temperature was linear with a correlation coefficient of 0.999. From the slope $\Delta H^{\ddagger}$ was calculated to be 75 kJ/mol.

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. We thank Prof. Cortlandt Pierpont and his research group for the use of their spectrometer.

Supplementary Material Available: Tables of all bond distances and angles, positional parameters, and complete crystal data, data collection conditions, and solution and refinement details for $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC_4H_3S)]Br$ and a table of ^1H NMR data for $(CpMo)_2(S_2CH_2)(SMe)(SR)$ derivatives (10 pages). Ordering information is given on any current masthead page.

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Sites of Electrophilic Attack in Neutral Dithiolate-Bridged Molybdenum Complexes

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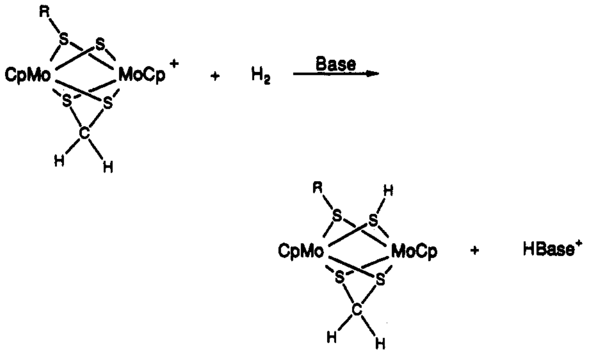
The reaction of $[CpMoS_2CH_2]_2$ (1) with 1 equiv of triflic acid at −70 °C resulted in the formation of a diamagnetic product which was formulated as $[CpMo(H)(S_2CH_2)_2MoCp]SO_3CF_3$ (2) on the basis of ^1H NMR data. When 2 was warmed above −50 °C, an intermolecular redox reaction occurred to form $[CpMoS_2CH_2]_2SO_3CF_3$ and $^1/_2$ mol of H_2. Similar chemistry was characterized for the related derivatives $[CpMoS_2CRR']_2$, where R = R′ = Me and R = Me, R′ = Ph. The reaction of 1 with methyl triflate resulted in alkylation of a sulfur ligand to form $[(CpMo)_2(S_2CH_2)(SCH_2SCH_3)]SO_3CF_3$ (6). Complex 6 was unstable in solution and rearranged to form $[CpMo(S_2CH_2)(\mu\text{-}SMe)(\mu\text{-}SCH_2)MoCp]SO_3CF_3$ (7). Complex 7 crystallized in space group *Pbca* with cell dimensions a = 14.287 (3) Å, b = 14.374 (3) Å, c = 20.045 (3) Å, V = 4116.5 (14) Å^3, and Z = 8. The crystal structure of 7 showed that the cation contained a bridging thioformaldehyde ligand which was η^1-bonded to one metal ion and η^2-bonded to the second. The protonated and alkylated products may be related to species formed in the addition of H_2 to the cations $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SR)]^+$. Chemical properties and reactivities of the cationic models of the hydrogen addition products are discussed.

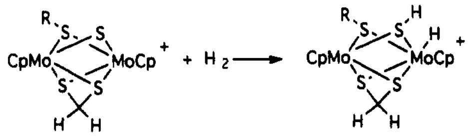
Introduction

In previous work we have reported that certain cationic thiolate-bridged molybdenum dimers reacted with hydrogen in the presence of base to form neutral products such as that shown in eq 1.[1] A kinetic study, described



(1)

in the preceding paper,[2] determined that the rate of reaction 1 was first order in molybdenum cation, first order in hydrogen, and independent of external base. Activation enthalpies determined for reaction 1 seemed most consistent with a heterolytic cleavage of hydrogen. Potential structures for the species resulting from initial hydrogen addition to the cation were discussed in the preceding paper, and some possibilities are reviewed in eqs 2–4.



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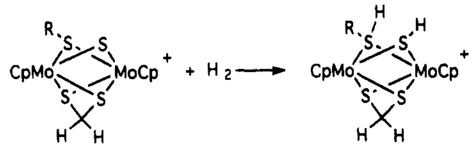

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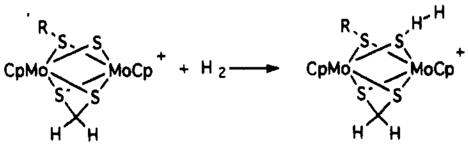
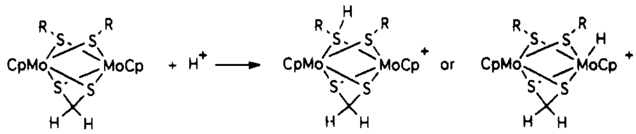


(4)

We wish to learn more about the mechanism of hydrogen activation in this system. Attempts to spectroscopically detect a hydrogen-addition product have been unsuccessful. An indirect method of assessing the relative stabilities of the products in eqs 2 and 3 may be to identify the site(s) of protonation in related neutral dimers, e.g. eq 5. For example, if the molybdenum ion served as a



(5)

Brønsted base, this might model the role of the metal ion in heterolytic hydrogen cleavage. Conversely, if the pro-

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[1] (a) Laurie, J. C. V.; Duncan, L.; Haltiwanger, R. C.; Weberg, R. T.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1986**, *108*, 6234. (b) Gabay, J. Masters Thesis, University of Colorado, Boulder, CO, 1991.

[2] Lopez, L. L.; Bernatis, P.; Birnbaum, J.; Haltiwanger, R. C.; Rakowski DuBois, M. *Organometallics*, preceding paper in this issue.

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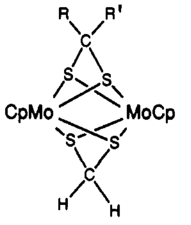
tonation could be shown to occur exclusively on a thiolate sulfur, the resulting cation would serve as a potential model for the hydrogen-addition product shown in eq 3.

In the previous paper we described the protonations of $(CpMo)_2(S_2CH_2)(\mu\text{-}SR)(\mu\text{-}SR')$ at −70 °C. These reactions generally led to a one-electron oxidation of the dimers, and no intermediates which would reveal the initial site of protonation were detected by NMR spectroscopy. In this paper we have extended our protonation studies to structurally related molybdenum(III) dimers containing 1,1-alkanedithiolate ligands of the general structure A,



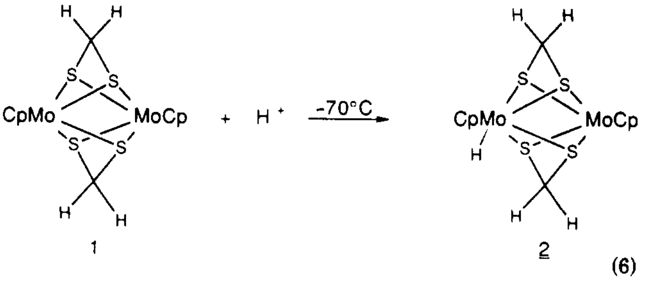
A

1: R = R' = H
R = R' = Me
R = Me , R' = Ph

which are somewhat less easily oxidized than the bis(thiolate) derivatives mentioned above. We report here characterization data for protonated derivatives of A which have been synthesized and characterized at −70 °C. Because the protonated complexes were too thermally unstable to isolate, we have also investigated the reactions of the neutral dimers with electrophilic alkylating agents. An example of an alkylated complex has been isolated and characterized by an X-ray diffraction study. The relationship between the site of electrophilic attack in these molecules and their further reactivity is explored, and the potential of the protonated complexes to serve as models for the hydrogen-addition products of eqs 2 and 3 is discussed.

Results

Reaction of Bis(methanedithiolate) Derivatives with Triflic Acid. $[CpMoS_2CH_2]_2$ (1) was reacted with 1 equiv of triflic acid in CH_2Cl_2 in an NMR tube which was maintained at −70 °C. The protonation reaction proceeded rapidly and apparently quantitatively to form a single product. The NMR spectrum of this protonated product, recorded at −70 °C (Figure 1) shows that the plane of symmetry which related the cyclopentadienyl ligands in 1 has been lost; two Cp resonances are observed in the product spectrum. The single AX pattern (pair of doublets) observed for the methanedithiolate protons indicates that the mirror plane which relates the two S_2CH_2 ligands in 1 remains intact in the protonated product or that the protonated structure is fluxional about this plane. Protonation of a lone pair of electrons on a sulfur ligand would not make the CpMo units inequivalent unless Mo–S bonds were also cleaved. In the latter case, the equivalency of the methylene groups is not likely to be maintained. The spectral data, therefore, seem most consistent with the formation of a metal–hydrogen bond, e.g., **2**, as shown in eq 6.[3] A singlet which was integrated for one proton was observed in the NMR spectrum at 2.63 ppm, and this resonance has been tentatively assigned to the hydride ligand. The chemical shift is unusually low for a metal hydride of intermediate oxidation state. However, examples of molybdenum and tungsten hydride complexes coordinated by thiolate ligands have been reported previously which showed hydride chemical shifts in the 2–4 ppm region.[4] We were unable to obtain infrared or mass spectral data on the proposed hydride because of its thermal instability (see below).



