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Dinuclear Cyclopentadienylmolybdenum Complexes Containing Thioether Ligands. Ligand Substitution and Desulfurization Reactions

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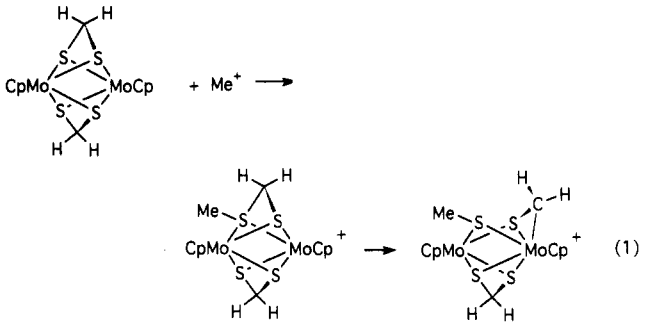
The cationic thioether complex $(CpMo)_2(S_2CH_2)(\mu\text{-}SMe)(\mu\text{-}SMe_2)]X$, 1, (X = OTf, BF_4) has been synthesized by the reaction of $(CpMo)_2(S_2CH_2)(\mu\text{-}SMe)_2$ with a methylating agent. Complex 1 undergoes dissociation of dimethyl sulfide when heated in acetonitrile solution at 50–60 °C. The thioether dissociation is partially reversed when the solution is cooled to room temperature. Reaction of 1 with ethyl methyl sulfide or with tetrahydrothiophene resulted in a thioether substitution into the dimer. The new ethyl methyl sulfide and tetrahydrothiophene complexes, synthesized by this route, have been isolated and characterized spectroscopically. The thermal reactions of 1 with the cyclic sulfides ethylene sulfide, trimethylene sulfide, and 2,5-dihydrothiophene resulted in the desulfurization of each heterocycle to form the known complex $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SMe)]^+$, 2, and ethylene, cyclopropane, or 1,3-butadiene, respectively. Free dimethyl sulfide is also produced in each reaction. The reactions are compared to those of single crystal Mo(110) surfaces with the same sulfur heterocycles.

Introduction

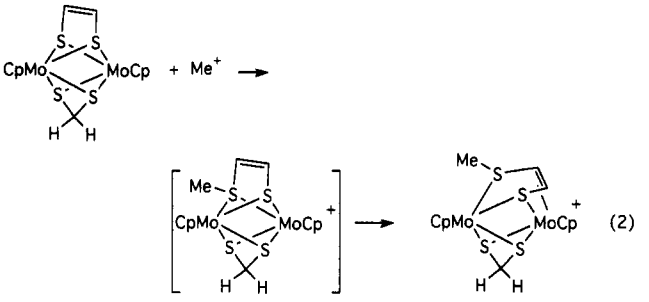
We have recently attempted to synthesize dinuclear cyclopentadienylmolybdenum complexes with bridging thioether ligands by the alkylation of a sulfur atom in a 1,2- or 1,1-dithiolate ligand.[1,2] The studies revealed that the resulting thioethers were not very stable as μ_2-η^2 ligands. For example, the thioether complex formed in eq 1 rearranged at room temperature by breaking a strained



(1)

carbon–sulfur bond of the thioether and forming a new molybdenum–carbon bond.[1] In the alkylation of a 1,2-dithiolate complex, we have observed cleavage of a molybdenum–sulfur bond of a thioether ligand in order to accommodate molybdenum–carbon bond formation, eq 2.[2]

More recently we have begun to explore the reactivity of thioethers in these types of dinuclear structures which are not chelated to a second sulfur atom. For example, we wished to determine whether the above tendency for metal–carbon bond formation was maintained in these systems by alkyl migration from sulfur to molybdenum. Other reaction possibilities for the bridging thioether



(2)

ligands which we hoped to explore were their potential for ligand substitution reactions, their susceptibility to external nucleophilic attack, and their ability to promote intramolecular hydrocarbon eliminations. We have found that the bridging thioether ligands in these systems are thermally labile, and in this paper we focus on ligand substitution reactions, particularly with saturated cyclic thioethers.

Recent studies of the reactions of a crystalline Mo(110) surface with sulfur heterocycles under ultrahigh vacuum have been reported by Friend and co-workers.[3] Several reaction pathways have been identified, and these depend, to some extent, on the nature of the substrate. For example, for tetrahydrothiophene, ring opening to form a surface thiolate intermediate was observed as a major pathway to the formation of butenes and butane. A similar ring opening on the molybdenum surface was observed for the thietane, trimethylene sulfide, but a second reaction mode was the intramolecular elimination of cyclopropane. In the reaction of the thiirane, ethylene sulfide, the intramolecular elimination of ethene was the dominant reaction pathway and the formation of ring-opened ethanethiolate species was not observed. The reaction of the molybdenum surface with 2,5-dihydrothiophene also resulted in hydrocarbon (butadiene) elimination.[4] The

* Abstract published in *Advance ACS Abstracts*, August 15, 1993.

(1) Bernatis, P.; Haltiwanger, R. C.; Rakowski DuBois, M. *Organometallics* **1992**, *11*, 2435.

(2) Birnbaum, J.; Haltiwanger, R. C.; Bernatis, P.; Teachout, C.; Parker, K.; Rakowski Dubois, M. *Organometallics* **1991**, *10*, 1779.

(3) (a) Wiegand, B. C.; Friend, C. M. *Chem. Rev.* **1992**, *92*, 491. (b) Friend, C. M.; Roberts, J. T. *Acc. Chem. Res.* **1988**, *21*, 394.

(4) Lui, A. C.; Friend, C. M. *J. Am. Chem. Soc.* **1991**, *113*, 820.

