Cleavage of Saturated Oxygen Heterocycles by a Dinuclear Molybdenum Complex Containing Sulfido and Hydrosulfido Ligands

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The cationic complex $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]SO_3CF_3$ (1) reacted with tetrahydrofuran to form a cationic derivative with a μ-4-hydroxybutanethiolate ligand, $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}S(CH_2)_4OH)]SO_3CF_3$. The product has been isolated and characterized by spectroscopic methods. Spectroscopic evidence for the deprotonation of 1 by THF suggests that the reaction proceeds by nucleophilic attack on the protonated heterocycle by a sulfido ligand in a neutral molybdenum(IV) complex. Similar ring opening reactions were observed for trimethylene oxide and propylene oxide. In each case a new dinuclear complex with a μ-hydroxy thiolate ligand has been isolated and characterized. No reactions were observed with the 6-membered rings tetrahydropyran and 1,3- or 1,4-dioxane. The reactivities of the new cations have been investigated. $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_2CH(Me)OH)]SO_3CF_3$ reacted under a deuterium atmosphere to form perdeuterioacetone and 1. Complex 1 effected the cleavage of the acylic ethers *t*-BuOEt and $(PhCH_2)_2O$, but $(n\text{-}Bu)_2O$ and MeOPh were unreactive under similar conditions.

Introduction

Many mechanistic studies have been carried out on the hydrotreating of aromatic heterocycles catalyzed by sulfided molybdenum surfaces. Although most of the studies have focused on the pathways involved in the hydrodesulfurization of thiophene,[1-5] mechanistic features of the hydrotreating of related nitrogen[6,7] and oxygen[8-10] containing rings have also been investigated. The latter systems are becoming of increased interest as dirtier feedstocks are utilized and as synthetic fuels are produced.[10] Reactions of oxygen containing aromatic rings, such as furan, benzofuran, and dibenzofuran, over sulfided molybdenum catalysts often proceed by a dual pathway; a mechanism that involves initial hydrogenation of the ring followed by hydrogenolysis of the C-O bonds has been proposed as well as a second pathway which involves direct hydrodeoxygenation (HDO) of the unsaturated ring.[8-10] The reactions of both saturated and unsaturated heterocycles with molybdenum sulfide complexes are therefore of interest as relevant models for the heterogeneous reactions. We report here our studies on the ring opening of saturated cyclic ethers by a cationic sulfido-bridged molybdenum complex in homogeneous solution. Tetrahydrofuran has been cleaved as well as the more highly strained rings trimethylene oxide and propylene oxide. In each system, a new dinuclear molybdenum complex that contains an μ-hydroxythiolate ligand has been isolated.

Many reagents are known to promote ether cleavage reactions, including Brønsted and Lewis acids, nucleophilic reagents, and halosilanes.[11] Hydrogenolysis of ethers has been catalyzed by platinum, palladium, and Raney nickel. The cleavage of the cyclic ether tetrahydrofuran follows similar reactivity patterns as the acyclic ethers.[12] For example, THF has been converted to butanol by $LiAl(o\text{-}t\text{-}Bu)_3H\cdot B(C_2H_5)_3$ or by hydrogen pressures over a platinum carbon catalyst;[12] the reaction of THF with HCl produces tetramethylene chlorohydrin, and with acetyl iodide, 4-iodobutyl acetate is formed.[13] THF is cleaved by butyllithium producing ethylene and the enolate anion of acetaldehyde.[14]

There are very few well-characterized examples of ring-opening reactions of tetrahydrofuran promoted by organometallic complexes of the transition metals, however. Finely divided magnesium inserts into THF to form a cyclic magnesium complex $\overline{MgOCH_2CH_2CH_2CH_2}$.[15] This reaction is promoted by transition-metal chlorides by a proposed mechanism which involves the initial addition of a Mg-M complex across the C-O bond of the ether. The insertion of aluminum into THF to form polymeric alkoxyalkylaluminum compounds was also promoted by metal halides.[17] The tungsten-aluminum complex $[(Me_3P)_3H_3W(\mu\text{-}H)_2Al(H)(\mu\text{-}H)]_2$ reacted in refluxing THF to form a related derivative in which the aluminum ions were bridged by butoxy ligands.[18] The reaction of an aluminum compound, AlR_2Br, with a chromium complex containing a diphenylphosphido ligand in THF resulted in the incorporation of a cleaved THF molecule into the product $Cr(CO)_5[PPh_2(CH_2)_4OAlR_2]$.[19] The ring cleavage reactions by the dinuclear molybdenum sulfide complex reported here do not require the presence

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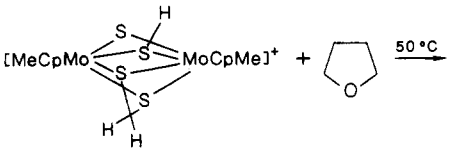
of an additional Lewis acid; the reactions appear to take advantage of the Brønsted acidity of the hydrosulfido ligand in the cation and the nucleophilicity of the sulfido ligand in the deprotonated complex.