1 2 (6)

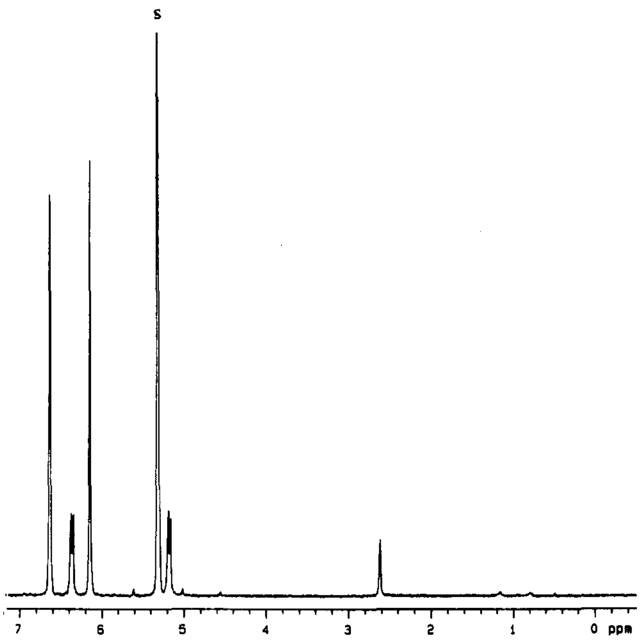


Figure 1. 300-MHz ^1H NMR spectrum of the product resulting from protonation of $[CpMoS_2CH_2]_2$ (1) wit 1 equiv of triflic acid in CD_2Cl_2 at −70 °C. See Table I for assignments.

Similar molybdenum hydride intermediates were observed when $(CpMo)_2(S_2CH_2)(S_2CMe_2)$ and $(CpMo)_2(S_2CH_2)(S_2C(Me)Ph)$ were protonated with 1 equiv of triflic acid at −70 °C. NMR data are summarized in Table I. For the latter complex, the substituents in the methanedithiolate ligand result in inequivalent MoCp sites. The spectrum of the protonated complex showed evidence for two isomers in a ratio of 6:1. Favored protonation at one of the two metal ions seems likely to be caused by electronic effects rather than steric factors.

As the solutions of the metal hydrides were warmed above −70 °C, the product resonances in the NMR spectrum shifted and broadened. A sharp singlet which appeared at 4.60 ppm in the spectrum of each reaction was assigned to molecular hydrogen, and a broad resonance at ca. 15 ppm was attributed to Cp ligands of the paramagnetic one-electron-oxidation products $[(CpMo)_2(S_2CH_2)(S_2CR_2)]^+$. Futher characterization data for this type of product are discussed below. As the solutions were warmed, a second molybdenum product was also observed in each NMR spectrum in low yield. The data for this

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[3] Alternate structures involving a metal–hydrogen bond can be proposed for 2. For example, a structure with a hydrogen bridging a molybdenum and two sulfur atoms would be consistent with the NMR data. This type of η^3-hydrogen has not been reported previously in metal sulfur complexes. A Mo–H–S interaction which is fluxional between two sulfurs of adjacent dithiolate ligands is also consistent with NMR data. A precedent for a M–H–S interaction has been reported: Darensbourg, M. Y.; Liaw, W.-F.; Riordan, C. G. *J. Am. Chem. Soc.* **1989**, *111*, 8051. A reviewer has noted that an interaction of the triflate counterion with the second molybdenum ion is possible.

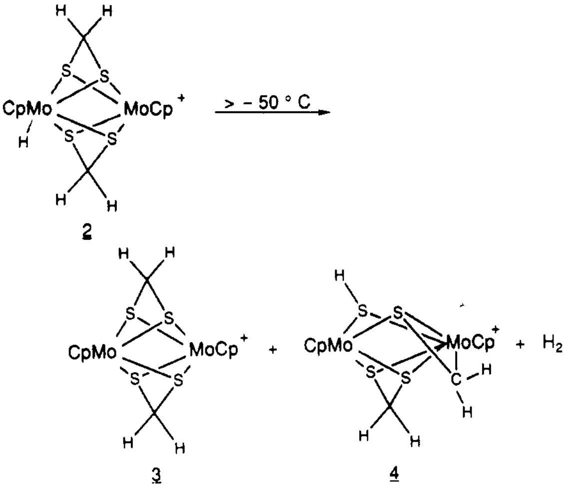
[4] (a) Burrow, T. E.; Lazarowych, N. J.; Morris, R. H. *Polyhedron* **1989**, *8*, 1701. (b) Boorman, P. M.; Moynihan, K. J.; Patel, V. D.; Richardson, J. F. *Inorg. Chem.* **1985**, *24*, 2989.

Table I. ^{1}H NMR Data[a] for the Protonated Complexes $[(CpMoH)(S_2CH_2)(S_2CRR')MoCp]SO_3CF_3$

alkyl substituent	C_5H_5	S_2CH_2 [J, Hz]	M-H	R
R = R' = H (2)	6.64, 6.15 (2 s)	6.37, 5.18 (2 d) [8.2]	2.63 (s)	
R = R' = CH_3	6.67, 6.11 (2 s)	6.57, 5.28 (2 d) [8.2]	3.04 (s)	2.00, 1.54 (2 s)
R = CH_3, R' = C_6H_5				
isomer A[b]	6.21, 5.94 (2 s)	6.46, 5.32 (2 d) [8.3]	2.64 (s)	1.57 (s) 7.46–7.02 (m)
isomer B	6.75, 5.50 (2 s)	6.54, 5.23 (2 d) [8.3]	3.5 (s)	1.91 (s) 7.46–7.02 (m)

[a] Recorded at 300 MHz at −70 °C in CD_2Cl_2. Chemical shifts are reported in ppm relative to residual solvent protons. [b] Isomers A and B were present in a 6:1 ratio, respectively.

diamagnetic product suggest the formulation $[(CpMo)(S_2CR_2)(\mu\text{-SH})(\overline{SCH_2})MoCp]^+$, e.g., 4 when R = H. Equation 7 summarizes the thermal decomposition of



(7)

the molybdenum hydride 2 and shows the proposed structure of 4. In the NMR spectrum of 4 singlets observed at 6.50 and 5.78 ppm were assigned to Cp ligands, and an AX pattern at 5.78 and 4.22 ppm corresponded to one methylene group. The remaining methylene protons gave rise to a doublet and an apparent triplet at 3.86 and 3.18 ppm, respectively. The triplet resulted from coupling to the hydrosulfido ligand as well as to the other methylene hydrogen. A doublet at −0.24 ppm was assigned to the SH proton, and irradiation of this resonance converted the apparent triplet to a doublet. The observed coupling with dithiolate protons served to distinguish the complexes with SH ligands from the molybdenum hydrides described above. Because of the low yield of 4, no further characterization data were obtained. However, structurally analogous products were synthesized using other electrophilic reagents, and complete characterization data for these products are presented later. Equation 7 suggests that facile migration of hydrogen from metal to sulfur sites is possible in these systems.

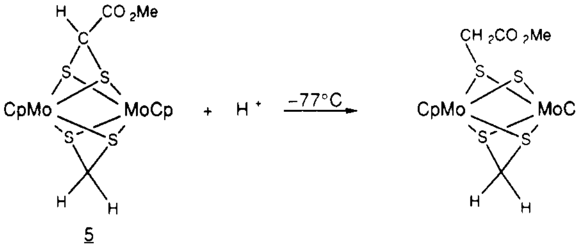
The major products formed at room temperature in reactions of the bis(methanedithiolate) derivatives with acid appeared to be paramagnetic mixed-valence cations of the type $[(CpMo)(S_2CH_2)(S_2CRR')]^+$ (3). For example, mass spectral data for the cation where R = R' = Me showed a parent ion envelope at m/e 506 consistent with the proposed formulation; a broad isotropic EPR signal was observed for the cation in CH_2Cl_2 solution at room temperature with a g value of 1.997. The data were identical with those obtained for the cationic oxidation product isolated from the reaction of silver triflate with $(CpMo)_2(S_2CH_2)(S_2CMe_2)$. In cyclic voltammetric studies, identical reversible one-electron waves were observed for the cation and the corresponding neutral complex, corresponding to the reduction and oxidation of the dimer, respectively. These mixed-valence cations undergo further thermally induced reactions which will be discussed later.