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reactions of several discrete transition metal complexes with the same thioethers have been reported,[5-7] and interesting ring opening reactions have been characterized in some systems. The dinuclear molybdenum complexes offered a good opportunity to systematically study the reactions with these thioethers as a function of ring size, and the systems provide relevant comparisons for the reactions observed on the crystalline molybdenum surface.[8]

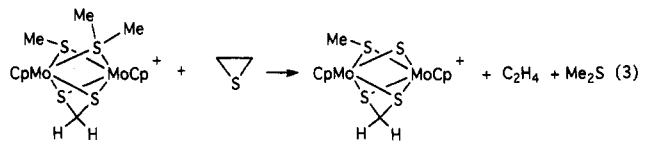
Results

Synthesis and Reactions of $[(CpMo)_2(S_2CH_2)(\mu\text{-}SMe)(\mu\text{-}SMe_2)]X, X = BF_4$ (1a), X = OTf (1b). A useful starting material in this project was the cationic dimethyl sulfide complex indicated in the heading. Complex 1 was readily synthesized by the reaction of the known compound $(CpMo)_2(S_2CH_2)(\mu\text{-}SMe)_2$[9] with trimethyloxonium tetrafluoroborate or with methyl triflate. The methylcyclopentadienyl analogue, 1b′, has also been prepared by a similar route. The products were isolated and characterized by spectroscopic techniques. The NMR spectrum for 1a or 1b showed evidence for only one isomer; the equivalency of the Cp ligands in the product suggested that a sulfur atom was the site of alkylation. The data are consistent with either alkylation of a methanethiolate or methanedithiolate sulfur. Previous studies have shown that alkylation of the dithiolate ligand leads to a structural rearrangement (see eq 1).[1] Evidence for such a rearrangement was not observed for 1, and the alkylation site was assigned to the methanethiolate sulfur. This assignment was supported by the reaction chemistry of 1. When the thermal decomposition of 1a in CD_3CN was monitored by NMR spectroscopy, the dissociation of free dimethyl sulfide was observed at a temperature of 50–60 °C. New NMR resonances near 5.6 ppm were assigned to the Cp ligands of a new dinuclear cyclopentadienyl complex. When the solution was cooled to room temperature, some of the starting complex, 1a, was reformed. However the reverse reaction was not quantitative, and after repeated thermal cycles, decomposition of the coordinatively unsaturated complex appeared to take place. Attempts to obtain a ^{13}C NMR spectrum of a proposed coordinatively unsaturated complex in a sealed NMR tube resulted in the decomposition of the material during data collection.

The thermal lability of dimethyl sulfide in 1 permitted us to carry out bridging ligand substitution reactions in the dinuclear complex. The reaction of 1 with ethyl methyl sulfide at 50–60 °C proceeded under a nitrogen purge to form the ethyl methyl sulfide complex $[(CpMo)_2(S_2CH_2)(\mu\text{-}SMe)(\mu\text{-}SMe(Et))]^+$. The product was isolated in pure form by column chromatography and characterized spectroscopically. Two isomers were observed in the NMR spectrum in a 1:1 ratio; these are attributed to complexes with different orientations of the ethyl methyl sulfide ligand (i.e. ethyl group in axial or equatorial position).

The thioether ligand of 1 was shown to be susceptible to nucleophilic attack. When the reaction of 1a with CN^- in DMSO-d_6 at 50 °C was monitored by NMR spectroscopy, the formation of acetonitrile and the known bis(methanethiolate) complex, $(CpMo)_2(S_2CH_2)(\mu\text{-}SMe)_2$, was observed. Further studies were not carried out to determine if dimethyl sulfide dissociation played a role in this reaction.

Reactions of 1 with Cyclic Thioethers. (a) Intramolecular Hydrocarbon Elimination. Complex 1a, 1b, or 1b′ was reacted with an excess (8–20 equiv) of ethylene sulfide in CD_3CN at 50–60 °C in a sealed NMR tube. A reaction was observed over a period of several days, resulting in the formation of $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SMe)]^+$, 2a, 2b, or 2b′. Other molybdenum products were not observed in the NMR spectra of the reaction solutions, but comparisons of integration values with that of an internal standard indicated that yields of 2 ranged from ca. 70 to 80%. No solids were observed in the solutions, and the fate of the remaining molybdenum was not established. Ethylene and free dimethyl sulfide were also formed in this reaction, eq 3, and identified in the NMR spectrum. The identity of the products was also confirmed by ^{13}C NMR spectroscopy.



An intermediate molybdenum complex containing a coordinated ethylene sulfide ligand was not detected under these experimental conditions, but such a complex is proposed as a likely intermediate. A thermal reaction of ethylene sulfide in the absence of molybdenum complex was compared to its reaction with 1b′ under identical conditions. No evidence for thermal decomposition or oligomerization of ethylene sulfide was observed in the NMR spectrum of the control solution.

The reaction of $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}SMe)(\mu\text{-}SMe_2)]$-OTf, 1b′, with 1 equiv of *cis*-stilbene sulfide was also carried out at 50 °C in CD_3CN for several days in a sealed NMR tube. In this case 2b′, dimethyl sulfide, and *cis*-stilbene were the only products observed in the NMR spectrum.

The reactions of 1b and 1b′ with trimethylene sulfide (1–5 equiv) were carried out under similar conditions. The dissociation of dimethyl sulfide from 1 was observed, but the formation of a dimer incorporating trimethylene sulfide as a bridging ligand was not detected. Instead, the reaction proceeded to form 2 and cyclopropane. The latter product was identified by ^1H and ^{13}C NMR spectroscopy. No

(5) Examples of reactions of metal complexes with thiiranes: (a) Amarasekera, J.; Rauchfuss, R. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1988**, *110*, 2332. (b) Adams, R. D.; Chen, G.; Sun, S.; Wolfe, T. A. *J. Am. Chem. Soc.* **1990**, *112*, 868. (c) Vergamini, P. J.; Kubas, G. *J. Prog. Inorg. Chem.* **1977**, *22*, 261. (d) Rakowski Dubois, M.; Haltiwanger, R. C.; Miller, D. J.; Glatzmaier, G. *J. Am. Chem. Soc.* **1979**, *101*, 5245. (e) Morrow, J. R.; Tonker, T. L.; Templeton, J. L. *Organometallics* **1985**, *4*, 745. (f) Schunn, R. A.; Fritchie, C. J.; Prewitt, C. T. *Inorg. Chem.* **1966**, *5*, 892. (g) King, R. B.; *Inorg. Chem.* **1963**, *2*, 326. (h) Adams, R. D.; Babin, J. E.; Tasi, M. *Inorg. Chem.* **1986**, *25*, 4514. (i) Lorenz, I.; Messelauser, J.; Hiller, W.; Conrad, M. *J. Organomet. Chem.* **1986**, *316*, 121. (j) Park, J. W.; Henling, L. M.; Schaefer, W. P.; Grubbs, R. H. *Organometallics* **1990**, *9*, 1650.