Results and Discussion

Reaction of 1 with Tetrahydrofuran. The cationic complex $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]SO_3CF_3$ (1) reacted with excess tetrahydrofuran in dry dichloromethane solvent at 50 °C under an atmosphere of nitrogen to form a cationic product with a 4-hydroxybutanethiolate ligand as shown in eq 1. The NMR spectrum of the crude



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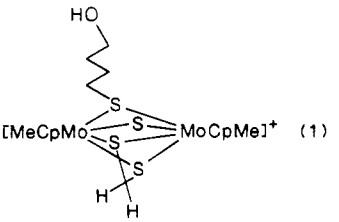


(1)

product mixture showed only one major molybdenum complex, and the cation was isolated as a purple crystalline material in ca. 60% yield. The product was characterized by elemental analyses, by fast atom bombardment mass spectroscopy, and by ^1H and ^{13}C NMR spectroscopy. In the ^1H NMR, the Cp and S_2CH_2 resonances occurred at frequencies normally observed for these ligands in cationic derivatives of this type.[20,21] The resonances of the hydroxybutanethiolate ligand in the ^1H and ^{13}C NMR spectra, with the exception of those assigned to the CH_2 group adjacent to the sulfur, were very similar in chemical shift to those of the corresponding atoms in 1-butanol. In particular, the ^{13}C chemical shift of the resonance assigned to the carbon adjacent to the OH group in the coordinated ligand was 61.8 ppm compared to a resonance at 61.4 ppm for the analogous carbon in free butanol.[22] The infrared spectrum, which showed a strong OH stretching absorption at 3600 cm^{-1}, also supported the proposed formulation of the ligand.

The hydrosulfido ligand in 1 is much more acidic than the S–H ligands in related neutral derivatives. The pK_a of 1 in dry acetonitrile solution has been found to be 8.3,[23] a value similar to the pK_a of HCl in this solvent.[24] In parts a and b of Figure 1, the visible spectrum of 1 in dried CH_2Cl_2 is compared to the spectrum of 1 in the THF/CH_2Cl_2 reaction solution. Evidence is observed in the latter spectrum for the presence of the deprotonated complex $(MeCpMo(\mu\text{-}S))_2(S_2CH_2)$, which has strong absorptions at 590 and 730 nm. The cleavage of THF, therefore, appears to proceed through formation of a protonated heterocycle. The degree of protonation of

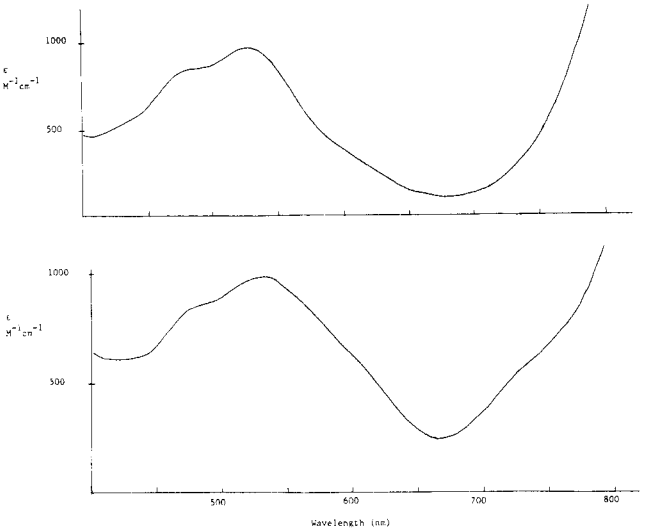
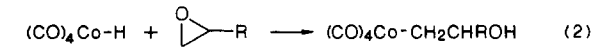


Figure 1. Visible spectra recorded in CH_2Cl_2: (a) $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]SO_3CF_3$ (1); (b) complex 1 plus tetrahydrofuran (150–200 equiv).

