ in the range 30–40°. [c] $R_{merge} = [\sum N(\sum[w(F_{mean} - F)^2])/\sum((N-1)\sum[wF^2])]^{1/2}$. [d] Sheldrick, G. M. SHELXTL, A Program For Crystal Structure Determination; Nicolet Analytical Instruments, Madison, WI, 1985; Version 5.1. [e] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4. [f] The quantity minimized in the least-squares procedures is $\sum[w(|F_o| - |F_c|)^2]$. $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. $R_2 = [\sum[w(|F_o| - |F_c|)^2]/\sum[w(F_o)^2]]^{1/2}$.

achieved in less than 24 h after which no further change occurs. In the course of the reaction, a dark red-purple precipitate forms which has been characterized as $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]Br$ (vide infra).

When the same reaction was carried out in the presence of 25 equiv of 2,6-lutidine, five turnovers occurred in 4 days. The components of the reaction mixture were separated by column chromatography on Al_2O_3. CH_2Cl_2 eluted *sym*-$(CpMo)_2(S_2CH_2)(SCH_2CO_2CH_3)_2$ (**4a**). $CHCl_3$ eluted the unsymmetrical isomer **4b** (vide infra).

Synthesis of $(CpMo)_2(S_2CH_2)(S_2CHCO_2CH_3)$ (3) and $(CpMo)_2(S_2CH_2)(S_2CH_2CO_2CH_3)_2$ (4). A 50-mL round-bottom flask was charged with 1 (0.067 g, 0.145 mmol), $CHCl_3$ (6 mL), and $BrCH_2CO_2CH_3$ (69 μL, 0.726 mmol). The solution was degassed; then Et_3N (101 μL, 0.726 mmol) was added. After the solution stirred at 25 °C for 5.5 h, volatiles were removed by vacuum, and the resulting material was chromatographed on Al_2O_3. CH_2Cl_2 eluted first a large yellow-brown band of **3** (0.040 g, 51% yield) and then a small brown band of **4a**, the symmetrical isomer. For **3**: ^1H NMR ($CDCl_3$) δ 6.98 (s, $S_2CHCO_2CH_3$), 6.31 (AB, S_2CH_2), 5.85, 5.82 (2s, Cp), 3.68 (s, OCH_3); FAB-MS, *m/e* 536 (P), 490 (P − SCH_2); 450 ($Cp_2Mo_2S_4$). Anal. Calcd for $C_{14}H_{16}Mo_2O_2S_4$: C, 31.35; H, 3.01; S, 23.91. Found: C, 31.50; H, 3.14; S, 23.56. For **4a**: ^1H NMR δ 5.70 (s, Cp), 5.41 (s, S_2CH_2), 3.57 (s, OCH_3), 2.39 (s, $SCH_2CO_2CH_3$); FAB-MS, *m/e* 610 (P), 536 (P − $CH_3CO_2CH_3$), 490 (P − $CH_3CO_2CH_3$ − SCH_2), 417 (P − $CH_3CO_2CH_3$ − SCH_2 − $CH_2CO_2CH_3$).

Reaction of 1 with $BrCH_2CO_2CH_3$, Et_3N, and H_2. A 500-mL Pyrex reactor equipped with a 10-mm Kontes O-ring stopcock was charged with 1 (0.020 g, 0.043 mmol), $BrCH_2CO_2CH_3$ (81.4 μL, 0.860 mmol), Et_3N (150 μL, 1.075 mmol), and 6 mL of $CDCl_3$. The mixture was degassed by three freeze–pump–thaw cycles and then charged with H_2 to 600 torr at −196 °C. The reactor was sealed and warmed to ambient temperature with stirring. Within 1 h, the color of the solution changed from blue to brown. Volatile components were removed by vacuum distillation. Column chromatography (Al_2O_3/CH_2Cl_2) of the resulting oil gave two yellow-brown bands. The first (smaller) band to elute was $(CpMo)_2(S_2CH_2)(S_2CHCO_2CH_3)$ (**3**). The second band (the major product) was $(CpMo)_2(S_2CH_2)(SCH_2CO_2CH_3)_2$ (**4b**), the unsymmetrical isomer only. For **4b**: ^1H NMR δ 5.72 (s, Cp), 5.57 (s, S_2CH_2), 3.61, 3.58 (2s, OCH_3), 2.80, 2.39 (2s, $SCH_2CO_2CH_3$); FAB-MS, *m/e* 610 (P), 537 (P − $CH_2CO_2CH_3$), 491 (P − $CH_2CO_2CH_3$ − SCH_2), 418 (P − $CH_2CO_2CH_3$ − SCH_2 − $CH_2CO_2CH_3$).