(6) Examples of reactions of metal complexes with thietanes: (a) Adams, R. D.; Pompeo, M. P. *Organometallics* **1990**, *9*, 1718, 2651; **1992**, *11*, 1460, 2281; *J. Am. Chem. Soc.* **1991**, *113*, 1619. (b) Adams, R. D.; Belinski, J. A.; Pompeo, M. P. *Organometallics* **1991**, *10*, 2016, 2539; **1992**, *11*, 2016. (c) Adams, R. D.; Belinski, J. A.; Yamamoto, J. H. *Organometallics* **1992**, *11*, 3422. (d) Adams, R. D.; Cortopassi, J. E.; Falloon, S. B. *Organometallics* **1992**, *11*, 3794. Adams, R. D.; Belinski, J. A.; Schierlman, J. *J. Am. Chem. Soc.* **1991**, *113*, 9004. (e) Yamamoto, J. H.; Yap, G. P. A.; Jensen, C. M. *J. Am. Chem. Soc.* **1991**, *113*, 5060.

(7) Examples of reactions of metal complexes with tetrahydrothiophenes: (a) Boorman, P. M.; Gao, X.; Freeman, G. K. W.; Fait, J. F. *J. Chem. Soc., Dalton Trans.* **1991**, *115*. (b) Boorman, P. M.; Gao, X.; Fait, J. F.; Parvez, M. *Inorg. Chem.* **1991**, *30*, 3886. (c) Moynihan, K. J.; Gao, X.; Boorman, P. M.; Fait, J. F.; Freeman, G. K. W.; Thorton, P.; Ironmonger, D. J. *Inorg. Chem.* **1990**, *29*, 1648. (d) Templeton, J. L.; Dorman, W. C.; Clardy, J. C.; McCarley, R. E. *Inorg. Chem.* **1978**, *17*, 1263. (e) Cotton, F. A.; Najjar, R. C. *Inorg. Chem.* **1981**, *20*, 2716.

(8) As the reactions proceed on the molybdenum surface, sulfur and hydrogen adsorbates on the surface increase; this has been found to influence the rates of some desulfurization reactions.[3,4]

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

cyclopropane was detected in a thermal reaction of trimethylene sulfide in the absence of molybdenum complex.

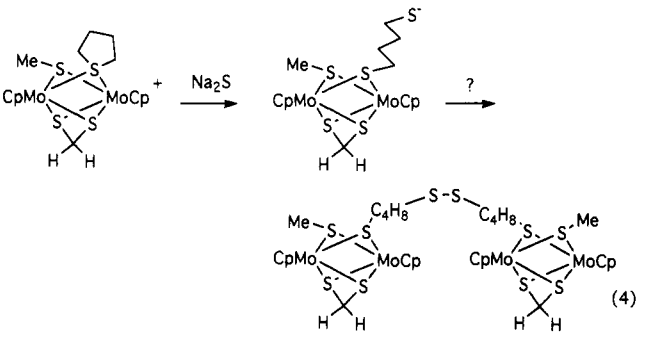
The reactions of **1b** and **1b′** with trimethylene sulfide each produced an additional molybdenum product(s) that was evidenced by additional Cp resonances in the NMR spectrum (see Experimental Section). This unidentified product did not appear to incorporate trimethylene sulfide, and its ratio to other products did not vary with time.

Complex **1b′** also reacted with 2,5-dihydrothiophene in acetonitrile solution at 50 °C. In this case 1,3-butadiene was produced and identified by comparison of its NMR spectrum with that of a standard sample. Complex **2b′** was the only molybdenum product observed; an intermediate dihydrothiophene complex was not detected. A small excess of dihydrothiophene was still present in the solution after the reaction was complete, and no evidence for its thermal decomposition was observed.

(b) Formation of a New Thioether Complex. The reaction of **1a** or **1b** with tetrahydrothiophene proceeded at a temperature of 50–60 °C to form a new complex with a bridging tetrahydrothiophene ligand, $[(CpMo)_2(S_2CH_2)(\mu\text{-SMe})(\mu\text{-}SC_4H_8)]^+$, **3**. The complex was isolated by column chromatography on alumina; a minor yellow band and major orange band were separated. Evaporation of solvent from each component produced apparent isomers of the product complex. NMR data for the two isomers are similar and are given in the Experimental Section. The isomers are assigned structures in which the orientation of the methanethiolate ligand is axial or equatorial. The major isomer was characterized by ^1H and ^{13}C NMR and by mass spectroscopy. An exact mass determination of the parent ion was consistent with the proposed formulation.

The thermal decomposition of **3** was studied in acetonitrile at 50–60 °C. In the presence of a small excess of tetrahydrothiophene, **3** was stable for extended periods. No intramolecular hydrocarbon (cyclobutane) elimination from the coordinated tetrahydrothiophene ligand was observed, and no evidence was observed for a ring opening reaction. When **3** was heated in the absence of free THT, dissociation of the bridging tetrahydrothiophene ligand was observed in the NMR spectrum. This dissociation was not observed at room temperature. The dissociation reaction did not appear to be significantly reversible, but the coordinatively unsaturated dimer could be trapped with an alternate thioether. For example, the thermal reaction of **3** in the presence of ethylene sulfide led to the formation of **2**, ethylene, and free tetrahydrothiophene.

The reaction of **3** with a slurry of excess sodium sulfide was carried out in acetonitrile solution in air at room temperature. Nucleophilic attack of sulfide on the C–S bond of the coordinated THT ligand led to a ring opening reaction. NMR data were consistent with the formation of a dimer with a η^1-μ-butanedithiolate ligand, $(CpMo)_2(S_2CH_2)(\mu\text{-SMe})(\mu\text{-}S(CH_2)_4S)]^-$. However, the mass spectrum of the product showed a parent ion at m/e 1134, suggesting a tetranuclear formulation. Since the reaction was carried out under aerobic conditions, it is possible that two dinuclear structures were linked through oxidation of the terminal thiolate and formation of a S–S bond, eq 4. Alternatively, such coupling may occur only under the conditions of the mass spectral experiment. Further characterization will be necessary to establish the structure of this product.