2,5-dimethyltetrahydrofuran was significantly greater than for the unsubstituted ring, but the rate of ring opening for the methyl-substituted heterocycle was much slower. This observation is consistent with a bimolecular mechanism involving nucleophilic attack on the heterocycle by a sulfido ligand of the deprotonated form of 1. The nucleophilic character of the sulfido ligands in $(MeCpMo(\mu\text{-}S))_2(S_2CH_2)$ has been observed in previous reactivity studies.[20] Such a bimolecular mechanism parallels that proposed for THF cleavage by simpler Brønsted acids.[25]

The ring cleavage reaction has also been carried out under a hydrogen atmosphere. Activation of hydrogen by $(MeCpMo(\mu\text{-}S))_2(S_2CH_2)$ has been postulated to form low concentrations of a nucleophilic Mo(III) complex, e.g. $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SH)_2$.[26] However, when rates of reaction 1 under H_2 and under N_2 were monitored by NMR spectroscopy, product formation was observed cleanly in each case at very similar rates. Hydrogen does not appear to increase the nucleophilic reactivity in this system.[27]

Reactions of 1 with Propylene Oxide and Trimethylene Oxide. Examples of reactions of oxetanes or epoxides with transition-metal complexes are more numerous than those involving THF. For example, simple epoxides have been isomerized to ketones by $Rh(PMe_3)_3Cl$[28] and other low-valent complexes.[29] The cis–trans isomerization of epoxides has been catalyzed recently by a ruthenium(II) porphyrin complex.[30] Metal complexes such as $[Rh(CO)_2Cl]_2$ promoted the rearrangement of oxetanes to olefins and aldehydes.[31] A metal–hydride addition to epoxides to form a β-hydroxyalkyl complex (eq 2) has been proposed as an initial step in the catalytic



(2)

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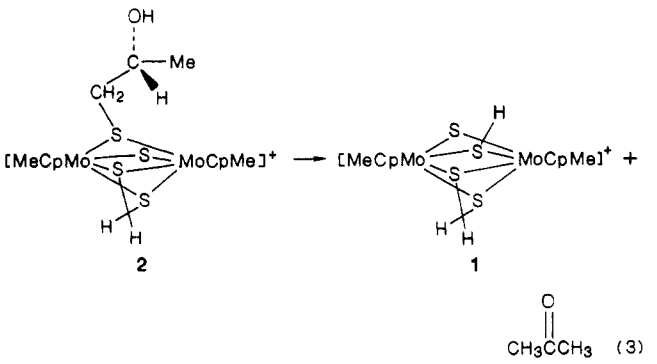
hydrogenation and hydroformylation of the epoxide substrate.[32-35] Although the addition of thiols to epoxides and oxetanes has been characterized,[36] this type of reaction has not been carried out within the coordination sphere of a metal ion to our knowledge.

The reaction of $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]SO_3CF_3$ with trimethylene oxide proceeded at 50 °C in acetonitrile in the presence of nitrogen to form the cationic product $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}S(CH_2)_3OH)]SO_3CF_3$ in 50% yield. The more strained ring propylene oxide reacted with the protonated complex at room temperature to produce the cation with a 2-hydroxypropane-1-thiolate ligand in 60% yield. Both product formulations have been confirmed by elemental analysis, by FAB mass spectra, and by ^1H and ^{13}C NMR data. In the propylene oxide reaction, only the regioisomer resulting from sulfide coordination to the unsubstituted carbon was observed. The isomer is consistent with a mechanism in which steric effects play a more dominant role than electronic factors in determining the position of nucleophilic attack.[32]

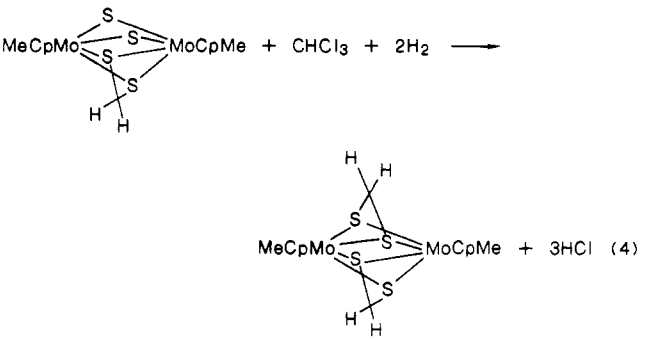
Reactivity of Hydroxy Thiolate Bridged Products. The products $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S(CH_2)_nOH)]SO_3CF_3$ (n = 3, 4), which resulted from the reaction with trimethylene oxide or THF, were thermally quite stable. No reaction was observed when the complexes were heated in CH_2Cl_2 at 70 °C for several days. A reaction commonly observed for the halide salts of related cationic complexes at elevated temperatures is the elimination of the alkyl halide from the bridging sulfonium-type complex.[37] However, no chlorohydrin was detected when the hydroxy thiolate bridged complexes were heated at 50 °C in the presence of [PPN]Cl. The new complexes also failed to react with hydrogen (1–3 atm) at temperatures ranging from 50 to 70 °C. For several related cationic derivatives, reaction with hydrogen has been found to result in hydrogenolysis of the C–S bond of the thiolate substituent R and formation of the corresponding hydrocarbon RH.[38,39]