Table II. Electrochemical Data for the Complexes $(CpMo)_2(S_2CH_2)(S_2CRR')$[a]

	$E_{1/2}$, V (ΔE_p, mV)	
R, R'	$Mo^{III}/Mo^{III} \rightleftharpoons Mo^{III}/Mo^{IV}$	$Mo^{III}/Mo^{IV} \rightleftharpoons Mo^{IV}/Mo^{IV}$
R = H, R' = H	−0.22 (84)	0.39 (169)
R = CH_3, R' = CH_3	−0.20 (88)	0.46 (224)
R = H, R' = CH_2CO_2Me	−0.089 (103)	0.63 (62)

[a] Potentials were recorded in a dichloromethane solution that contained 0.1 M tetra-n-butylammonium tetrafluoroborate. Potentials are reported relative to ferrocene. Other conditions are given in the Experimental Section.

The molybdenum dithiolate complex with an electron-withdrawing substituent $(CpMo)_2(S_2CH_2)(S_2CHCO_2Me)$ (5) reacted with triflic acid at −70 °C to form a product which differed from the metal hydrides postulated above. The spectrum of the protonated product at low temperature showed single sharp resonances for the Cp and methanedithiolate ligands and two singlets which were assigned to methylene and methyl protons in the thiolate ligand in the cation $[(CpMo)_2(S_2CH_2)(\mu\text{-S})(\mu\text{-}SCH_2CO_2Me)]^+$ (eq 8). When the solution was warmed



(8)

to room temperature, a new spectrum was observed with similar resonances at slightly different chemical shifts. This spectral change is attributed to an inversion of the thiolate ligand from the initially formed axial isomer to the more stable equatorial isomer of the product. The latter complex has been synthesized previously, and spectral data agree with those of the final product of eq 8.[5]

The electron-withdrawing substituent increases the oxidation potential of the complex, and this disfavors the electron-transfer oxidation pathway. Cyclic voltammetric data for the dithiolate-bridged dimers are given in Table II. The potential for the first one-electron oxidation of 5 shows an anodic shift of approximately 110 mV relative to that for 1. Since the HOMO in the neutral dimers is primarily derived from metal ion orbitals,[6] the oxidation

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(5) Coons, D. E.; Haltiwanger, R. C.; Rakowski DuBois, M. *Organometallics* 1987, *6*, 2417.

(6) DuBois, D. L.; Miller, W. K.; Rakowski DuBois, M. *J. Am. Chem. Soc.* 1981, *103*, 3429.

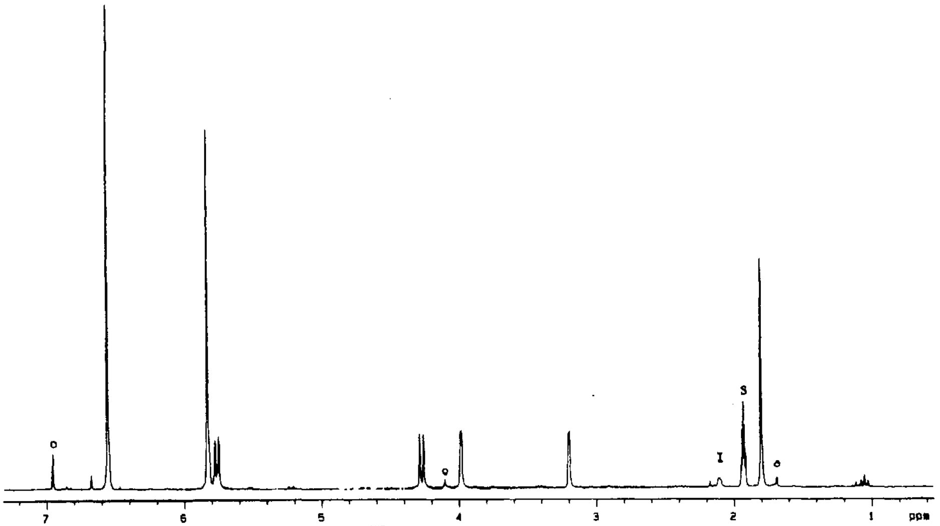
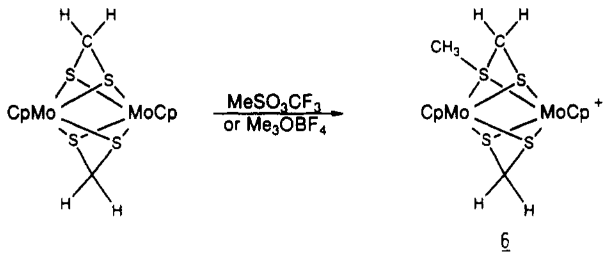


Figure 2. 300-MHz ^1H NMR spectrum of $[(CpMo)(S_2CH_2)(\mu\text{-}SCH_2)(\mu\text{-}SCH_3)(MoCp)]SO_3CF_3$ (7) in CD_3CN at room temperature. Resonances marked o correspond to $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_3)]^+$, and I indicates an unidentified impurity. Assignments are given in the Experimental Section.

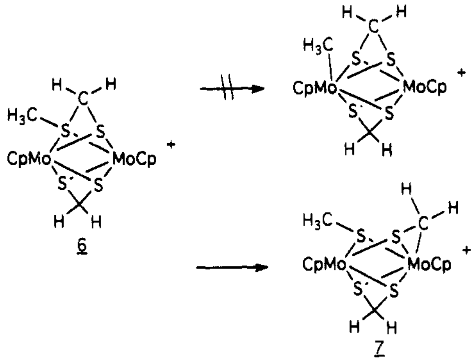
potentials reflect the relative ease with which metal ions should undergo protonation and oxidation in these complexes.

Reactions of Bis(methanedithiolate) Derivatives with Methyl Cation. Because the protonated complexes were too unstable to isolate, the reactions of the neutral species $(CpMo)_2(S_2CH_2)(S_2CRR')$ with trimethyloxonium ion were examined to determine if similar reactivity patterns were followed and if thermally stable complexes could be isolated. The reaction of $[CpMoS_2CH_2]_2$ (1) with Me_3OBF_4 was too slow to monitor at −70 °C but proceeded at room temperature over a period of 1–2 days. When the reaction was monitored by NMR spectroscopy, two products were observed which were distinguished by their symmetry characteristics. Complex 6 was formulated as shown in eq 9 because the product maintained a mirror plane through the sulfur atoms. In the NMR spectrum of 6 a single sharp Cp resonance was observed at 6.28 ppm, two singlets at 7.30 and 6.22 ppm were assigned to inequivalent methanedithiolate ligands, and the methyl resonance was observed at 2.55 ppm. Complex 6 was relatively unstable and slowly converted to 7 in the reaction solution. As a result, we were not successful in isolating 6.



(9)

The second, more stable product formed in the alkylation reaction, 7, was isolated by column chromatography. The ^1H NMR spectrum for 7 (Figure 2) suggested that this complex was an isomer of 6; resonances for the same ligands were observed in the NMR spectrum. However, the spectroscopic data indicated that 7 was a product of significantly lower symmetry than 6 with inequivalent Cp rings and four inequivalent methanedithiolate protons. (See the Experimental Section for chemical shift data.) Our initial interpretation of the data was that a sulfur-alkylated cation was the kinetic product (6), which rearranged to a more stable molybdenum-alkylated isomer (7), similar to the molybdenum hydrides discussed above (eq 10a). However, the inequivalency of the two CH_2 groups in 7 indicated a lower symmetry than was observed for the proposed molybdenum hydride (see Figure 1). An X-ray diffraction study (see below) was necessary to clarify the structure of 7. The product resulted from rearrangement of the methanedithiolate ligand rather than methyl migration (eq 10b).