Discussion

Characteristics of Thioether Complexes. In the preceding section we have described the syntheses and spectroscopic characterization of new dinuclear molybdenum complexes with bridging thioether ligands. The complexes containing dimethyl sulfide and ethyl methyl sulfide ligands were readily isolated. The complexes did not display the tendency to undergo alkyl migration from sulfur to molybdenum that was observed in studies of dithiolate–thioether derivatives, e.g., eq 1. However, an unusual feature of these complexes is the thermal lability of the μ_2-thioether ligand. Although facile dissociation of thioether ligands in mononuclear complexes has been established,[10,11] we are unaware of previously reported examples of the reversible dissociation of such ligands from μ_2 coordination sites. Other early transition metal complexes with bridging thioether ligands have been established to have quite short M–S distances,[6a,7b–e] suggesting kinetically stable metal sulfur bonds.

The coordinatively unsaturated dinuclear molybdenum complex which results from the loss of dimethyl sulfide from **1** has not been characterized in detail because it appears to undergo facile decomposition. However, the partial reversibility, observed by NMR spectroscopy, suggested that the initial ligand dissociation occurred without disruption of other bonds in the dimer. This was confirmed by our characterization of clean thioether substitution reactions. For example the thermal reaction of **1** in the presence of less volatile ethyl methyl sulfide led to the isolation of the ethyl methyl sulfide complex.

Reactions with Cyclic Thioethers. The primary focus of this work was the study of the thermal reactivity of **1** with a series of cyclic thioethers. The reactions showed many similarities to those of a Mo(110) single crystal surface with this series of substrates. For example, the reaction of **1** with the strained rings of a thiirane or thietane led to an intramolecular hydrocarbon elimination to form a sulfide bridged dimer, **2**, and ethylene or cyclopropane, respectively. A related hydrocarbon elimination of butadiene was also observed in the reaction of **1** with 2,5-dihydrothiophene. These hydrocarbon elimination products were also identified in reactions of the heterocycles with the molybdenum single crystal surface.[3,4]

It is instructive to compare these reactions of sulfur heterocycles to reactions with other discrete metal complexes. The reactions of episulfides with a variety of metal complexes have often been found to lead to rapid olefin elimination,[5b–j] and this reagent has been used frequently in the syntheses of metal sulfide complexes. Only one

(10) Eckhof, J. H.; Hogeneen, H.; Kellog, R. M.; Klei, E. *J. Organomet. Chem.* **1978**, *161*, 183.
(11) Sauer, N. N.; Markel, E. J.; Schroder, G. L.; Angelici, R. J. *J. Catal.* **1989**, *117*, 295.

example of a well characterized episulfide complex has been reported.[5a]

Metal complexes containing intact thietane and 2,5-dihydrothiophene ligands are somewhat more numerous.[6,10,11] There is one previous example of the partial elimination of butadiene from a coordinated dihydrothiophene ligand in an iron carbonyl complex. However dissociation of the intact heterocyclic ligand from the metal was the primary thermal reaction observed in this system.[11] Quite extensive studies of the reactions of metal clusters with thietanes have been reported.[6] Metallocycle formation resulting from metal insertion into the coordinated thietane has been shown to precede thermally and photochemically promoted ring opening reactions. Nucleophilic attack on a bridging thietane ligand has also resulted in ring opening reactions (vide infra). However cyclopropane elimination has not been reported for the previously studied thietane complexes. The molybdenum complexes studied here and the molybdenum single crystal (110) surface appear to be unique among the reported systems in promoting the facile elimination of cyclopropane from thietanes.

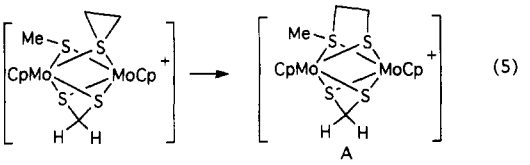
The substitution of dimethylsulfide in 1 by tetrahydrothiophene led to a stable complex. Hydrocarbon elimination from this heterocycle was not expected in either the surface or solution reactions because of the lack of ring strain in the molecule. The tetrahydrothiophene complex showed thermal lability similar to the other isolated thioether complexes, and further ligand substitution reactions could be carried out with this derivative. The dissociative behavior of tetrahydrothiophene in 3 provides a low temperature solution analogue to the observed desorption of this molecule from the molybdenum (110) surface.

The major reaction pathway for tetrahydrothiophene on the molybdenum single crystal was the ring opening reaction with surface hydrogen to produce an adsorbed linear thiolate species.[3] The soluble tetrahydrothiophene complex 3 did not react with molecular hydrogen to form a thiolate bridged derivative. Nor did the addition of the hydrogen activating complex $(CpMo\mu\text{-}S)_2S_2CH_2$[9] promote the reaction of 3 with hydrogen. However, the cyclic ligand in 3 was opened in a room temperature reaction with the nucleophile sulfide ion. This reactivity is similar to that characterized previously for a bridging tetrahydrothiophene ligand in a tungsten(III) dimer.[7b]

Mechanistic Aspects of Hydrocarbon Elimination. Since the sulfur heterocycles do not decompose under identical thermal conditions in the absence of molybdenum complex, initial coordination of the sulfur atom of the heterocycle to one or both molybdenum ions is proposed to precede a hydrocarbon elimination from this undetected adduct. In previous studies of interactions of episulfides with metal complexes, several possible ring opening pathways have been suggested. For example, in the reaction of a titanocene methylidene complex with episulfides, metal–sulfur coordination followed by a stepwise opening of the episulfide ring to give a diradical intermediate was proposed.[5j] The reaction of styrene-d_1 sulfide with the titanocene complex produced ca. a 1:1 ratio of *cis*- and *trans*-styrene-d_1. In the reaction of the molybdenum complex 1 with *cis*-stilbene sulfide, only the cis isomer of stilbene was formed. Since inversion of a radical carbon center should be very facile, the stereoselectivity in this reaction suggests that a stepwise homolytic cleavage of a C–S bond does not occur in the present system.