The cationic complex with the 2-hydroxypropane-1-thiolate ligand, **2**, did undergo a reaction under nitrogen at 50 °C to eliminate acetone and form the protonated molybdenum complex (eq 3). The elimination of acetone is proposed to involve a hydride shift from the carbon which is β to the thiolate sulfur to the adjacent μ-sulfido ligand, accompanied or followed by elimination of the enol. Similar eliminations of olefins from branched alkanethiolate ligands in cationic molybdenum complexes have also been observed.[40] Such eliminations display an interesting parallel to β-elimination reactions at a transition-metal center and provide a facile mechanism for the cleavage of a carbon–sulfur bond in these complexes.



When **2** was heated under deuterium, perdeuterioacetone was produced. The same result was observed when **1** and acetone were heated under deuterium pressure. Formation of the enol form of acetone is believed to be catalyzed by the acidic proton of **1**,[41] and the H–D exchange process is therefore likely to involve a reversible addition to this tautomer by an S–D ligand in **1** or a related neutral derivative. The insertion of an olefin into a μ-SH ligand has been characterized previously for both cationic and neutral hydrosulfido derivatives of the cyclopentadienylmolybdenum dimers.[40,42]

Reactions of $(MeCpMo(\mu\text{-}S))_2S_2CH_2$ with Trimethylene Oxide and Propylene Oxide. The reactions of the strained oxygen heterocycles with the protonated cation, described above, were compared to similar reactions with the unprotonated complex. $(MeCpMo(\mu\text{-}S))_2S_2CH_2$ in chloroform solution was reacted with propylene oxide (2 equiv) at 50 °C. The reaction was carried out under an atmosphere of hydrogen in order to promote the formation of a nucleophilic complex with SH ligands (vide supra). However, the product with a ring-opened hydroxypropanethiolate ligand was not detected. After several days reaction time, the starting molybdenum complex as well as a second molybdenum product were identified by NMR. The new complex was $[MeCpMo(\mu\text{-}S_2CH_2)]_2$, which has been characterized previously.[43] It is produced from a slow reaction of $(MeCpMo(\mu\text{-}S))_2S_2CH_2$ with chloroform under hydrogen (eq 4). No propylene oxide remained in the reaction mixture. It had been, in part, isomerized to acetone and, in part, converted to 3-chloro-2-propanol. The latter product resulted from the reaction of propylene oxide with HCl, produced in reaction 4.



Similarly the reaction of trimethylene oxide with $(MeCpMo(\mu\text{-}S))_2S_2CH_2$ in chloroform solution under hydrogen resulted in the formation of $[MeCpMo(\mu\text{-}S_2CH_2)]_2$ and 3-chloro-1-propanol. When the neutral molybdenum complex was heated with propylene oxide or trimethylene oxide under hydrogen in a non-chlorinated solvent such

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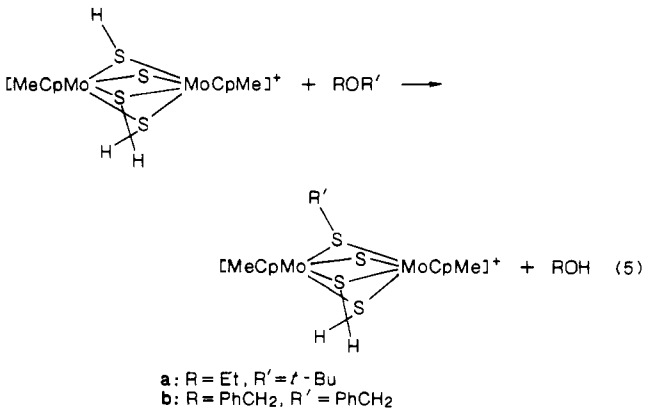
as THF, no reaction was observed.