(10a)

(10b)

The alkylations of other bis(alkanedithiolate) derivatives have also been investigated. For example, the reaction of $(CpMo)_2(S_2CH_2)(S_2C(Me)_2)$ with trimethyloxonium ion was characterized by NMR spectroscopy. Spectroscopic data (see the Experimental Section) supported the conclusion that products analogous to 6 and 7 were formed, but the products appeared to decompose during attempts to isolate them by column chromatography. The reaction of $(CpMo)_2(S_2CH_2)(S_2CHCO_2Me)$ with Me_3OBF_4 led to a complex mixture of products which appeared to be unstable in solution and were not further characterized.

X-ray Diffraction Study of $[(CpMo)(S_2CH_2)(SCH_2)(SCH_3)(MoCp)]^+$ (7). Cation 7 was also prepared by the reaction of 1 with methyl triflate. Single crystals of the triflate salt of 7 were obtained by addition of hexane to a dichloromethane solution. A perspective drawing of the cation's structure determined by X-ray crystallography is shown in Figure 3. Selected bond distances and angles

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(7) (a) Boorman, P. M.; Freeman, G. K. W. *Abstracts of Papers*, 199th National Meeting of the American Chemical Society, Boston, MA, April 1990; American Chemical Society: Washington, DC, 1990; INOR 468. (b) Freeman, G. K. W. Ph.D. Thesis, University of Calgary, Calgary, Alberta, Canada, 1990.

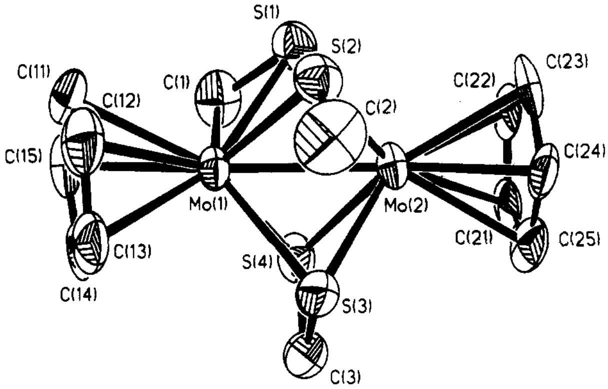

Figure 3. Perspective drawing and numbering scheme for [(CpMo)(S_2CH_2)(μ-SCH_2)(μ-SCH_3)(MoCp)]SO_3CF_3 (7). Thermal ellipsoids are shown at the 50% probability level.

Table III. Selected Bond Distances and Angles for [CpMo(S_2CH_2)(μ-SCH_2)(μ-SCH_3)MoCp]SO_3CF_3 (7)

	Distances (Å)		
Mo(1)–Mo(2)	2.625 (1)	Mo(1)–C(1)	2.277 (7)
Mo(1)–S(1)	2.433 (2)	Mo(2)–S(1)	2.449 (2)
Mo(1)–S(2)	2.477 (2)	Mo(2)–S(2)	2.473 (2)
Mo(1)–S(3)	2.472 (2)	Mo(2)–S(3)	2.423 (2)
Mo(1)–S(4)	2.476 (2)	Mo(2)–S(4)	2.448 (2)
S(1)–C(1)	1.697 (7)	S(2)–C(2)	1.826 (8)
S(3)–C(3)	1.774 (7)	S(4)–C(3)	1.805 (8)
	Angles (deg)		
Mo(1)–S(1)–Mo(2)	65.1 (1)	Mo(1)–C(1)–S(1)	73.9 (2)
Mo(1)–S(2)–Mo(2)	64.1 (1)	Mo(1)–S(3)–C(3)	92.4 (3)
Mo(1)–S(3)–Mo(2)	64.9 (1)	Mo(2)–S(3)–C(3)	92.6 (3)
Mo(1)–S(4)–Mo(2)	64.4 (1)	Mo(1)–S(4)–C(3)	91.5 (2)
Mo(1)–S(1)–C(1)	64.0 (2)	Mo(2)–S(4)–C(3)	91.0 (2)
Mo(2)–S(1)–C(1)	105.6 (3)	S(3)–C(3)–S(4)	95.9 (3)
Mo(1)–S(2)–C(2)	114.2 (3)	S(1)–Mo(1)–S(2)	68.6 (1)
Mo(2)–S(2)–C(2)	116.1 (3)	S(3)–Mo(1)–S(4)	65.0 (1)

are given in Table III, and atomic coordinates are given in Table IV. The structure of the cation confirmed that the product contained an alkylated molybdenum ion. However, the isomerization of 6 to 7 did not involve methyl transfer from the thioether sulfur but, rather, transfer of the methylene group of the strained thiolate–thioether ligand. The resulting cation contains a thioformaldehyde ligand which is η^2-bonded to Mo(1) and η^1-bonded to Mo(2). The μ-sulfur atom of the thioformaldehyde ligand remains in the plane of the other sulfur atoms and maintains the normal Mo_2S_4 core observed for these cyclopentadienyl systems. The metal–metal distance of 2.62 Å is similar to that observed in other cationic derivatives of these CpMo dimers.[8] The bond distances and angles associated with the methanedithiolate and methanethiolate ligands in 7 are normal.[8b] The Mo–C bond length for the thioformaldehyde ligand (2.28 Å) is similar to other Mo–C bond lengths in organometallic complexes.[5,9]

The carbon–sulfur bond distance for the thioformaldehyde ligand (1.696 Å) lies midway between those observed for single carbon–sulfur bonds in organic compounds (($(CH_3)_2S$, 1.80 Å; CH_3SH, 1.81 Å[10]) and those found for C=S bonds in organic thiocarbonyls (1.60 Å).[10] The thioformaldehyde C–S distance is unusually short relative to the bond length for other metal complexes containing this ligand. For example, the C–S bond length in [CpRe(NO)(PPh_3)(CH_2S)]PF_6 was reported as 1.742 Å[11] and for several di- and trinuclear Os complexes the C–S bond length ranged from 1.77 to 1.86 Å.[12] A dinuclear molybdenum complex containing a thioketone ligand in a similar η^1:η^2-bonding mode has been structurally characterized.[13] The complex $(CpMo)_2(CO)_3(\mu\text{-}CO)(\mu\text{-}R_2CS)$, where R_2CS = thiocamphor, included a semibridging carbonyl ligand. The Mo–Mo distance was significantly longer in this complex (3.145 Å) than in the tetrasulfur-bridged structures, and as a result, the S–C, C–Mo, and S–Mo distances associated with the thioketone ligand in the former complex were also longer.

The isomerization of 6 to 7 resulted in an inversion at sulfur 1, and the environment about sulfur 1 is significantly distorted from the normal trigonal-pyramidal geometry. While the Mo(2)–S(1)–C(1) angle has a close to expected value of 105.6°, the Mo(1)–S(1)–C(1) and Mo(1)–S(1)–Mo(2) angles are near 65°. Such distortion appears necessary to obtain significant overlap between molybdenum and carbon bonding orbitals. The orientation of the molybdenum–carbon bond approaches that proposed on the basis of spectroscopic data for the molybdenum–hydride

Table IV. Atomic Coordinates[a] (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for [CpMo(S_2CH_2)(μ-SCH_2)(μ-SCH_3)MoCp]SO_3CF_3 (7)