Reaction of 2 with Base. A 20-mL Schlenk flask was charged with **2** (0.064 g, 0.104 mmol) and 5 mL of THF. The resulting suspension was degassed and then stirred at −78 °C. $LiN(i\text{-}Pr)_2{\cdot}2THF$ (1.5 M in cyclohexane, 0.125 mmol) was added by syringe, and the mixture was stirred for 30 min at −78 °C and then for 16 h at ambient temperature. Volatiles were removed by vacuum, and the remaining solid was chromatographed on Al_2O_3. CH_2Cl_2 eluted first a yellow-brown band of $(CpMo)_2(S_2CH_2)(S_2CHCO_2CH_3)$ (**3**) and then the blue $(CpMo)_2(\mu\text{-}S)_2(S_2CH_2)$ (**1**). $CHCl_3$ eluted a yellow-brown band of $(CpMo)_2(S_2CH_2)(SCH_2CO_2CH_3)_2$ (**4**). The remaining purple band was eluted with CH_3OH but was not characterized. The same products were identified in the reaction of **2** with triethylamine (3 equiv).

Reaction of 3 with H_2. In a thin-wall 5-mm o.d. NMR tube, a solution of **3** in $CDCl_3$ was degassed and cooled to −196 °C. The tube was filled with H_2 to 550 torr and flame-sealed. The yellow-brown solution gradually turned blue at ambient temperature. After 4 days, the ^1H NMR spectrum showed that the reaction was 95% complete with clean conversion to **1** and methyl acetate.

Reaction of 3 with CF_3SO_3H. In a 20-mL Schlenk tube, **3** (0.040 g, 0.074 mmol) was dissolved in 2–3 mL of $CDCl_3$ and the resulting solution was degassed by three freeze–pump–thaw cycles. With the solution at −196 °C, CF_3SO_3H (10 μL, 0.111 mmol) was added by syringe. The mixture was then allowed to warm to room temperature and stirred. The color of the solution changed from yellow-brown to deep purple well below 0 °C. As the reaction proceeded, it was monitored by ^1H NMR spectroscopy. An unidentified intermediate species exhibited resonances at δ 6.88 (s, Cp), 4.61 (s, S_2CH_2), 3.69 (s, OCH_3), and 2.79 (s, SCH_2). During several hours these resonances were replaced by those of the final product $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_2CO_2CH_3)]SO_3CF_3$. After 18 h, the solution was evaporated to dryness in vacuo. The residue was dissolved in a few milliliters of methanol and precipitated by addition of Et_2O and pentane. The product was washed with Et_2O and dried by vacuum. Yield: 0.041 g, 80.7%. ^1H NMR ($CDCl_3$): δ 6.96 (s, Cp), 4.25 (s, S_2CH_2), 3.67 (s, OCH_3), and 2.65 (s, SCH_2). The FAB-MS was identical with that observed for the bromide salt of **2**.

Reaction of 4a with H_2. In a thin-wall 5-mm o.d. NMR tube, a solution of **4a** in $CDCl_3$ was degassed and cooled to −196 °C. The tube was filled with H_2 to 550 torr and flame-sealed. By ^1H NMR spectroscopy, no reaction was observed after 24 h at 25 °C. At 65 °C, the yellow-brown solution turned blue in 30 min. The ^1H NMR spectrum at this point showed complete reaction to **1** and methyl acetate.