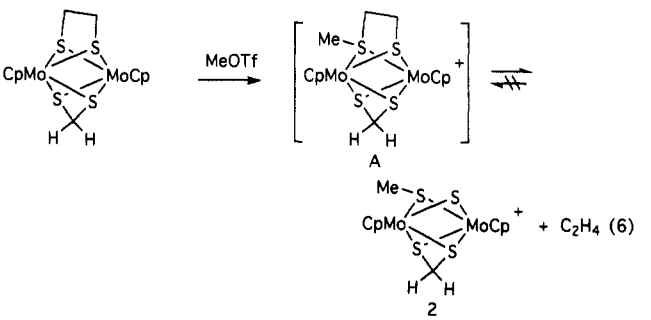
A second suggested stepwise mechanism for ring opening of a coordinated thiirane or thietane involves nucleophilic attack on the ligand. For example, Adams and co-workers have observed the formation of ethanedithiolate ligands in the reactions of ethylene sulfide with osmium carbonyl clusters, and suggested that a sulfide ligand may play a role in the thiirane ring opening process.[5b] Ring opening of thietanes in osmium and rhenium carbonyl clusters has also been achieved by nucleophilic attack.[6,a,b,d]

In the molybdenum systems studied here, the adjacent thiolate sulfur in a proposed intermediate episulfide complex could serve as a nucleophile to promote ring opening and the formation of the thiolate–thioether complex A, eq 5.[12] Structures analogous to A have been



(5)

characterized for related dinuclear molybdenum systems.[2] Complex A was not detected by NMR spectroscopy during the course of reaction 3. Independent studies have established that A undergoes very rapid ethylene elimination. For example, the reaction of the ethanedithiolate complex with methyl triflate is presumed to form A initially, but only 2 and ethylene are observed as products in the instantaneous reaction, eq 6.[2] Neither was A observed when excess ethene was added to 2 in an attempt to reverse eq 6.



Our studies suggest that structure A could serve as an intermediate in reaction 3. However the release of ethylene in this reaction could also occur by a concerted elimination from the proposed episulfide intermediate. A concerted elimination of ethylene has been considered likely for the reaction of ethylene sulfide with the molybdenum single crystal surface.[13]

Although stereochemical studies of butadiene elimination were beyond the scope of the present work, such studies may be important in developing a more complete mechanistic understanding of these reactions. It is not clear, however, that symmetry guidelines devised for ring opening reactions in organic compounds will be entirely applicable to these dimeric metallosulfur complexes which contain a number of closely spaced frontier orbitals.

Summary and Conclusions. Cationic thioether complexes of the formula $[(CpMo)_2(S_2CH_2)(\mu\text{-}SMe)(\mu\text{-}SR_2)]^+$ have been synthesized and characterized. Thermal lability of the bridging thioether ligand permits, for the first time,

(12) The geometry of A may lead to stereospecific sulfide substitution in reaction 5. Elimination of olefins from 1,2-dithiolate ligands in these systems has been found to proceed without olefin isomerization.[9]

(13) Calhorda, M. J.; Hoffman, R.; Friend, C. M. *J. Am. Chem. Soc.* **1990**, *112*, 50.

bridging ligand substitution in these dinuclear complexes. Thioether dissociation provides a homogeneous model for the formation of anion vacancies on a sulfided molybdenum surface. In keeping with this idea, the thermal thioether dissociations were carried out in the presence of cyclic thioether substrates. Facile desulfurization of thiiranes, thietanes, and 2,5-dihydrothiophene was found to occur, producing olefins, cyclopropane, or butadiene, respectively, and the sulfide bridged dimer $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SMe)]^+$. In contrast, the thioether ligand exchange with tetrahydrothiophene produced a stable THT complex. Work is currently in progress to determine whether ligand lability can be promoted by variation of steric or electronic properties of the thioether substituents. We have also begun to investigate the substitution reactions of the thioether complexes with other potential ligands, including thiophenes, nitrogen and oxygen heterocycles, carbon monoxide, and alkynes.

Experimental Section

Materials. $(CpMo)_2(S_2CH_2)(\mu\text{-}SMe)_2$ and $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SMe)_2$ were synthesized by the published procedure.[9] Trimethyloxonium tetrafluoroborate, methyl triflate, and most of the thioethers were purchased and used without purification. *cis*-Stilbene sulfide[14] and 2,5-dihydrothiophene[15] were synthesized according to published procedures. Dichloromethane and acetonitrile were distilled from CaH_2 immediately before use.

Synthesis of $[(CpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}S(CH_3)_2)]BF_4$, 1a. $(CpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)_2$ (0.050 g, 0.11 mmol) and $(CH_3)_3OBF_4$ (0.016 g, 0.11 mmol) were combined in 10 mL of dichloromethane and stirred at room temperature. Over 2 days the reaction mixture remained red-brown and a white precipitate disappeared. Solvent was removed at reduced pressure and the residue recrystallized from CH_2Cl_2/Et_2O giving 0.052 g (87% yield) of orange-brown crystals of the title complex. ^1H NMR (CD_3CN), δ (ppm): 6.05 (s, Cp), 5.59 (s, S_2CH_2), 2.31, 2.21, 1.49 (3s, $S(CH_3)$ and $S(CH_3)_2$). FAB-MS: *m/e* 509 (P^+), 494 ($P^+ - CH_3$), 479 ($P^+ - 2CH_3$), 447 ($P^+ - S(CH_3)_2$), 432 ($P^+ - CH_3 - S(CH_3)_2$), 418, 400. Anal. Calcd for $C_{14}H_{21}Mo_2S_4BF_4$: C, 28.18; H, 3.54; S, 21.49. Found: C, 28.22; H, 3.68; S, 21.48.

A similar procedure with methyl triflate produced the triflate salts **1b** and **1b′**. For **1b**: ^1H NMR ($CDCl_3$) [δ (ppm)] 6.05 (s, 10, Cp), 5.58 (s, 2, S_2CH_2), 2.31 (s, 3, SCH_3), 2.21 (s, 3, SCH_3), 1.48 (s, 3, SCH_3); ^{13}C NMR (CD_3CN) [δ (ppm)] 95.2 (Cp), 75.3 (CH_2), 36.7 (SCH_3), 23.5 (SCH_3), 20.8 (SCH_3), 19.6 (SCH_3).