	x/a	y/b	z/c	U(eq)[b]
Mo(1)	437 (1)	2680 (1)	951 (1)	34 (1)*
Mo(2)	149 (1)	2483 (1)	−335 (1)	37 (1)*
S(1)	1053 (1)	3773 (1)	135 (1)	52 (1)*
S(2)	1599 (1)	1928 (1)	209 (1)	46 (1)*
S(3)	−372 (1)	1323 (1)	460 (1)	46 (1)*
S(4)	−1085 (1)	3030 (1)	416 (1)	50 (1)*
S(5)	1964 (1)	5492 (1)	2657 (1)	53 (1)*
O(1)	2195 (4)	6426 (3)	2845 (2)	68 (2)*
O(2)	1121 (4)	5140 (4)	2937 (3)	95 (2) *
O(3)	2103 (5)	5286 (4)	1966 (2)	84 (2)*
F(1)	2862 (6)	4975 (5)	3712 (3)	149 (4)*
F(2)	3695 (4)	5027 (4)	2847 (4)	143 (3)*
F(3)	2744 (4)	3914 (3)	2995 (3)	97 (2)*
C(1)	369 (6)	4236 (5)	743 (3)	62 (3)*
C(2)	1700 (6)	672 (5)	322 (4)	73 (3)*
C(3)	−1487 (5)	1853 (6)	547 (3)	61 (3)*
C(4)	2856 (7)	4822 (6)	3067 (4)	73 (3)*
C(11)	1347 (5)	3067 (6)	1869 (3)	58 (3)*
C(12)	1341 (6)	2099 (6)	1824 (3)	61 (3)*
C(13)	426 (6)	1793 (6)	1916 (3)	59 (3)*
C(14)	−144 (5)	2567 (6)	2018 (3)	58 (3)*
C(15)	417 (6)	3364 (6)	2000 (3)	63 (3)*
C(21)†	−804 (14)	2811 (20)	−1270 (5)	52 (6)*
C(22)†	86 (24)	3191 (12)	−1389 (7)	58 (7)*
C(23)†	754 (11)	2465 (19)	−1388 (6)	53 (6)*
C(24)†	243 (20)	1604 (13)	−1266 (8)	51 (6)*
C(25)†	−704 (18)	1841 (19)	−1190 (7)	56 (6)*
C(21′)†	−339 (33)	3091 (29)	−1295 (17)	67 (12)
C(22′)†	575 (29)	2860 (31)	−1385 (18)	69 (12)
C(23′)†	629 (25)	1870 (29)	−1348 (15)	61 (9)
C(24′)†	−252 (31)	1550 (22)	−1233 (15)	57 (9)
C(25′)†	−860 (28)	2284 (30)	−1196 (17)	63 (11)

[a] Atoms have occupancies of 1.0 except as marked with †: C(21), 0.59; C(22), 0.59; C(23), 0.59; C(24), 0.59; C(25), 0.59; C(21′), 0.41; C(22′), 0.41; C(23′), 0.41; C(24′), 0.41; C(25′), 0.41. [b] For values marked with *, the equivalent isotropic U is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

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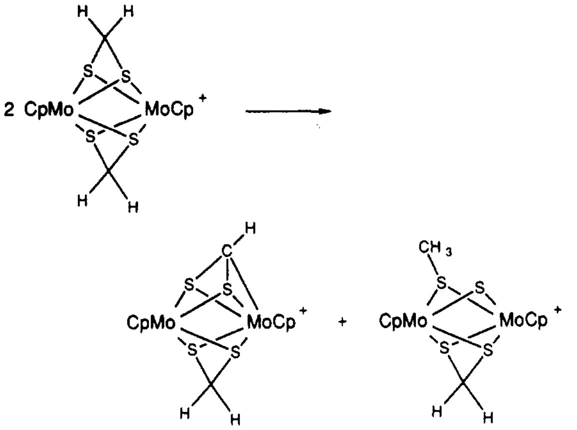
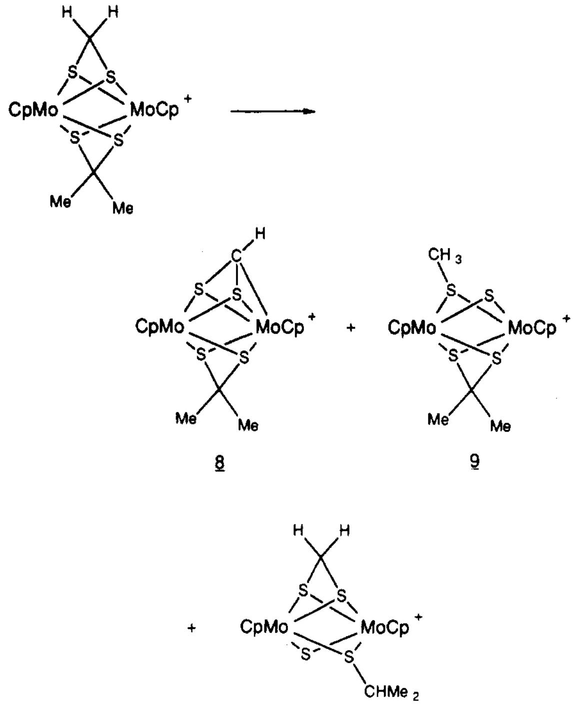
bond formed in the protonation of 1 if the latter is nonfluxional.

Reactions of Oxidized Cations. The Mo(III)/Mo(IV) cations produced in the redox reactions with protic acid were thermally unstable. For example, $[CpMoS_2CH_2]_2^+$ (**3**) underwent a further reaction slowly at room temperature and more rapidly when heated. This reaction involved formal hydrogen atom transfer to form the product cations, shown in eq 11, in roughly equimolar ratios. Each of the product cations in eq 11 has been synthesized by independent routes and characterized previously.[8b,14]



(11)

When $[(CpMo)_2(S_2CH_2)(S_2CMe_2)]SO_3CF_3$, prepared either from HSO_3CF_3 or from $AgSO_3CF_3$, was heated at 65–70 °C, a similar reaction occurred over a period of several days to form a mixture of diamagnetic products shown in eq 12. Complexes 8 and 9 have been isolated by chromatography and characterized by NMR and mass spectroscopy. Complex 10 was identified by comparison of its NMR spectrum to that of a sample prepared by an independent route.[15]



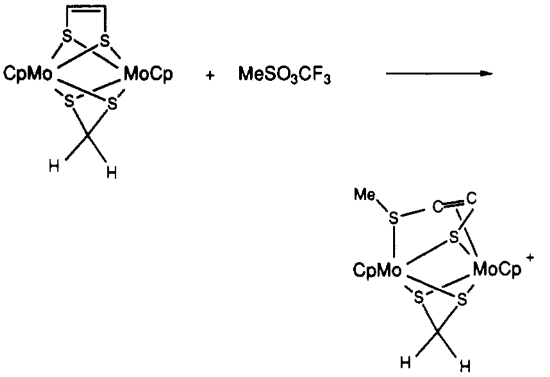
8 9 10

(12)

Discussion

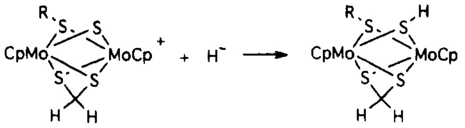
The protonation studies at low temperatures have provided data to suggest that in most cases the molybdenum ions are the most basic sites in these structures. Formation of a metal hydride appears to precede a bimolecular interaction that results in the evolution of hydrogen and the one-electron oxidation of the dimers. The ester-substituted derivative 5 provided an exception to this trend by reacting via C–S bond protonolysis. While it might be expected that an electron-withdrawing substituent would disfavor an oxidation reaction, the tendency for such ligands in the molybdenum dimers to undergo C–S bond cleavage upon protonation is somewhat unexpected. A rationale for this reactivity has been discussed in the previous paper.[2] It suggested that the inductive effect of the substituent may increase electron density on S and C atoms in the thiolate ligand of the dimer. It is interesting to speculate on whether the site of initial protonation in these systems is therefore altered. However, no spectroscopic evidence for intermediates in the protonolysis reactions described here or in the previous paper have been obtained, and the mechanism of C–S bond protonolysis therefore remains unestablished.

A comparison of the alkylation reactions of the dimers with the protonations has expanded the types of reaction products observed. A sulfur ligand appears to be the kinetically favored site of alkylation in $(CpMoS_2CH_2)_2$, perhaps because it is the most sterically accessible site. However, the sulfur-alkylated product isomerizes to a molybdenum-alkylated structure at room temperature, suggesting that there is an instability associated with a bridging thioether ligand in these dimers. Evidence has been observed previously for the instability of an alkenethiolate–thioether bridge in a related dinuclear molybdenum complex.[16] In that system, an isomerization of the thioether ligand involved the breaking of a Mo–S bond rather than a C–S bond, but the rearrangement was similar to that of eq 10b in that a product with new Mo–C bonds was ultimately formed (eq 13).



(13)

In the Introduction we discussed the heterolytic addition of hydrogen to cationic molybdenum complexes and speculated on the site of hydride and proton coordination. In previous work we have shown that hydrides and other nucleophiles react with the sulfide ligand of the cations to form neutral Mo(III) complexes (eq 14).[17,18] In this



(14)

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paper we have shown that neutral Mo(III) dimers can be further protonated at the Mo ion. The reactions provide a model for the stepwise addition of hydrogen across a Mo–S bond in the thiolate cations (see eq 2) and suggest that this is a feasible pathway in heterolytic hydrogen activation. We have also presented evidence in this paper for kinetically favored electrophilic attack at thiolate sulfur sites. These results suggest that under kinetic control an alternate pathway for heterolytic hydrogen addition could involve sulfur ligands, as suggested in eq 3. We conclude that both sulfur- and metal-protonated species may contribute to the reaction chemistry observed in the hydrogen-activating systems.