Reaction of 4 with CF_3SO_3H. A thin-wall 5-mm o.d. NMR tube was charged with a $CDCl_3$ solution of **4** (**4a**:**4b** = 1:2). The solution was degassed and cooled to −196 °C. Under a flow of N_2, CF_3SO_3H (8.8 μL, 0.100 mmol) was added. The tube was evacuated, flame-sealed, and then warmed to room temperature. The color of the solution changed from yellow-brown to purple well below 0 °C, and solid was observed. Addition of a few drops of CD_3OD caused dissolution of most of the precipitate. A ^1H NMR spectrum of this mixture showed resonances of $CH_3CO_2CH_3$ and $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_2CO_2CH_3)]^+$. This triflate salt was isolated by dissolving it in methanol and precipitating it from solution with Et_2O. The ^1H NMR spectral peaks of this material in CD_3OD were shifted slightly from those observed in $CDCl_3$. In CD_3OD: δ 7.08 (s, Cp), 4.28 (s, S_2CH_2), 3.68 (s, OCH_3), 2.78 (s, SCH_2).

Preparation of $(CpMo)_2(S_2CH_2)(\mu\text{-}SCH_2CO_2CH_3)(\mu\text{-}SCH_2CH_3)$ (5). Complex **2** (0.083 g, 0.134 mmol) was suspended in 10 mL of THF in a 25-mL Schlenk tube. The mixture was degassed by three freeze–pump–thaw cycles and then stirred at −78 °C. EtMgBr (0.140 mmol in THF) was added by syringe. After 30 min at −78 °C, the mixture was warmed to ambient temperature and stirred for an additional 30 min. Volatiles were removed by vacuum, and the product **5** was isolated by column chromatography (Al_2O_3/CH_2Cl_2). Collection of the large red-brown band followed by removal of solvent in vacuo gave **5** in >90% purity. By ^1H NMR spectroscopy, the compound is obtained as a mixture of two isomers with axial and equatorial ethanethiolato ligands, respectively. Ratios of these isomers varied considerably in different runs. ^1H NMR ($CDCl_3$): δ 5.68, 5.67 (2s, Cp), 5.70, 5.58 (2AB, S_2CH_2), 3.60, 3.57 (2s, OCH_3), 2.34, 2.40 (2s, $SCH_2CO_2CH_3$), 2.10, 1.73 (q, SCH_2CH_3), 0.83 (t, SCH_2CH_3). FAB-MS: *m/e* 565 (P), 535 (P − C_2H_6), 493 (P − $CH_2CO_2CH_3$), 464 (P − $CH_2CO_2CH_3$ − CH_2CH_3), 448 (P − $CH_2CO_2CH_3$ − SCH_2), 420 (P − $CH_2CO_2CH_3$ − CH_2CH_3 − SCH_2).

Reaction of 5 with H_2. A solution of **5** in C_6D_6 was degassed and then flame-sealed in an NMR tube under ca. 500 torr of H_2. After the tube was heated at 80 °C for 6 d, the sample consisted of a blue solution with some brown solid. The ^1H NMR spectrum of this sample showed resonances for $(CpMoS)_2S_2CH_2$ and $CH_3CO_2CH_3$.