Characterization data for $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}SMe)(\mu\text{-}SMe_2)]OTf$, **1b′**: ^1H NMR (CD_3CN, 20 °C) [δ (ppm)] 6.05 (m, 2, Cp), 5.93 (m, 2, Cp), 5.84 (m, 2, Cp), 5.75 (m, 2, Cp), 5.56 (s, 2, S_2CH_2), 2.29 (s, 3, SMe), 2.18 (s, 9, MeCp + SMe), 1.48 (s, 3, Me), FAB$^+$-MS: *m/e* 537 (P^+), 523 ($P^+ - CH_2$), 508 ($P^+ - CH_2 - CH_3$), 460 ($P^+ - S(CH_3)_2 - CH_3$), 446 ($P^+ - S(CH_3)_2 - CH_3 - CH_2$).

Thermal Decomposition of $[(CpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}S(CH_3)_2)]^+$, 1. In an NMR tube was combined complex **1a** (0.010 g, 0.17 mmol) and thiophene (14 μL, 0.17 mmol) in 0.7 mL of CD_3CN. The brown solution was sealed under vacuum at −196 °C and warmed to 65 °C. Resonances slowly grew into the NMR spectrum over 2 days for an unidentified organometallic product(s) at 5.61, 5.60 (2s), 5.53, 5.37 (2s), 1.97, 1.63 (2s). A singlet at 2.06 ppm, assigned to $(CH_3)_2S$, was observed, and weak resonances assigned to $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SMe)]BF_4$, **2** were present. No change in the thiophene resonances was observed. When the solution was cooled to room temperature for 24 h, resonances for the unidentified compound nearly disappeared and the concentration of complex **1a** increased. The resonance for dimethyl sulfide at the early stages of the reaction also decreased when the solution was cooled. After the reaction was heated for several days, numerous weak resonances were observed in the Cp region of the NMR spectrum, and the resonance for dimethyl sulfide did not decrease appreciably on cooling. Similar irreversible decomposition was observed for **1b** after several days of heating in acetonitrile. Small amounts of $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SMe)]^+$ (10-30%) and of $[CpMo(\mu\text{-}S)]_4$ were identified by NMR and mass spectroscopy, respectively, but most of the molybdenum decomposition products were not identified.

When **1b′** was heated in CD_3CN in a sealed NMR tube for 8 days, resonances for the starting material were still present, but several new resonances in the region 5.2–5.6 ppm and a singlet at 2.06 ppm (Me_2S) were observed in the spectrum. Resonances for **2b′** were not present in the spectrum.

An attempt was made to isolate a complex formed by dimethyl sulfide dissociation. $[(CpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}S(CH_3)_2)]BF_4$, **1a**, (0.047 g, 7.9×10^{-5} mol), was placed in a 50-mL round bottom flask, distilled CH_3CN was injected into the flask, and the system was flushed with N_2 for several minutes. The flask was attached to an external bubbler and a reflux condenser and was placed in a 60–65 °C oil bath. The reaction was stirred under a positive N_2 flow for 7 days. During the course of the reaction no color change was observed. The solvent was removed under vacuum and the orange-brown oil dried for several hours under dynamic vacuum. A sample of the crude material was dissolved in $CDCl_3$ under N_2 and analyzed by ^1H NMR spectroscopy. ^1H NMR ($CDCl_3$), δ (ppm): 6.21 (s, 9, Cp?), 6.15 (s, 5, Cp?), 6.00 (b, 8, Cp?), 1.20 (s, 6, SCH_3). A sample of this material was prepared for ^{13}C NMR analysis by dissolving the molybdenum complex under N_2 in $CDCl_3$ in a NMR tube. The solution was degassed in three freeze–pump–thaw cycles, and the tube was sealed under N_2 at −196 °C. Over the course of a 2-h accumulation period, a pink insoluble material formed, suggesting decomposition. Further attempts gave the same decomposition after 2 h.

Reaction of $[(CpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}S(CH_3)_2)]BF_4$, 1a, with Sodium Cyanide. Complex **1a** (0.010 g, 0.017 mmol) and NaCN (0.002 g, 0.04 mmol) were combined in ~0.8 mL $(CD_3)_2SO$ in an NMR tube. The solution was degassed in three freeze–pump–thaw cycles and sealed under vacuum at −196 °C. The brown solution containing a white precipitate was warmed to 50 °C, and over 2 h the precipitate largely disappeared. The proton NMR spectrum of the reaction mixture gave resonances consistent with a 1:1 ratio of $(CpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)_2$[9] and acetonitrile (s, 2.07 ppm). A singlet at 2.03 ppm (<10% of Cp resonance) may be due to free Me_2S. The reaction mixture was combined with 2 mL of CH_2Cl_2 and purified by chromatography on an alumina column. Elution with dichloromethane gave a brown band that, after removal of solvent at reduced pressure, gave brown crystals of $(CpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)_2$. ^1H NMR, δ (ppm): isomer A 5.65 (s, Cp), 5.46 (s, S_2CH_2), 1.36 (s, SCH_3); isomer B 5.66 (s, Cp), 5.56 (s, S_2CH_2), 1.49, 1.34 (2s, $2SCH_3$).

Reaction of $[(CpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}S(CH_3)_2)]CF_3SO_3$, 1b, with Ethyl Methyl Sulfide. Complex **1b** (0.045 g, 6.8×10^{-5} mol) was dissolved in ca. 10 mL of distilled CH_3CN in a Schlenk tube. $CH_3CH_2SCH_3$ (2 mL, 2×10^{-2} mol) was added, the reaction mixture was degassed, and the tube was sealed under vacuum. The Schlenk tube was stirred in a 50–60 °C oil bath for 10 days, and the orange solution became orange-brown after a few days. The solvent was removed under a dynamic vacuum, and the reaction mixture was eluted in air on acidic alumina beginning with 60/40 hexanes/CH_2Cl_2 as eluent. The eluent was gradually increased to 95% CH_2Cl_2/5% EtOH. The second orange fraction was collected and dried to give a 1:1 mixture of two isomers of $[(CpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SCH_3(CH_2CH_3))]CF_3SO_3$. Yield: 0.019 g, 41%. ^1H NMR (CD_3CN), δ (ppm): 6.08 (s, 20, Cp), 5.54 (s, 2, S_2CH_2), 5.51 (s, 2, S_2CH_2), 3.21 (q, 2, CH_2CH_3), 2.89 (q, 2, CH_2CH_3), 2.67 (s, 3, $S(CH_3)CH_2CH_3$), 2.60 (s, 3, $S(CH_3)CH_2CH_3$), 1.45 (s, 6, SCH_3), 1.11 (2 overlapping t, 6, CH_2CH_3). ^{13}C NMR (CD_3CN), δ (ppm): isomer a 95.0 (Cp), 75.3 (S_2CH_2), 47.8 (CH_2CH_3), 19.8 ($S(CH_2CH_3)CH_3$), 19.6 (SCH_3), 13.4 ($S(CH_2CH_3)CH_3$); isomer b 95.0 (Cp), 74.7 (S_2CH_2), 34.2 (CH_2CH_3), 32.8 ($S(CH_2CH_3)CH_3$), 19.4 (SCH_3), 13.2 ($(S(CH_2CH_3)CH_3$). FAB-MS: *m/e* 523 (P), 508 ($P - CH_3$), 494 ($P - CH_2CH_3$),