A second interesting conclusion from this study is that a decrease in electron density in the Mo_2S_4 core, achieved by oxidation, by addition of electrophiles, or by incorporation of an electron-withdrawing group, appears to promote C–S bond cleavage in the complexes. Alkyl radical transfer and other carbon–sulfur bond cleavage reactions have been observed previously for related Mo(III)/Mo(IV) structures,[8b,17,18] and these appear to be characteristic reactions for the electron-deficient systems.

Experimental Section

Materials and Instrumentation. $(CpMo(\mu\text{-}S))_2S_2CH_2$,[19] $CpMo(S_2CH_2)(S_2CMePh)$,[1] and $(CpMo)_2(S_2CH_2)(S_2CHCO_2Me)$[5] were prepared according to the published procedures. Triflic acid, methyl triflate, and trimethyloxonium tetrafluoroborate were purchased from Aldrich and used without further purification. Dichloromethane and acetonitrile were distilled from CaH_2 immediately before use.

Proton NMR spectra were recorded on a Varian VXR-300 NMR spectrometer. Chemical shifts were referenced to tetramethylsilane by using the deuterated solvent as the secondary reference. Mass spectra were obtained on a VG Analytical 7070 EQ-HF mass spectrometer. Elemental analyses were performed by Spang Microanalytical Laboratories. Electrochemical measurements were made on a Cypress Systems CYSY-1 electroanalysis system equipped with a Cypress Systems CYSY-1h potentiostat. A platinum disk and platinum wire were used as working and auxiliary electrodes, and a copper wire was used for a reference electrode. Acetonitrile or dichloromethane solutions of 0.1 M tetra-*n*-butylammonium tetrafluoroborate were used to record measurements. Potentials are reported relative to ferrocene (0.42 V vs SCE), which was dissolved in the electrolyte solution. Potentials were scanned at 150 mV/s unless otherwise noted.

Synthesis of $[CpMoS_2CH_2]_2$ (1). $(CpMo(\mu\text{-}S))_2S_2CH_2$ (0.10 g, 0.22 mmol) was dissolved in ~20 mL of $CHCl_3$ or CH_2Cl_2, and propylamine (54 μL, 0.66 mmol) was added. The solution was freeze–pump–thaw-degassed two times and ~0.50 atm of H_2 was added at −196 °C. The flask was sealed and placed in a 60 °C oil bath, and the contents were stirred for 1–2 weeks until the color changed from blue to brown. The solution was then filtered and the filtrate evaporated. The resulting residue was purified by elution through an alumina column with dichloromethane and collection of the first yellow-brown band. Yield: ~70%. ^1H NMR of 1 ($CDCl_3$; δ, ppm): 6.27 (s, S_2CH_2), 5.88 (s, Cp). Analytical data have been reported previously.[19]

Synthesis of $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_3C{=}CH_2)]Br$. $(CpMo(\mu\text{-}S))_2S_2CH_2$ (0.40 g, 0.86 mmol) and $CH_3CBr{=}CH_2$ (190 μL, 2.13 mmol) were combined in 30 mL of CH_2Cl_2 in a Schlenk flask. The mixture was stirred at ambient temperature for 6 h, and the color changed from blue to purple with a purple precipitate. The solvent volume was reduced by half at reduced pressure, and addition of diethyl ether gave purple crystals. The solution was filtered, and the crystals were washed with diethyl ether. The crystals were dried in vacuo to give 0.46 g (91% yield) of the title compound. ^1H NMR ($CDCl_3$; δ, ppm): 7.03 (s, Cp), 5.22, 4.68 (2 m, $=CH_2$), 4.09 (s, S_2CH_2), 1.74 (m, Me). A second isomer of this complex, similar to those described in ref 1, was also detected in solution. Alternate syntheses of the title cation have been developed.[16,20]

Table V. X-ray Data Collection Parameters for $[(CpMo)(S_2CH_2)(SCH_3(SCH_2)(MoCp)]SO_3CF_3$ (7)

formula	$C_{14}H_{17}O_3F_3S_5Mo_2$
fw	642.5
space group	*Pbca*
unit cell dimens	
a, Å	14.287 (3)
b, Å	14.374 (3)
c, Å	20.045 (3)
V, Å^3	4116.5 (14)
Z	8
calcd density, g/cm^3	2.073
cryst size, mm	0.15 × 0.20 × 0.25
λ, Å	0.71073 (Mo Kα)
μ, mm^{-1}	1.718
temp, °C	24–28
scan type	θ–2θ
2θ range, deg	3.0–50.0
scan speed, deg/min	2.02–58.59
index ranges	$-16 \leq h \leq 16$, $-17 \leq k \leq 17$, $-2 \leq l \leq 23$
no. of unique rflns	3629 (R_{int} = 3.42%)
no. of obsd rflns	2489 ($F > 6.0\sigma(F)$)
data-to-param ratio	9.4:1
R, %	5.83
R_w, %	5.78

Synthesis of $(CpMo)_2(S_2CH_2)(S_2C(CH_3)_2)$. $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_3C{=}CH_2)]Br$ (0.50 g, 0.85 mmol) was partially dissolved in 10 mL of CH_3CN in a Schlenk flask. The reaction mixture was degassed and sealed under 500 Torr of hydrogen at −196 °C. The solution was warmed to 65 °C for 5 days and changed from purple with a purple precipitate to brown with a brown precipitate. Solvent was removed at reduced pressure and the residue chromatographed on alumina with CH_2Cl_2. The first brown band eluted was collected, and after removal of solvent at reduced pressure, 0.29 g (55% yield) of brown microcrystals of the title complex was collected. ^1H NMR ($CDCl_3$; δ, ppm): 6.45 (s, S_2CH_2), 5.85 (s, Cp), 1.45 (s, $S_2(CH_3)_2$). An alternate synthesis and analytical data have been reported previously.[19]

Reaction of $(CpMo)_2(S_2CH_2)(S_2CRR')$ with Protic Acid. In a typical procedure 0.7 mL of degassed CD_2Cl_2 and CF_3SO_3H (1.9 μL, 0.021 mmol) were combined in an NMR tube and frozen at −131 °C (*n*-pentane ice bath). $(CpMo)_2(S_2CH_2)(S_2CRR')$ (0.010 g, ~0.02 mmol) was added on top of the frozen solution, and the NMR tube was sealed under vacuum. The reaction mixture was thawed at −77 °C (dry ice–acetone), and the tube containing brown solution and precipitate was rapidly transferred to the NMR probe precooled to −70 °C. The ^1H NMR spectra of the reaction mixtures gave sharp resonances tentatively assigned to $[(CpMoH)(S_2CH_2)(S_2CRR')(MoCp)]CF_3SO_3$ (see Table I for NMR data). An attempt to regenerate the starting complex by addition of triethylamine (1 equiv) to the cooled solution immediately upon removal from the probe was unsuccessful. Only broadened resonances were observed, as described below.

As the reaction mixtures were warmed, the resonances of the hydride complexes disappeared and a broad resonance near 14–15 ppm was attributed to the Cp ligands of the oxidized product $[(CpMo)_2(S_2CH_2)(S_2CR_2)]^+$. A singlet assigned to molecular hydrogen was also observed at 4.6 ppm. Recooling the mixture in the reaction where R, R′ = CH_3 did not regenerate the spectrum of the hydride intermediate. New sharp resonances were observed in the room-temperature spectrum in addition to the broad resonances of the paramagnetic cations. There were tentatively assigned to $(CpMo)(S_2CRR')(\mu\text{-}SCH_2)(\mu\text{-}SH)(MoCp)]CF_3SO_3$. The intensities of the resonances for the latter products were very weak, and it was estimated that they were present in <10% yield. ^1H NMR (CD_2Cl_2; δ): R = R′ = H, 6.50, 5.78 (2 s, Cp), 3.86 (d, J = 2.6 Hz, SCH_2), 3.18 (app t, J = 2.6 and 2.4 Hz, SCH_2), −0.24 (d, J = 2.4 Hz, SH), 5.78, 4.22 (2 d, J = 8.4 Hz, S_2CH_2); R = R′ = Me, 6.41, 5.72 (2 s, Cp), 3.96 (d, J = 2.7 Hz, SCH_2), 3.12 (app

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t, J = 2.7 and 2.5 Hz, SCH$_2$), −0.14 (d, J = 2.5 Hz, SH), 1.91, 1.20 (2 s, Me); R = Me, R′ = Ph, 7.4–7.1 (m, Ph), 5.84, 5.79 (2 s, Cp), 3.8 and 3.3 (br, SCH$_2$), −0.1 (br, SH), 1.44 (s, Me).