Reactions of 1 with Acyclic Ethers. The cation $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]SO_3CF_3$ reacted slowly with *t*-BuOEt and $(PhCH_2)_2O$ under a nitrogen atmosphere at 50 °C as shown in eq 5. These ethers are particularly susceptible to cleavage by acidic reagents because of the relative stability of the leaving group R'^+.[11] The dinuclear molybdenum complexes with the alkylated sulfide ligand were identified by comparison of NMR data with those of authentic cations prepared by alternate routes.[40,45] The product alcohol in eq 5a was identified by GC/mass spectroscopy and by NMR spectroscopy.



No reactions were observed when the protonated cation 1 was heated under a hydrogen atmosphere with other acyclic ethers such as $(n\text{-}Bu)_2O$ or PhOMe. The lower basicity of these molecules relative to the cyclic ether THF is expected to be a factor in their reduced reactivity. Studies of the reactivities of other heterocycles with 1 and related derivatives are in progress.

Experimental Section

Materials and Instrumentation. The molybdenum complexes $(MeCpMo(\mu\text{-}S))_2S_2CH_2$[43] and $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]SO_3CF_3$[44] were synthesized by published procedures. Dichloromethane was distilled from either P_4O_{10} or CaH_2. Acetonitrile and tetrahydrofuran were distilled from CaH_2. Anhydrous diethyl ether was used without further purification. All other reagents and solvents were purchased from Aldrich and were used without further purification.

Proton NMR spectra were recorded on either a Chemagnetics A-200, a Bruker WM-250, or a Varian Gemini-300 spectrometer. Carbon-13 NMR spectra were recorded on either a Bruker WM-250 or a Varian VXR-500 spectrometer. Signal positions were referenced to $Si(CH_3)_4$ by using the solvent signal as a secondary reference. Visible spectra were recorded on a Hewlett-Packard 8451A diode array spectrophotometer. Mass spectra were obtained on a VG Analytical 7070 EQ-HF mass spectrometer. GC/MS analyses were carried out on a Hewlett-Packard 5988A GC/MS system equipped with a Hewlett-Packard 5890 gas chromatograph. The GC contained a 25-m fused silica capillary column of cross-linked 5% phenyl methyl silicone. Elemental analyses were performed by Spang Laboratories.

Synthesis of $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}S\text{-}CH_2CH(OH)CH_3)]SO_3CF_3$. $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]SO_3CF_3$ (0.12 g, 0.19 mmol), 5.0 mL of freshly distilled acetonitrile, and propylene oxide (75 μL, 1.1 mmol) were placed in a Schlenk tube. The resulting solution was freeze–pump–thaw degassed three times. The tube was sealed, and the solution was stirred at 50 °C for about 6 days. The solvent was removed under vacuum, and the resulting red product was crystallized from acetonitrile/diethyl ether. The product was isolated as 73 mg (56% yield) of a dark purple microcrystalline solid. ^1H NMR (CD_2Cl_2): δ 6.82, 6.79 (br, 8, Cp); 4.08 (s, 2, S_2CH_2); 3.68 (m, 1, $-CH(OH)$); 2.51 (s, 6, Cp–Me); 1.98 (d, J = 5.6 Hz, 2, $CH_2CH(OH)CH_3$); 1.08 (d, J = 6.0 Hz, 3, $CH_2CH(OH)CH_3$). ^{13}C NMR (CD_3CN): δ 124.64, 105.43, 105.35, 103.85, 103.73 (Cp); 68.97 ($-CH(OH)$); 49.35 (S_2CH_2); 44.63 ($CH_2CH(OH)CH_3$); 23.09 ($CH_2CH(OH)CH_3$); 16.89 (Cp–Me). MS(FAB): m/e 551 (P^+). Anal. Calcd for $C_{17}H_{23}Mo_2S_5O_4F_3$: C, 29.15; H, 3.31; S, 22.89. Found: C, 29.21; H, 3.27; S, 22.89.

