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(C<sub>6</sub>H<sub>5</sub>)SiMe<sub>3</sub>, 768-32-1; (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Hg, 587-85-9; Sm, 7440-19-9; C<sub>5</sub>Me<sub>5</sub>H, 4045-44-7; C<sub>5</sub>Me<sub>4</sub>EtH, 93473-76-8.

**Supplementary Material Available:** Tables of thermal parameters and structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

## A Study of Ionic and Radical Reactivities of Bridging Sulfido Ligands in Dimeric Cyclopentadienyl Complexes of Molybdenum<sup>†</sup>

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Reaction of (CpMo-μ-S)<sub>2</sub>S<sub>2</sub>CH<sub>2</sub> (I, Cp = C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>) with methyl iodide or methyl fluorosulfate leads to the formation of the cationic dimer [(CpMo)<sub>2</sub>(μ-S)(μ-SCH<sub>3</sub>)S<sub>2</sub>CH<sub>2</sub>]<sup>+</sup> (II). The bisulfate salt of II has been characterized by an X-ray diffraction study which confirms that a bridging sulfido ligand in I is the site of electrophilic attack. The salt crystallizes in space group P2<sub>1</sub>/n with *a* = 10.155 (2) Å, *b* = 17.478 (9) Å, *c* = 22.201 (7) Å, β = 97.89 (2)°, and *V* = 3903 (2) Å<sup>3</sup>. The electrochemical characteristics of II are compared to those of related molybdenum dimers. II undergoes two reversible one-electron reductions in acetonitrile at -0.34 and -1.24 V vs. SCE to form a neutral mixed valence Mo(III)/Mo(IV) dimer, V, and an anionic Mo(III)/Mo(III) derivative, VII, respectively. The reactivity of each member of this redox series has been characterized. The bridging sulfido ligand in II reacts readily with carbanions and alkyl-substituted borohydride reagents. In contrast, the sulfido ligand in VII is strongly nucleophilic. For example, VII reacts with acetylene to form, upon protonation, the ethenyl thiolate bridged derivative (CpMo)<sub>2</sub>(μ-SC<sub>2</sub>H<sub>3</sub>)(μ-SCH<sub>3</sub>)S<sub>2</sub>CH<sub>2</sub> (IV). The reactivity of the unsaturated ligand in IV toward further reduction has been investigated.

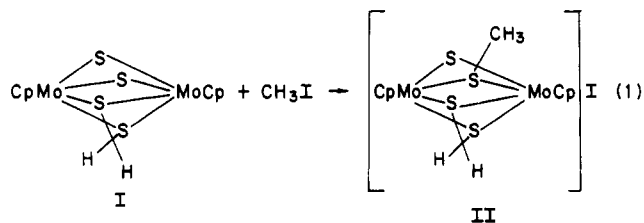
### Introduction

We have recently reported that the molybdenum(IV) dimer (CpMo-μ-S)<sub>2</sub>S<sub>2</sub>CH<sub>2</sub> (I) promotes the hydrogenation of alkynes to cis alkenes, allenes to alkenes, and ketenes to aldehydes<sup>2</sup> and the hydrogenolysis of carbon disulfide to hydrogen sulfide and thioformaldehyde.<sup>3</sup> The bridging cis sulfido ligands in the molybdenum complex are proposed to be the reactive site that reacts with hydrogen and substrate. However, mechanistic details of these reactions have not been established. In order to obtain information on both the ionic and radical reactivity of bridging sulfur ligands in molybdenum dimers of this type, we have undertaken a study of the sulfur-alkylated derivative of I [(CpMo)<sub>2</sub>(μ-S)(μ-SR)S<sub>2</sub>CH<sub>2</sub>]<sup>+</sup> (II). The redox-active nature of this cationic Mo(IV) dimer has enabled us to vary the formal oxidation states of the metal ions in order to induce potential electrophilic, nucleophilic, or radical characteristics at one bridging sulfido ligand. The alkylation of the other sulfido bridge has served the purpose of preventing the facile side reaction of adduct formation that is known to occur between unsaturated substrates and a pair of cis sulfido ligands.<sup>2</sup> The investigations have helped to define the range of reactivity to be expected for sulfur ligands in these dimers. For example, the sulfido bridge in a neutral mixed-valence dimer does not show the reactivity characteristic of a sulfur-based radical; but the ligand in an anionic molybdenum(III) dimer has been shown to be strongly nucleophilic. Its reaction with acetylene to form, upon protonation, a dimer with an alkenyl thiolate bridge