Synthesis of $[(CpMo)_2(S_2CH_2)(S_2C(CH_3)_2)]CF_3SO_3$. (a) $(CpMo)_2(S_2CH_2)(S_2CH_3)_2)$ (0.030 g, 0.059 mmol) and $AgCF_3SO_3$ (0.014 g, 0.056 mmol) were combined in 5 mL of CH_3CN and stirred at ambient temperature. The colorless solution containing brown precipitate quickly turned brown, and gray and brown precipitates were present. After 18 h the solution was filtered and the solvent removed from the filtrate at reduced pressure. Recrystallization from CH_2Cl_2/Et_2O gave 0.020 g (53% yield) of a brown microcrystalline solid. EPR (CH_2Cl_2, 25 °): broad signal with g = 1.977. FAB-MS (m/e): 506 (P of cation), 465 ($P^+ - C(CH_3)_2$), 432 ($P^+ - SC(CH_3)_2$), 418 ($P^+ - SCH_2 - C(CH_3)_2$).

(b) $(CpMo)_2(S_2CH_2)(S_2CMe_2)$ (0.040 g, 0.079 mmol) and CF_3SO_3H (10 μL, 0.11 mmol) were dissolved in 5 mL of dichloromethane at room temperature and stirred. The solution rapidly (3 min) became darker brown, and after 30 min, ~75 mL of diethyl ether was added, precipitating a brown solid. Brown crystals of the cationic product was washed with diethyl ether (3 × 10 mL) and dried in vacuo. Yield: 0.033 g, 64% yield. Mass spectral and EPR data are similar to those reported above. Note: When the solid product was exposed to air for an extended time, a significant amount of $[(CpMo)_2(S_2C(CH_3)_2)(S_2CH)(MoCp)]^+$ (8) formed.

Reaction of $(CpMo)_2(S_2CH_2)(S_2CHCO_2CH_3)$ (5) with Protic Acid. Using a procedure similar to that reported for other bis(methanedithiolate) derivatives, 5[5] (0.010 g, 0.018 mmol) and CF_3SO_3H (1.8 μL, 0.020 mmol) were combined in ~0.7 mL of CD_2Cl_2 in an NMR tube at −77 °C. The reaction mixture rapidly turned from brown to purple. Resonances in the ^{1}H NMR spectrum were assigned to $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_2CO_2CH_3)]^+$. ^{1}H NMR ($CD_2Cl_2$): δ 6.85 (s, Cp), 4.48 (s, S$_2$CH$_2$), 3.64 (s, OMe), 2.83 (s, CH$_2$). No further change was noted between −70 and 0 °C. On further warming, resonances were observed at 6.96 (s, Cp), 4.20 (s, S$_2$CH$_2$), 3.64 (s, OMe), and 2.66 (s, CH$_2$) and were assigned to a second isomer of the thiolate cation.[5]

Reaction of $[CpMoS_2CH_2]_2$ with Trimethyloxonium Tetrafluoroborate. In an NMR tube was combined $[CpMoS_2CH_2]_2$ (1; 0.010 g, 0.021 mmol) and Me_3OBF_4 (0.003 g, 0.02 mmol) in 0.8 mL of CD_2Cl_2. The brown reaction mixture was degassed in three freeze–pump–thaw cycles and sealed under vacuum at −196 °C. The solution was warmed to room temperature, and after 2 h, resonances for Me_2O (3.29 ppm, s) and for $[(CpMo)_2(S_2CH_2)(SCH_2SCH_3)]BF_4$ (6) were observed. ^{1}H NMR (δ): 7.30, 6.22 (2 s, S$_2$CH$_2$ and SCH$_2$SMe), 6.28 (s, Cp), 2.57 (s, CH$_3$). The resonances for this product disappeared over the next 22 h, and resonances for 7 (see below) were observed as the major product.

Synthesis of $[(CpMo)(S_2CH_2)(\mu\text{-}SCH_2)(\mu\text{-}SCH_3)(MoCp)]CF_3SO_3$ (7). $[CpMoS_2CH_2]_2$ (1; 0.10 g, 0.21 mmol) and $CF_3SO_3CH_3$ (29 μL, 0.26 mmol) were combined in 10 mL of dichloromethane and stirred at room temperature. Over the next 10 days the mixture became darker brown and a brown precipitate was present throughout the reaction. The solution was filtered, and ^{1}H NMR and mass spectral data for the precipitate were consistent with those of the starting material. Solvent was removed from the filtrate at reduced pressure and the residue chromatographed on acidic alumina. Elution with 80/20 (v/v) CH_3CN–CH_2Cl_2 gave a brown band, which yielded the brown title complex. Solvent was removed at reduced pressure, and product was recrystallized from CH_3CN–Et_2O. Yield: 0.061 g, 45%. ^{1}H NMR (CD_3CN; δ): 6.56, 5.83 (2 s, Cp), 3.98, 3.20 (2 d, J = 2.6 Hz, SCH$_2$), 5.76, 4.27 (2 d, J = 8.3 Hz, S$_2$CH$_2$), 1.79 (s, Me). ^{13}C{^{1}H} NMR (CD_3CN; δ, ppm): 101.13, 94.92 (2 s, Cp), 78.88, 63.31, 15.68 (3 s, SCH$_2$ or S$_2$CH$_2$; SCH$_3$). FAB-MS (m/e): 493 (P of cation), 479 ($P^+ - CH_2$), 464 ($P^+ - CH_2 - CH_3$), 432 ($P^+ - CH_2 - SCH_3$), 418, 400.

X-ray Diffraction Study of 7. Crystals suitable for X-ray diffraction were obtained by layering hexanes over a saturated dichloromethane solution of the title complex and allowing slow diffusion of the two layers to occur. A crystal was mounted with epoxy resin and examined on the diffractometer. Crystal data are summarized in Table V. The structure was solved by direct methods and expanded by Fourier techniques. Table IV gives final parameters for the non-hydrogen atoms in the final model. The hydrogen atoms were included in fixed idealized positions. We were particularly interested in the positions of the hydrogens on C(1). The idealized positions of these atoms corresponded within 0.2 Å to the peaks for these atoms as seen in difference electron density maps. Complete results of the X-ray diffraction study are included in the supplmentary material.

Reaction of $(CpMo)_2(S_2CH_2)(S_2C(CH_3)_2)$ with Trimethyloxonium Tetrafluoroborate. The title complex (0.010 g, 0.020 mmol) and Me_3OBF_4 (0.003 g, 0.02 mmol) were combined in an NMR tube in ~0.8 mL of degassed CD_2Cl_2. The brown mixture was sealed under vacuum at −196 °C and warmed to room temperature. The mixture was monitored by ^{1}H NMR spectroscopy. After 6 h major products observed in a 1/1 ratio were $[(CpMo)(S_2C(CH_3)_2)(\mu\text{-}SCH_2)(\mu\text{-}SCH_3)(MoCp)]^+$ and $[(CpMo)_2(S_2C(CH_3)_2)(SCH_2SCH_3)]^+$. ^{1}H NMR for the former complex (CD_2Cl_2; δ): 6.49, 5.78 (2 s, Cp), 4.04, 3.27 (2 d, J = 2.9 Hz, SCH$_2$), 1.88, 1.89, 1.19 (3 s, Me). ^{1}H NMR for the latter complex ($CDCl_3$; δ): 6.39 (s, S$_2$CH$_2$), 6.26 (s, Cp), 2.39 (s, SCH$_3$), 1.75 (s, S$_2$C(CH$_3$)$_2$). Attempts to separate the products from a similar reaction mixture using chromatography on acidic alumina were unsuccessul.