Synthesis of $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_2CH_2CH_2OH)]SO_3CF_3$. $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]SO_3CF_3$ (0.18 g, 0.28 mmol), trimethylene oxide (40 μL, 0.61 mmol), and 5.0 mL of freshly distilled dichloromethane were put into a Schlenk tube. The solution was freeze–pump–thaw degassed three times. Then, while the tube was immersed in liquid N_2, 600 mm of N_2 was added to the tube. The tube was sealed and stirred at 50 °C for 42 h. The solvent was removed under vacuum, and the product was crystallized from acetonitrile/diethyl ether. The product was isolated as 126 mg (65% yield) of a dark purple microcrystalline solid. ^1H NMR (CD_2Cl_2): δ 6.81 (s, 8, Cp); 4.09 (s, 2, S_2CH_2); 3.50 (t, J = 5.9 Hz, 2, $\mu\text{-}SCH_2CH_2CH_2OH$); 2.51 (s, 6, Cp–Me); 2.08 (t, J = 7.5 Hz, 2, $\mu\text{-}SCH_2CH_2CH_2OH$); 1.61 (m, 2, $\mu\text{-}SCH_2CH_2CH_2OH$). ^{13}C NMR (CD_3CN): δ 124.69, 105.43, 105.19, 103.56 (Cp); 60.51 ($\mu\text{-}SCH_2CH_2CH_2OH$); 49.65 ($S_2CH_2$); 36.21, 33.47 ($\mu\text{-}SCH_2CH_2CH_2OH$); 17.03 (Cp–Me). MS (FAB): m/e 551 (P^+). Anal. Calcd for $C_{17}H_{23}Mo_2S_5O_4F_3$: C, 29.15; H, 3.31; S, 22.88. Found: C, 29.17; H, 3.29; S, 22.77.

Synthesis of $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_2CH_2CH_2CH_2OH)]SO_3CF_3$. $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]SO_3CF_3$ (0.15 g, 0.23 mmol), 2.0 mL of freshly distilled tetrahydrofuran, and 5.0 mL of freshly distilled dichloromethane were put into a Schlenk tube. The solution was freeze–pump–thaw degassed three times. Then, with the tube immersed in liquid N_2, 600 mm of N_2 was added to the tube. The tube was sealed, and the solution was allowed to stir for 20 h at 50 °C. The solvent was removed under vacuum, and the resulting solid was crystallized from acetonitrile/diethyl ether. The product was isolated as 96 mg (58% yield) of a dark purple microcrystalline solid. ^1H NMR (CD_2Cl_2): δ 6.80 (s, 8, Cp); 4.12 (s, 2, S_2CH_2); 3.50 (t, J = 5.7 Hz, 2, ($\mu\text{-}SCH_2CH_2CH_2CH_2OH$); 2.50 (s, 6, Cp–Me); 1.98 (t, J = 6.5 Hz, $\mu\text{-}SCH_2CH_2CH_2CH_2OH$); 1.44 (m, 4, $\mu\text{-}SCH_2CH_2CH_2CH_2OH$). ^{13}C NMR (CD_3CN): δ 124.59, 105.31, 105.10, 103.58, 103.46 (Cp); 61.79 ($\mu\text{-}SCH_2CH_2CH_2CH_2OH$); 49.60 ($S_2CH_2$); 36.61 ($\mu\text{-}SCH_2CH_2CH_2CH_2OH$); 32.26, 30.14 ($\mu\text{-}SCH_2CH_2CH_2CH_2OH$); 17.02 (Cp–Me). MS (FAB): m/e 565 (P^+). Anal. Calcd for $C_{18}H_{25}Mo_2S_5O_4F_3$: C, 30.26; H, 3.53; S, 22.43. Found: C, 30.13; H, 3.62; S, 22.32.

Relative Rates of the Formation of $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}S(CH_2)_4OH)]SO_3CF_3$ under N_2 and under H_2. Two reactions were carried out as described above under ca. 600 mm of H_2 and N_2, respectively. Aliquots were withdrawn periodically, and reaction vessels were repressurized. NMR analysis showed that both reactions were ca. 76% complete after 6 h at 50 °C and 90–100% complete after 12 h.

Deprotonation of 1 by Tetrahydrofuran. The visible spectrum of a dichloromethane solution of 1 (4.64×10^{-4} M) and THF (6.50×10^{-2} M) was recorded. Extinction coefficients for 1 at 730 and 525 nm (233 and 988 M^{-1} cm^{-1}, respectively) and for $(MeCpMo(\mu\text{-}S))_2S_2CH_2$ at the same wavelengths (1814 and 890 M^{-1} cm^{-1}, respectively) were determined from Beer's law plots.[27] The absorptivities and extinction coefficients at the two wavelengths were used to calculate that ca. 8% of the deprotonated complex was present in solution. No ring cleavage product was detected at this early stage of the reaction.

Relative Rates of Reaction of 1 with Tetrahydrofuran and with 2,5-Dimethyltetrahydrofuran. The reaction of 1 with THF, described above, was repeated with 2,5-dimethyltetrahydrofuran under the same conditions. The color of the dimethyltetrahydrofuran reaction solution was blue, indicating significant deprotonation of 1. After 18 h at 50 °C, the reaction solution was cooled and a portion was analyzed by NMR. Resonances that might be assigned to a ring opened product were observed in very low intensity (<5%), and the product was not further characterized. In contrast, the THF reaction proceeded to completion within this time period.