Preparation of $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_2C(O)CH_2CH_3)]Br$ (6). Complex **1** (0.158 g, 0.340 mmol) and 1-bromo-2-butanone (69.5 μL, 0.68 mmol) were combined in 10 mL of $CHCl_3$. After the solution was stirred for 2 h at room temperature, all volatiles were removed from the purple solution by vacuum distillation. The resulting solid was dissolved in $CHCl_3$. Addition of Et_2O resulted in precipitation of a dark solid which was washed with Et_2O and dried by vacuum. Yield: 0.193 g, 92%. The ^1H NMR spectrum of this material in $CDCl_3$ indicates the presence of two compounds, **6a** and **6b**. ^1H NMR: **6a**, δ 7.03 (s, 10, Cp), 4.54 (s, 2, S_2CH_2), 3.06 (s, 2, SCH_2), 2.40 (q, 2, CH_2CH_3), 0.95 (t, 3, CH_2CH_3); **6b**, 6.56 (s, 5, Cp), 6.48 (s, 5, Cp), 4.52 (AB, 2, S_2CH_2), 3.32 (2, SCH_2), 2.08 (q, 2, CH_2CH_3), 0.94 (t, 3, CH_2CH_3). FAB-MS: **6a**, *m/e* 535 (P), 489 (P − SCH_2), 465 (P − $CHC(O)CH_2CH_3$), 418 (P − $CH_2C(O)CH_2CH_3$ − SCH_2); **6b**, *m/e* 535 (P), 489 (P − SCH_2), 465 (P − $CHC(O)CH_2CH_3$), 418 (P − $CH_2C(O)CH_2CH_3$ − SCH_2).

Recrystallization and ^1H NMR Spectra of 6. Recrystallization of **6** from $CDCl_3$ by slow diffusion of diethyl ether gave mixtures of purple and brown crystals. Identification of these as isomers **6a** and **6b**, respectively, was achieved by manual separation of the crystals and examination of their respective ^1H NMR spectra. Samples >90% in either isomer were obtained

in this manner. Starting with either isomer, the equilibrium ratio of 56:44 (**a**/**b**) was reached in several hours. Crystals of **6b** suitable for structure determination by X-ray diffraction were not obtained.

Reaction of 6 with H_2. A solution of **6** (mixed isomers) in $CDCl_3$ was degassed in an NMR tube and cooled to −196 °C. H_2 was admitted to 600 torr. The tube was flame-sealed and warmed to ambient temperature. After 17 h, the ^1H NMR spectrum indicated complete reaction to form **1** and butanone.

Synthesis of $(CpMo)_2(S_2CH_2)(S_2CHC(O)CH_2CH_3)$ (7). A 25-mL Schlenk tube was charged with **1** (0.106 g, 0.229 mmol), 5 mL of $CDCl_3$, 1-bromo-2-butanone (47 μL, 0.458 mmol), and Et_3N (160 μL, 1.15 mmol). The resulting solution was degassed and then stirred under N_2 at room temperature. After 1.5 h, the color had changed from deep blue to green-brown. Although the reaction was probably complete after 2–3 h, it was not examined until 18 h had passed. All volatiles were removed from the mixture by vacuum distillation. The resulting brown solid was dissolved in 3–4 mL of $CHCl_3$. This solution was washed with H_2O to remove $Et_3NH^+Br^-$. After the $CHCl_3$ layer was evaporated to dryness, a small portion of the resulting solid was examined by ^1H NMR in $CDCl_3$. The spectrum was that of pure **7**. Crystallization from $CHCl_3/Et_2O$ gave golden crystals with metallic luster. Yield: 0.067 g, 55%. ^1H NMR ($CDCl_3$): δ 7.06 (s, $S_2CHC(O)CH_2CH_3$), 6.30 (AB, S_2CH_2), 5.88, 5.75 (2s, Cp), 2.23 (q, CH_2CH_3), 0.99 (t, CH_2CH_3). FAB-MS: *m/e* 534 (P), 487 (P − SCH_3), 464 (P − $CH_2C(O)CH_2CH_3$), 417 (P − SCH_3 − $CH_2C(O)CH_2CH_3$). Anal. Calcd for $C_{15}H_{18}Mo_2OS_4$: C, 33.71; H, 3.39; S, 24.00. Found: C, 34.24; H, 3.46; S, 24.01. Complex **7** has also been synthesized from the reaction of **6** with triethylamine (3 equiv).