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479 (P – CH_3, CH_2CH_3), 464 (P – CH_3, CH_2CH_3 CH_3). Exact mass calcd for $Mo_2S_4C_{15}H_{23}$ (based on ^{98}Mo): 526.8791. Found: 526.8794.

Reaction of $[(CpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}S(CH_3)_2]^+$, 1, with Ethylene Sulfide. In a typical procedure, **1a** (0.007 g, 1 × 10^{-5} mol) was weighed in air and placed in an NMR tube. Ethylene sulfide (10 μL, 2 × 10^{-4} mol) was combined with ca. 1 mL of CD_3CN, and the solution was added to the NMR tube. The reaction mixture was degassed in freeze–pump–thaw cycles, and the tube was flame sealed under vacuum at –196 °C. The reaction was monitored by ^1H NMR spectroscopy. The initial NMR spectrum indicated the presence of only the starting materials. The reaction mixture was heated in an oil bath for the first 2 days at 70–80 °C and for the remaining 4 days at 50–60 °C. After 4 days the starting material was gone and $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_3)]BF_4$, **2a**, (72%), ethylene (63%), and free dimethyl sulfide (ca. 100%) were the products observed in the NMR spectrum. The ^{13}C NMR spectrum confirmed the product assignments. ^1H NMR for **2a** (CD_3CN), δ (ppm): 6.94 (s, 10, Cp), 4.08 (s, 2, S_2CH_2), 1.67 (s, 3, CH_3) (very weak resonances at 6.8 and a multiplet at 2.7 ppm were unassigned). ^{13}C NMR (CD_3CN), δ (ppm): 123.80 (s, C_2H_4), 105.01 (Cp), 16.45 ($S(CH_3)_2$).

A similar reaction was observed for **1b′** (0.005 g, 0.007 mmol) after heating with ethylene sulfide (0.037 mmol) in CD_3CN at 50 °C for 5 days. Yields: **2b′**, 78%; ethylene, 28%; dimethyl sulfide, ca. 50%. No other products were observed in the spectrum. ^1H NMR for **2b′** (CD_3CN, 20 °C), δ (ppm): 6.86 (m, 4, Cp), 6.80 (m, 4, Cp), 4.08 (s, 2, S_2CH_2), 2.45 (s, 6, MeCp), 1.65 (s, 3, SCH_3). FAB$^+$-MS: *m/e* 507 (P^+), 493 ($P^+ - CH_2$), 460 ($P^+ - SCH_3$), 446 ($P^+ - CH_2 - SCH_3$).

Control Reaction with Ethylene Sulfide. Ethylene sulfide (0.0020 mL, 0.037 mmol) was added to CD_3CN in an NMR tube via syringe. The solution was cooled to –196 °C, and the tube sealed under a dynamic vacuum. The tube was heated in an oil bath at 50 °C. After 5 days ^1H NMR spectroscopy showed that the ethylene sulfide remained unchanged.

Reaction of 1b′ with *cis*-Stilbene Sulfide. Complex **1b′** (0.005 g, 0.007 mmol) and *cis*-stilbene sulfide (0.0015 g, 0.0071 mmol) dissolved in CD_3CN with an internal standard (CH_2Cl_2) were added to an NMR tube. The solution was cooled to –196 °C, and the tube was sealed under a dynamic vacuum. The tube was heated in an oil bath at 50 °C. After 7 days the solution color had changed from orange to purple. ^1H NMR spectroscopy of the reaction mixture showed formation of $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SMe)]OTf$, **2b′**, (43%), *cis*-stilbene (ca. 90%), and dimethyl sulfide (60%). No other products were observed. ^1H NMR for *cis*-stilbene (CD_3CN), δ (ppm): 7.21 (s, 10, Ph), 6.65 (s, 2, =CH). Our sample of *cis*-stilbene sulfide contained a 20% impurity of *trans*-stilbene. When the reaction was complete, the fraction of *trans*-stilbene (0.20–0.23) had not increased significantly.

A control reaction with *cis*-stilbene sulfide was carried out. *cis*-Stilbene sulfide (0.005 g, 0.02 mmol) dissolved in CD_3CN was placed in an NMR tube. The solution was cooled to –196 °C and the tube sealed under a dynamic vacuum. The tube was heated in an oil bath at 50 °C. After 7 days ^1H NMR spectroscopy showed that the *cis*-stilbene sulfide remained unchanged.

Reaction of 1b′ with Trimethylene Sulfide. $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}S(CH_3)_2)]CF_3SO_3$, **1b′** (0.007 g, 1 × 10^{-5} mol), was placed in an NMR tube and combined with trimethylene sulfide (1 μL, 1 × 10^{-5} mol) and ca. 1 mL of CD_3CN with an internal standard (CH_2Cl_2, 2 μL). The reaction mixture was degassed and flame sealed under vacuum at –196 °C. The NMR tube was placed in a 50–60 °C oil bath and monitored by ^1H NMR spectroscopy. As the reaction progressed, the solution color changed from orange to burgundy. The ^1H spectrum indicated the formation of $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_3)]CF_3SO_3$, **2b′** (19%), as well as cyclopropane (5%). New molybdenum products with somewhat broad multiplets from 5.7 to 6.1 ppm were observed. These unassigned peaks appeared to account for ca. 44% of the molybdenum. The ^{13}C NMR spectrum confirmed the presence of **2** and cyclopropane. ^1H NMR (CD_3CN) for cyclopropane, δ (ppm): 0.23 (s, C_3H_6). ^{13}C NMR (CD_3CN), δ (ppm): –2.8 (C_3H_6). Similar results were observed for reaction of **1b** with trimethylene sulfide.