Attempted Reactions of $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]SO_3CF_3$ (1) with 6-Membered Heterocycles. Complex 1 (9.0 mg, 0.01 mmol) and tetrahydropyran (10 μL, 0.10 mmol) in 0.40 mL of CD_2Cl_2 were placed in an NMR tube. The solution

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was freeze–pump–thaw degassed three times. With the tube immersed in liquid N_2, 590 mm of H_2 was added and the tube was sealed. The reaction was allowed to proceed for 30 days at 50 °C and 7 days at 70 °C. After this time, the ^1H NMR spectrum showed no evidence for a new cationic molybdenum derivative in solution.

Similar procedures were followed for reactions of 1 with 1,3- or 1,4-dioxane. Reactions were heated for 19 and 7 days, respectively, at 50 °C. New cationic molybdenum derivatives were not observed in the NMR spectrum.

Attempted Reactions of $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}S(CH_2)_nOH)]SO_3CF_3$ (n = 3, 4) with Hydrogen. The molybdenum complex (0.01–0.02 mmol) was dissolved in CD_2Cl_2 or CD_3CN in an NMR tube. The solution was freeze–pump–thaw degassed three times. With the tube immersed in liquid N_2, 590 mm of H_2 was added and the tube was sealed. No reaction was detected by NMR spectroscopy after 5–7 days at 50 °C for n = 3 or after 25 days at 50 °C and 7 days at 70 °C for n = 4.

Attempted Reaction of $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_2CH(Me)OH]SO_3CF_3$ with Hydrogen. The molybdenum complex (0.02 mmol) was dissolved in CD_2Cl_2 (0.6 mL) in an NMR tube. The solution was freeze–pump–thaw degassed three times, and 600 mm of H_2 was added as described in the previous paragraph. The solution was heated at 50 °C for ca. 7 days. The ^1H NMR spectrum of the products showed the presence of 1 (in equilibrium with its deprotonated form) and acetone. Acetone formation was confirmed by ^{13}C NMR: δ 31.0 (CH_3); 206.6 (C=O). When the reaction was carried out under deuterium, the resonances of the starting complex disappeared, but no acetone resonance was observed in the ^1H NMR.

The reaction of 1 with acetone under D_2 was carried out under similar conditions. The ^1H NMR spectrum showed the gradual disappearance of the acetone resonance. Molybdenum products were a mixture of 1 and its deprotonated form.

Reaction of $(MeCpMo(\mu\text{-}S))_2(\mu\text{-}S_2CH_2)$ with Trimethylene Oxide in the Presence of Hydrogen. The neutral molybdenum complex (0.02 mmol), trimethylene oxide (0.05 mmol), and 0.60 mL of $CDCl_3$ were placed in an NMR tube. The solution was freeze–pump–thaw degassed three times, and then 590 mm of hydrogen was added at −196 °C. The tube was sealed. The reaction was allowed to proceed for 9 days at 50 °C. After this time the volatile materials were transferred into another NMR tube. The resulting solid was found to contain primarily $(MeCpMo)_2(\mu\text{-}S_2CH_2)_2$.[38] ^1H NMR ($CDCl_3$): δ 6.24 (s, S_2CH_2); 5.74, 5.72 (br, Cp); 2.13 (s, Cp–Me). The volatile fraction was analyzed by ^1H NMR and GC/MS and was found to contain only $ClCH_2$–CH_2–CH_2OH. ^1H NMR ($CDCl_3$): δ 3.81 (t, J = 5.9 Hz, 2, $ClCH_2CH_2CH_2OH$); 3.67 (t, J = 6.5 Hz, 2, $ClCH_2CH_2CH_2OH$); 2.00 (m, 2, $ClCH_2CH_2CH_2OH$).

When the same reagents were heated in THF-d_8 at 50 °C for 11 days, no reaction was observed by ^1H NMR.

Reaction of $(MeCpMo(\mu\text{-}S))_2S_2CH_2$ with Propylene Oxide in the Presence of Hydrogen. The molybdenum complex (0.03 mmol), propylene oxide (0.04 mmol), and 0.60 mL of $CDCl_3$ were put into an NMR tube. The solution was freeze–pump–thaw degassed three times, and then 590 mm of H_2 was added at −196 °C. The tube was sealed. The reaction mixture was kept at 50 °C for 18 days. After this time the volatile materials were transferred to another NMR tube. The resulting solid was found to contain the starting complex and $(MeCpMo)_2(\mu\text{-}S_2CH_2)_2$.[38] The volatile fraction was analyzed by both ^1H NMR and GC/MS and was found to contain acetone and 1-chloro-2-propanol along with a small amount of an unidentified product (^1H NMR δ 1.48 ppm (d)).