Reaction of $(CpMo)_2(S_2CH_2)(S_2CHCO_2Me)$ (5) with Trimethyloxonium Tetrafluoroborate. Complex 5 (0.010 g, 0.019 mmol) and Me_3OBF_4 (0.003 g, 0.02 mmol) were combined in ~0.7 mL of CD_2Cl_2 in an NMR tube. The brown mixture was degassed in three freeze–pump–thaw cycles and the tube sealed under vacuum at −196 °C. The reaction mixture was warmed to room temperature and became purple, and a purple precipitate formed. Three sets of Cp resonances were observed at 6.57 and 5.71, 6.50 and 5.88, and 6.47 and 5.85 ppm which were tentatively assigned to three isomers of a product with a structure analogous to 7. The products were unstable in solution and were not isolated.

Thermal Decomposition of $[CpMoS_2CH_2]_2SO_3CF_3$ (3). The CD_2Cl_2 solution of 3, obtained from protonation of 1, was heated in a sealed NMR tube to 70 °C for 18 days. The color changed from brown to purple after 1 day of heating, and the gradual conversion to products was monitored by NMR spectroscopy. When the reaction was stopped, $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_3)]^+$ and $[(CpMo)(S_2CH_2)(S_2CH)(MoCp)]^+$[14] were present in a 1:0.9 ratio, respectively, in >90% yield based upon integration of Cp resonances. Weak resonances for 3 were still present. ^{1}H NMR of $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_3)]SO_3CF_3$ (CD_2Cl_2; δ): 6.92 (s, Cp), 4.12 (s, S$_2$CH$_2$), 1.71 (s, Me).

Thermal Decomposition of $[(CpMo)_2(S_2CH_2)(S_2CMe_2)]SO_3CF_3$. The reaction mixture resulting from the addition of 1 equiv of triflic acid to the neutral complex was heated to 60 °C for 10 days. The color slowly changed from brown to purple. When the reaction wa stopped, major products observed in the NMR spectrum were $[(CpMo(S_2C(CH_3)_2)(S_2CH)(MoCp)]^+$ (8), $[(CpMo)_2(S_2C(CH_3)_2)(\mu\text{-}S)(\mu\text{-}SCH_3)]^+$ (9), and $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH(CH_3)_2)]^+$ (10)[15] in a 1.2:3.8:1 ratio, respectively, based upon integration of methyl resonances (differences in solubilities may affect the observed ratio of products formed). In a similar reaction carried out at room temperature, complexes 8 and 9 were purified by removing solvent at reduced pressure and dissolving the purple residue in CH_3CN. Addition of diethyl ether gave yellow crystals of complex 8, which were filtered and dried. ^{1}H NMR ($CDCl_3$; δ, ppm): 8.12 (s, S$_2$CH), 6.66, 5.69 (2 s, Cp's), 2.22, 1.36 (2 s, C(CH$_3$)$_2$). FAB-MS (m/e): 505 (P^+), 431 ($P^+ - SC(CH_3)_2$). Removal of the solvent from the above filtrate at reduced pressure gave a solid which was chromatographed on acidic alumina with 50/50 (v/v) CH_3CN–MeOH. Collection of the first purple band gave pure 9. ^{1}H NMR for 9 (CD_2Cl_2; δ, ppm): 6.89 (s, Cp), 1.75 (s, SCH$_3$), 1.58 (s, S$_2$C(CH$_3$)$_2$). FAB-MS (m/e): 507 (P of cation), 492 ($P^+ - CH_3$), 465 ($P^+ - C(CH_3)_2$), 433 ($P^+ - SC(CH_3)_2$), 418, 386. ^{1}H NMR for 10 (CD_2Cl_2; δ, ppm): 6.93 (s, Cp), 4.18 (s, S$_2$CH$_2$), 2.1 (hept, CH(CH$_3$)$_2$), 1.10 (d, J = 6.8 Hz, CH(CH$_3$)$_2$).

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Supplementary Material Available: Complete tables of data collection parameters, bond distances and angles, and displacement parameters for 7, a figure giving an alternate view of 7, and a 300-MHz ^1H NMR spectrum of $[(CpMo)(S_2CH_2)(\mu\text{-}SH)(\overline{SCH_2)}MoCp]SO_3CF_3$ (4) in CD_2Cl_2 (12 pages). Ordering information is given on any current masthead page.

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Elimination Process from the [(Diphenylphosphino)methyl]zirconium Hydride $[Cp_2ZrH(CH_2PPh_2)]_n$[†]

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The synthesis of $[Cp_2ZrH(CH_2PPh_2)]_n$, 1, and its chemical behavior toward different organic or organometallic substrates are described. The chemical reduction of the hydride 1 produced a paramagnetic Zr(III) species formulated as $[CpZr(\eta^2\text{-}CH_2PPh_2)_2]$, and a redistribution reaction from the unstable $[Cp_2ZrH(CH_2PPh_2)]^-$ is suggested. The thermolytic experiment of 1 led to the Zr(III) species "Cp_2ZrH" and $[Cp_2Zn(\eta^2\text{-}CH_2PPh_2)]$, and a mechanistic pathway implying the reductive elimination of the phosphine CH_3PPh_2 is proposed. Indirect evidence comes from the thermolysis of $[Cp_2ZrD(CH_2PPh_2)]_n$ and $[(C_5D_5)_2ZrD(CH_2PPh_2)]_n$ or from the reactivity of 1 with PhC≡CPh, $Cp_2Zr(Ph)_2$, or $Cp_2Zr(\eta^4\text{-butadiene})$. A Zr(IV)–Zr(II) homodimetallic hydride $[Cp_2Zr(\mu\text{-}H)(\mu\text{-}CH_2PPh_2)ZrCp_2]$ is postulated as an intermediate in the decomposition scheme of 1.

Introduction

The organometallic chemistry of Zr(IV) containing a Zr–H bond provides many examples of thermally and photolytically unstable products.[1–5] Mechanisms have been investigated, and their decomposition pathways have proved difficult to establish due to cyclopentadienyl CH activation, which complicates the nature of the reaction.[4a,5e,f,6,7] Intramolecular reductive elimination of the alkyl and hydride ligand, as RH, with formation of the zirconocene species "Cp_2Zr", which in some instances can be trapped, is one proposed mechanism for the autodecomposition of hydride alkyl complexes.[5a,b,d,e] Early work in this area introduced the paramagnetic Zr(III) species $Cp_2Zr(\eta^2\text{-}CH_2PPh_2)$ in the activation of cyclopentadienyl C–H bonds.[8] The related compound, $[Cp_2ZrH(CH_2PPh_2)]_n$ (1), has shown by thermolysis at 60 °C the formation of a zirconium(III) hydride species, "Cp_2ZrH" (2), and the [(diphenylphosphino)methyl]zirconium $Cp_2Zr(\eta^2\text{-}CH_2PPh_2)$ (3).[9] The catalytic hydrogenation properties of 1 were investigated, and the presence of 3 was revealed during the hydrogenation of various organic unsaturated substrates.[10] Consequently, we were intrigued by the formation of species 3 when 1 was mixed with olefins, even at room temperature.

Herein we present a study on the chemical properties of 1, to learn as much as possible about the formation of Zr(III) species observed in the thermolytic experiments as well as toward olefinic substrates and to propose a picture about the decomposition of 1.

Results and Discussion

Synthesis, Chemical Reduction, Photolysis, and Thermolysis of $[Cp_2ZrH(CH_2PPh_2)]_n$, 1. The reaction of $Cp_2ZrCl(CH_2PPh_2)$ with $LiAlH(O\text{-}t\text{-}Bu)_3$ in THF or $NaAlH_2(OCH_2CH_2OMe)_2$ in toluene produces the insoluble polymeric white hydride complex $[Cp_2ZrH(CH_2PPh_2)]_n$, 1, in 60% yield.[9] Complex 1 is also accessible in a one-pot synthesis, with the same yield, starting from a mixture of Cp_2ZrCl_2 and $LiCH_2PPh_2(TMEDA)$ in THF at −78 °C,[13b]

Scheme I

$$(1/n)[Cp_2ZrH(CH_2PPh_2)]_n \xrightarrow{Na(np)} [Cp_2ZrH(CH_2PPh_2)]^- + Na^+ + Np$$

$$[Cp_2ZrH(CH_2PPh_2)]^- \longrightarrow {}^1/_2[Cp_2ZrH_2]^- + {}^1/_2[Cp_2Zr(CH_2PPh_2)_2]^-$$

$$ {}^1/_2[Cp_2Zr(CH_2PPh_2)_2]^- \longrightarrow {}^1/_2[Cp_2Zr(\eta^2\text{-}CH_2PPh_2)_2]^- \ (+{}^1/_2Cp^-)$$

[†] In memory of Prof. D. Gervais.

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