Reaction of 1 with 1-Bromo-2-butanone, Et_3N, and H_2. A 150-mL reactor equipped with a 10-mm Kontes O-ring stopcock was charged with **1** (0.073 g, 0.158 mmol), 10 mL of $CDCl_3$, and 1-bromo-2-butanone (322 μL, 3.13 mmol). After this solution was degassed, Et_3N (551 μL, 3.95 mmol) was added at −196 °C under N_2 flow. The reactor was evacuated, charged with H_2 to 600 torr, then warmed to room temperature, and stirred. After 1.5 h, the mixture was brown and homogeneous. All volatiles were removed by vacuum distillation. The resulting solid was dissolved in CH_2Cl_2. Addition of Et_2O to this solution caused precipitation of $Et_3NH^+Br^-$. It was filtered, and the filtrate was evaporated to dryness in vacuo. The ^1H NMR spectrum of the resulting solid in $CDCl_3$ exhibited the resonances due to **7** (see above) plus resonances at δ 5.66 (s, Cp), 5.44 (s, S_2CH_2), 2.44 (s, $SCH_2C(O)CH_2CH_3$), 2.33 (q, CH_2CH_3), and 0.90 (t, CH_2CH_3) which have been assigned to $(CpMo)_2(S_2CH_2)(SCH_2C(O)CH_2CH_3)_2$ (**8**). The mole ratio of **8** to **7** in this sample was ca. 2 on the basis of ^1H NMR data. The mixture was not separated.

Reaction of 7 with H_2. A solution of **7** in $CDCl_3$ was degassed in a thin-wall 5-mm o.d. NMR tube. At −196 °C, H_2 was admitted to 550 torr, and the tube was flame-sealed. The sample was warmed to 25 °C, and its ^1H NMR spectrum was examined periodically. The color of the solution changed from brown to blue within 30 min, and reaction was complete in 2 h. The ^1H NMR spectrum at this point showed resonances of **1** and butanone plus an unidentified peak at δ 5.49.

An NMR tube reaction of **7** with H_2 in C_6D_6 solution gave the same products as the reaction in $CDCl_3$ solution and at a similar rate. However, in the presence of proton sponge (0.0010 g, 0.0046 mmol), **7** (0.0036 g, 0.0067 mmol) in 0.5 mL of C_6D_6 in a sealed NMR tube gave no reaction with H_2 in 3 days at 25 °C. At 70 °C the reaction was 80–85% complete in 53 h (by ^1H NMR) and was complete in 5 days.

Reaction of 7 with CF_3SO_3H. In a 20-mL Schlenk tube, **7** (0.037 g, 0.069 mmol) was dissolved in 5 mL of $CDCl_3$. The solution was degassed. At −196 °C under N_2, CF_3SO_3H (9.2 μL, 0.104 mmol) was added by syringe. The mixture was warmed to ambient temperature slowly with stirring. Reaction was evident at low temperature by a color change from brown to purple. The product was crystallized from $CHCl_3/Et_2O/n$-pentane. Obtained was 0.0291 g (0.043 mmol, 61% yield) of **6** (triflate salt) as a mixture of **a** and **b** isomers.

Preparation of $[(CpMo)_2(S_2CH_2)(S_2CCH_3)]Cl$ (9). Typically, a 500-mL reaction flask equipped with a 10-mm Kontes O-ring stopcock was charged with **1** (0.650 g, 1.40 mmol), 15 mL of $CHCl_3$, and CH_3COCl (0.200 mL, 2.81 mmol). The mixture was degassed by three freeze–pump–thaw cycles. H_2 was admitted at −196 °C to 600 torr. The reaction mixture was stirred at room temperature for 12 h. At this point, it consisted of a brown solution with much brown precipitate. Removal of all volatile components by vacuum distillation gave a brown residue that was dissolved in methanol. Addition of diethyl ether to this solution caused precipitation of **9**·CH_3OH. The precipitate was washed with ether and vacuum dried to give 0.660 g (1.18 mmol), 84.3%. Extended exposure to dynamic vacuum caused gradual loss of the methanol of solvation. Similar runs in $CDCl_3$ were examined by ^1H NMR spectroscopy. From integration of spectra of the initial brown solution, ca. 0.4 of the original CH_3COCl was converted to CH_3CHO (0.8 turnover). The bromide salt of **9** was prepared analogously. $CHCl_3$ or CH_2Cl_2 may be used as solvent in either reaction. However, in $CHCl_3$ use of greater than 2 equiv of CH_3COBr/mol of **1** resulted in the precipitation of $[(CpMo)_2(S_2CH_2)(S)(SH)]Br$ (**10**), and **9(Br)** was not obtained.