A control reaction was prepared by dissolving trimethylene sulfide (4 μL, 4 × 10^{-5} mol) in 1 mL of CD_3CN in a NMR tube. The reaction mixture was degassed in three freeze–pump–thaw cycles and flame sealed under vacuum at –196 °C. The NMR tube was placed in a 50–60 °C oil bath and monitored by ^1H NMR spectroscopy. After 1 week no change was observed in the resonances of the starting material.

Reaction of 1b′ with 2,5-Dihydrothiophene. Complex **1b′** (0.005 g, 0.007 mmol) dissolved in CD_3CN was placed in an NMR tube. 2,5-Dihydrothiophene (0.001 mL, 0.01 mmol) and an internal standard, CH_2Cl_2 (2 μL), were added via syringe. The solution was cooled to –196 °C, and the tube was sealed under a dynamic vacuum. The tube was heated in an oil bath at 50 °C. After 7 days the solution color had changed from orange to purple. ^1H NMR spectroscopy of the reaction mixture showed the presence of $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SMe)]OTf$, **2b′** (53%). 1,3-Butadiene (34%), dimethyl sulfide (ca. 45%), and excess 2,5-dihydrothiophene were also observed in the spectrum. ^1H NMR for 1,3-butadiene (CD_3CN), δ (ppm): 6.40–6.35 (m, 2, =CH), 5.25 (d, 2, J = 15 Hz), 5.12 (d, 2, J = 8.3 Hz).

Reaction of $[(CpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}S(CH_3)_2)]BF_4$, 2a, with Tetrahydrothiophene). In a typical procedure, **2a** (0.03 g, 5 × 10^{-5} mol) was placed in a 50-mL round bottom flask fitted with a side arm, distilled CH_3CN (20 mL) was injected into the round bottom flask, and the system was flushed with N_2 for several minutes. Tetrahydrothiophene (3 mL, 3 × 10^{-2} mol) was added to the solution, and the round bottom flask was attached to an external bubbler and a reflux condenser and was placed in a 60–65 °C oil bath. The reaction was stirred under a positive N_2 flow for 6–7 days. During the course of the reaction the solution color changed from orange to brown-orange. The solvent was removed under vacuum and the resulting oil dried for several hours under dynamic vacuum. The crude material was eluted in air on acidic alumina beginning with a 60/40 hexanes/CH_2Cl_2 eluent. The eluent was gradually increased to 95/5 CH_2Cl_2/EtOH to give a yellow fraction. An orange fraction was eluted with a slightly greater percentage of EtOH. Both fractions gave ^1H NMR spectral data consistent with the formulation $[(CpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SCH_2CH_2CH_2CH_2)]BF_4$, **3**. Yield of the yellow fraction: ca. 10%. ^1H NMR ($CDCl_3$), δ (ppm): 6.08 (s, 10, Cp), 5.57 (s, 2, S_2CH_2), 3.05 (b, 2, $S(CH_2)_4$), 2.76 (b, 2, $S(CH_2)_4$, 2.14 (b, 4, $S(CH_2)_4$), 1.44 (s, 3, SCH_3). Yield of the orange fraction: ca. 0.012 g, 40%. ^1H NMR ($CDCl_3$), δ (ppm): 6.05 (s, 10, Cp), 5.57 (s, 2, S_2CH_2), 2.97 (m, 2, $S(CH_2)_4$), 2.67 (m, 2, $S(CH_2)_4$), 2.09 (m, 4, $S(CH_2)_4$), 1.43 (s, 3, SCH_3). ^{13}C NMR (CD_3CN), δ (ppm): 95.8 (Cp), 73.1 (S_2CH_2), 52.0 ($S(CH_2)_4$, 41.5 ($S(CH_2)_4$), 29.8 ($S(CH_2)_4$), 29.0 ($S(CH_2)_4$), 20.0 (SCH_3). FAB-MS: *m/e* 535 (P), 521 (P – CH_3), 505 (P – CH_3, CH_3), 479 (P – C_4H_4), 464 (P – C_4H_4, CH_3), 432 (P – C_4H_4, CH_3, S), 418 (P – C_4H_4, CH_3, SCH_2). Exact mass calcd for $C_{16}H_{23}Mo_2S_4$: 538.8791. Found: 538.8839.

Reaction of $[(CpMo)_2(S_2CH_2)(\mu\text{-}SMe)(\mu\text{-}SC_4H_8)]^+$, 3, with Lithium Sulfide. Complex **3a** (0.047 g, 7.6 × 10^{-5} mol) was dissolved in CH_2Cl_2 in a round bottom flask. Li_2S (>100-fold excess) was added to the flask, and the milky colored solution was stirred in air for 4 days. The solution was filtered, and the filtrate was evaporated. The orange solid obtained was dried under a dynamic vacuum for several hours. The spectral data for this product were consistent with the formation of $[(CpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(SCH_2CH_2CH_2CH_2S)]^-$ or its dimer. ^1H NMR ($CDCl_3$), δ (ppm): 5.6 (s, 10, Cp), 5.5 (s, 2, S_2CH_2), 2.6 (m, 2, $S(CH_2)_4$), 2.5 (m, 2, $(CH_2)_4$), 1.7 (b, 2, $S(CH_2)_4$), 1.4 (b, 2, $S(CH_2)_4$). ^{13}C NMR ($CDCl_3$), δ (ppm): 91.28 (Cp). FAB-MS: *m/e* 1134 (P), 687 (P – $Cp_2Mo_2S_3CH_2$), 599 (P/2 + S – Me), 567 (P/2), 552 (P/2 – Me), 479 ($Cp_2Mo_2S_4CH_2(CH_3)$). Other unidentified fragments were observed at *m/e* 905, 817, 781, and 732.

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