Reaction of $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]SO_3CF_3$ (1) with *tert*-Butyl Ethyl Ether. Complex 1 (0.02 mmol), *tert*-butyl ethyl ether (0.04 mmol), and 0.60 mL of CD_2Cl_2 were placed in an NMR tube. The solution was freeze–pump–thaw degassed three times, and 600 mm of N_2 was added at −196 °C. The tube was then sealed. After the reaction was allowed to proceed for $15^1/_2$ days at 50 °C, the volatile products were separated from the solid Mo products. Analysis of the volatile portion of the reaction mixture by both ^1H NMR and GC/MS showed that the major organic product was ethanol. The red solid produced in the reaction was found to contain both $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC(CH_3)_3)]SO_3CF_3$ and $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_2CH(CH_3)_2)]SO_3CF_3$. Previous work from this laboratory has shown that the former product cation rearranges to the latter.[40]

$[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC(CH_3)_3)]SO_3CF_3$: ^1H NMR (CD_2Cl_2) δ 6.80 (br, Cp); 4.13 (s, S_2CH_2); 2.53 (s, Cp–Me); 1.21 (s, $-C(CH_3)_3$).

$[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_2CH(CH_3)_2)]SO_3CF_3$: ^1H NMR (CD_2Cl_2) δ 6.77 (br, 8, Cp); 4.16 (s, 2, S_2CH_2); 2.51 (s, 6, Cp–Me); 1.77 (d, J = 7.0 Hz, 2, $-CH_2CH(CH_3)_2$); 1.53 (m, 1, $-CH_2CH(CH_3)_2$); 0.86 (d, J = 6.5 Hz, 6, $-CH_2CH(CH_3)_2$).

Reaction of 1 with Benzyl Ether. Complex 1 (0.02 mmol), benzyl ether (0.03 mmol), and 0.60 mL of CD_2Cl_2 were placed in an NMR tube. The solution was freeze–pump–thaw degassed three times, then 600 mm of N_2 or H_2 was added at −196 °C, and the tube was sealed. The reaction was allowed to proceed for $12^1/_2$ days at 50 °C and $4^1/_2$ days at 70 °C. The solvent was then removed by vacuum distillation, and the resulting red oil was washed several times with diethyl ether. The red solid was characterized as $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_2C_6H_5)]SO_3CF_3$. ^1H NMR (CD_3CN): δ 7.36, 7.07 (m, Ph); 6.64, 6.62 (m, Cp); 4.12 (s, S_2CH_2); 3.17 (s, CH_2Ph); 2.39 (s, *Me*–Cp). The bromide salt of this compound has been synthesized previously.[45] The second expected product, benzyl alcohol, was not separated from the excess benzyl ether.

Attempted Reactions 1 with Anisole and with *n*-Butyl Ether. Complex 1 (0.02 mmol) and the ether (0.03–0.04 mmol) were dissolved in CD_2Cl_2 in an NMR tube, and the tube was sealed under H_2 as described above. No reactions were detected by NMR after the tube was heated for 5 days at 50 °C.

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Registry No. 1, 121919-57-1; $2\cdot CF_3SO_3$, 121919-59-3; $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}S(CH_2)_3OH)]SO_3CF_3$, 121919-61-7; $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}S(CH_2)_4OH)]SO_3CF_3$, 121919-63-9; $(MeCpMo(\mu\text{-}S))_2S_2CH_2$, 86163-45-3; $(MeCpMo)_2(\mu\text{-}S_2CH_2)_2$, 121919-64-0; $Cl(CH_2)_3OH$, 627-30-5; $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC(CH_3)_3)]SO_3CF_3$, 121919-66-2; $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_2CH(CH_3)_2]SO_3CF_3$, 121919-68-4; $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_2C_6H_5)]SO_3CF_3$, 121919-70-8; propylene oxide, 75-56-9; trimethylene oxide, 503-30-0; tetrahydrofuran, 109-99-9; 2,5-dimethyltetrahydrofuran, 1003-38-9; tetrahydropyran, 142-68-7; 1,3-dioxane, 505-22-6; 1,4-dioxane, 123-91-1; 1-chloro-2-propanol, 127-00-4; *tert*-butyl ethyl ether, 637-92-3; benzyl ether, 103-50-4; anisole, 100-66-3; *n*-butyl ether, 142-96-1; acetone, 67-64-1.