$[(CpMo)_2(S_2CH_2)(S_2CR)]Cl$ (R = Ph, CH_2Ph) were prepared in analogous reactions of **1** with excess (20–25 equiv) PhCOCl and $PhCH_2COCl$, respectively, under H_2.

$[(CpMo)_2(S_2CH_2)(S_2CCH_3)]Br$. ^1H NMR (CD_3OD): δ 6.74, 5.69 (2 s, Cp), 7.16, 5.31 (2d, S_2CH_2), 2.57 (s, CH_3). $\{^1H\}^{13}C$ NMR: δ 150.8 (CH_3CS_2), 102.6, 95.2 (Cp), 80.9 (S_2CH_2), 36.2 (CH_3CS_2). FAB-MS: *m/e* 491 (P of cation), 445 (P − SCH_2), 418 (P − SCH_2 − CCH_3), 386 (P − SCH_2 − CCH_3 − S), 354 (P − SCH_2 − S_2CCH_3). Anal. Calcd for $C_{13}H_{15}BrMo_2S_4$: C, 34.03; H, 3.01; S, 20.19; Br, 12.56. Found: C, 34.10; H, 2.95; S, 19.91; Br, 12.65.

$[(CpMo)_2(S_2CH_2)(S_2CC_6H_5)]Cl$. ^1H NMR ($CDCl_3$): δ 7.38–6.99 (m, C_6H_5), 6.39, 5.76 (2s, Cp), ~6.9, 5.38 (2d, S_2CH_2). FAB-MS: *m/e* 522 (P of cation), 506 (P − SCH_2), 474 (P − S_2CH_2), 417 (P − SCH_2 − CC_6H_5), 385 (P − S_2CH_2 − CC_6H_5). Anal. Calcd for $C_{18}H_{17}ClMo_2S_4$: C, 36.71; H, 2.91; Cl, 6.02; S, 21.78. Found: C, 36.60; H, 3.03; Cl, 5.91; S, 21.71.

$[(CpMo)_2(S_2CH_2)(S_2CCH_2C_6H_5)]Cl$. ^1H NMR (CD_3OD): δ 7.37 (s, C_6H_5), 6.86, 5.71 (2s, Cp), 6.82, 5.29 (2d, S_2CH_2), 3.43 (s, S_2CCH_2Ph). FAB-MS: *m/e* 566 (P of cation), 520 (P − SCH_2), 418 (P − SCH_2 − $CCH_2C_6H_5$), 386 (P − S_2CH_2 − $CCH_2C_6H_5$). Anal. Calcd for $C_{19}H_{19}ClMo_2S_4$: C, 37.85; H, 3.18; Cl, 5.88; S, 21.27. Found: C, 37.74; H, 3.21; Cl, 5.87; S, 21.31.

Reaction of 1 with Acetyl Bromide and Acetyl-d_3 Chloride. An NMR tube was charged with **1** (6–7 mg, ca. 0.014 mmol), 0.5 mL of $CDCl_3$, CH_3COBr (10 μL, 0.135 mmol), and CD_3COCl (9.6 μL, 0.135 mmol). The solution was degassed in two freeze–pump–thaw cycles, and the tube was flame-sealed. Immediately after the mixture was warmed to 25 °C, the ^1H NMR spectrum was obtained. The methyl resonances due to the acetyl chloride and bromide were of essentially equal areas, indicating complete equilibration of acetyl and acetyl-d_3 with chloride and bromide ions. In a separate experiment, CD_3COCl and CH_3COBr in the absence of **1** required over 6 h to reach equilibrium.

Thermolysis of $[(CpMo)_2(S_2CH_2)(S_2CCH_3)]Cl$ (9). A solution of **9** in CD_3OD was degassed in an NMR tube, and the tube was flame-sealed. The ^1H NMR spectrum of the sample was monitored periodically as the tube was heated in an oven at 80–82 °C for 9 h and then at 120–130 °C for 5 days. No change was observed. Under similar conditions, no reaction was observed between **9** and H_2, CO, 1-butene, or CF_3SO_3H.

Reaction of 9 with Li[Et_3BH]. Complex **9** (0.116 g, 0.20 mmol) was suspended in 5 mL of THF. The mixture was degassed and stirred under N_2 at −78 °C. $LiEt_3BH$ (0.60 mL of 1.0 M solution in THF, 0.60 mmol) was added slowly by syringe. The solution gradually became dark brown, but much brown solid remained. After ca. 30 min, the reaction was warmed slowly to 25 °C. At this point, the color was green brown. After 1 h, all volatiles were removed by vacuum distillation. The remaining solid was chromatographed on an Al_2O_3 column. CH_2Cl_2 eluted a small brown band followed by a large green one. The brown substance has been characterized as $(CpMo)_2(S_2CH_2)(S_2CHCH_3)$: ^1H NMR δ 6.43 (q, S_2CHCH_3), 6.34 (AB, S_2CH_2), 5.88, 5.83 (2s, Cp), 1.35 (d, S_2CHCH_3). FAB-MS: *m/e* 492 (P), 432 (P − $SCHCH_3$), 388 (calcd 386) (P − $SCHCH_3$ − SCH_2). The ^1H NMR spectrum of the green substance indicated primarily the same product, but less pure. An analogous reaction between **9** and CH_3Li also gave a low yield of $(CpMo)_2(S_2CH_2)(S_2CHCH_3)$.

Reaction of 1 with Methyl Chloroformate and Hydrogen. A 150-mL reaction vessel equipped with a 10-mm Kontes O-ring

stopcock was charged with 1 (0.074 g, 0.159 mmol), 5 mL of $CDCl_3$, and $ClCO_2CH_3$ (3.187 mmol, 20 equiv). The solution was degassed in three freeze–pump–thaw cycles, and then hydrogen was admitted to 600 torr at −196 °C. The flask was sealed and warmed to ambient temperature. The solution was stirred for 22.5 h. A ^1H NMR spectrum of the blue solution at this point exhibited resonances due to 1, HCO_2CH_3, and $ClCO_2CH_3$, the latter two in a ratio of 0.13 (2.3 turnovers). The NMR sample was returned to the flask, and hydrogen was admitted as before. The lower portion of the reactor was then immersed in a 70 °C oil bath. after the solution was stirred for 24 h, the ^1H NMR spectrum showed a formate:chloroformate ratio of 6.0 (17.1 turnovers). After another 24 h at 70 °C, the ratio was 16.0 (18.0 turnovers). A considerable amount of solid was present in the reaction mixture at this point. Attempts to characterize the solid were unsuccessful.

Reaction of 1 with *N,N*-Dimethylcarbamoyl Chloride and Hydrogen. The reaction of $(Me)_2NC(O)Cl$ (20 equiv) with 1 and H_2 in $CDCl_3$ gave no reaction at 25 °C or after 8 days at 50 °C. After 6 days at 75 °C, new resonances were observed in the ^1H NMR spectrum at δ 8.1 and 5.9 and between 2.6 and 3.0 ppm. Some of these may correspond to *N,N*-dimethylformamide (lit.[16] δ 8.01, 2.91, 2.74). However, the total conversion would be less than 7%.

Reaction of $(CpMoS)_2S_2CH_2$ (1) with HBr. Complex 1 (0.106 g, 0.228 mmol) was dissolved in 10 mL of CH_2Cl_2 in a 150-mL reactor. The solution was degassed on a high-vacuum line by three freeze–pump–thaw cycles. One equivalent of HBr was condensed onto the frozen solution at −196 °C. As the solution was warmed, the initial blue color turned deep red and then back to blue as it reached room temperature. The mixture was cooled to −196 °C, and another equivalent of HBr was added. When the mixture was warmed, to room temperature, the red color persisted and dark solid precipitated. Volatile components were removed by vacuum distillation, and the resulting solid $[(CpMo)_2(S_2CH_2)(S)(SH)]Br$ was washed with CH_2Cl_2 to remove 1 and dried by vacuum. Yield: 0.090 g, 0.165 mmol, 72.4%. When the above reaction was carried out in an NMR tube in $CDCl_3$, the solution turned from blue to red and most of the colored material precipitated leaving a pale red solution. ^1H NMR: δ 6.92 (Cp) and 4.20 (s, S_2CH_2). The data are similar to those reported for the triflate and tetrafluoroborate salts of this cation.[4] Also observed was a large singlet at δ −1.95, probably an average resonance arising from exchange of H_2O, HBr, and the SH ligand. EI-MS: *m/e* 80/82 (P, HBr), 464 (P of 1), 418 (P − SCH_2), 386 (P − S_2CH_2), 354 (P − S_2CH_2 − S). $[(CpMo)_2(S_2CH_2)(S)(SH)]Br$ is insoluble in CH_2Cl_2, $CHCl_3$, and acetone. It deprotonates in H_2O, CH_3OH, and wet CH_3CN to give 1. When a suspension of the salt (0.0172 g, 0.0315 mmol) in $CHCl_3$ was extracted with H_2O, titration of the aqueous phase with 0.0106 M NaOH solution using a pH meter required addition of 3.35 mL (0.0355 mmol) to reach pH 7. The observed HBr concentration was 113% of calculated.

Acknowledgment. This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy. Purchase of the X-ray diffraction equipment was made possible by the National Science Foundation (CHE 84-12182). M.R.D. is grateful for fellowships as a Camille and Henry Dreyfus Teacher-Scholar, 1981–1986, and from the John Simon Guggenheim Foundation, 1984–1985.

Registry No. 1, 86163-42-0; 2, 110077-41-3; 3, 110077-46-8; 4a, 110077-47-9; 4b, 110169-77-2; 5, 110077-48-0; 6a, 110077-49-1; 6b, 110169-76-1; 7, 110077-50-4; 8, 110077-51-5; 9(Cl), 110077-45-7; 9(Br), 106017-51-0; 10, 110077-52-6; $[(CpMo)_2(S_2cH_2)(\mu\text{-}S)(\mu\text{-}SCH_2CO_2CH_3)]SO_3CF_3$, 110077-44-6; $[(CpMo)_2(S_2CH_2)(S_2CPh)]Cl$, 110077-42-4; $[(CpMo)_2(S_2CH_2)(S_2CH_2Ph)]Cl$, 110077-53-7; $(CpMo)_2(S_2CH_2)(S_2CHCH_3)$, 110077-54-8; $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_2CO_2CH_3)]^+$, 110077-43-5; $BrCH_2CO_2CH_3$, 96-32-2; $CH_3CO_2CH_3$, 79-20-9; CF_3SO_3H, 1493-13-6; CH_3COCl, 75-36-5; $PhCOCl$, 98-88-4; $PhCH_2COCl$, 103-80-0; CH_3COBr, 618-32-6; $ClCO_2CH_3$, 79-22-1; HCO_2CH_3, 107-31-3; $(Me)_2NC(O)Cl$, 79-44-7; $LiEt_3BH$, 22560-16-3; 2,6-lutidine, 108-48-5; 1-bromo-2-butanone, 816-40-0; 2-butanone, 78-93-3; *N,N*-dimethylformamide, 68-12-2.

Supplementary Material Available: A table of anisotropic thermal parameters and complete listings of bond distances and bond angles for 9 (5 pages); a table of structure factor amplitudes for 9 (32 pages). Ordering information is given on any current masthead page.

(16) Pouchert, C. J., Campbell, J. R., Eds. *Aldrich Library of NMR Spectra*; Aldrich Chemical Co.: Milwaukee, WI, 1974; Vol. 3, p 108D.