demonstrates one pathway in which alkyne reduction may be mediated by sulfur sites in metal sulfur catalysts. The possible relationship of these derivatives to hydrogenation intermediates is discussed.

### Results and Discussion

**Reactivity of Sulfido Ligands in (CpMo-μ-S)<sub>2</sub>S<sub>2</sub>CH<sub>2</sub>.** Previous work in this laboratory has shown that the nature of the thiolate ligands in quadruply bridged molybdenum dimers significantly alters the reactivity of sulfido bridges in the complex.<sup>2</sup> An additional example of this type of effect on reactivity has been observed in this study. While [(CpMo(μ-S)SCH<sub>3</sub>)<sub>2</sub>]<sup>5</sup> does not react with methyl iodide, the related Mo(IV) dimer I reacts readily to form the air-stable cation II (reaction 1). Other electrophilic alkylating agents



(1) Alfred, P. Sloan Fellow 1981-1984; Camille and Henry Dreyfus Teacher Scholar 1981-1986.

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

(3) Rakowski DuBois, M. *J. Am. Chem. Soc.* 1983, 105, 3710.

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

(5) Rakowski DuBois, M.; VanDerveer, M. C.; DuBois, D. L.; Haltiwanger, R. C.; Miller, W. K. *J. Am. Chem. Soc.* 1980, 102, 7456.

<sup>†</sup>This paper is dedicated to the memory of Professor Earl L. Muettterties, whose catholicity of interests inspired new growth in organometallic chemistry.

Table I. Intramolecular Distances and Angles for  $[(\text{CpMo})_2(\mu\text{-S})(\mu\text{-SCH}_3)(\text{S}_2\text{CH}_2)]\text{HSO}_4^a$ 

molecule 1		molecule 2 <sup>b</sup>	
Distances, Å			
Mo(1)-Mo(2)	2.610 (1)	Mo(3)-Mo(4)	2.602 (1)
Mo(1)-S(1)	2.445 (3)	Mo(3)-S(8)	2.444 (3)
Mo(1)-S(2)	2.440 (3)	Mo(3)-S(5)	2.439 (3)
Mo(1)-S(3)	2.437 (3)	Mo(3)-S(6)	2.450 (3)
Mo(1)-S(4)	2.315 (3)	Mo(3)-S(7)	2.311 (3)
Mo(2)-S(1)	2.457 (3)	Mo(4)-S(8)	2.456 (3)
Mo(2)-S(2)	2.450 (3)	Mo(4)-S(5)	2.430 (3)
Mo(2)-S(3)	2.437 (3)	Mo(4)-S(6)	2.454 (3)
Mo(2)-S(4)	2.307 (3)	Mo(4)-S(7)	2.315 (3)
S(1)-C(13)	1.795 (11)	S(8)-C(27)	1.927 (11)
S(2)-C(13)	1.845 (11)	S(5)-C(27)	1.812 (12)
S(3)-C(14)	1.802 (10)	S(6)-C(28)	1.799 (13)
S(1)···S(2)	2.674 (4)	S(5)···S(8)	2.696 (4)
S-O(anion)(av)	1.445 (13)	S-O(av)	1.446 (13)
Angles, deg			
Mo(1)-S(1)-Mo(2)	64.3 (1)	Mo(3)-S(8)-Mo(4)	64.1 (1)
Mo(1)-S(2)-Mo(2)	64.5 (1)	Mo(3)-S(5)-Mo(4)	64.1 (1)
Mo(1)-S(3)-Mo(2)	64.8 (1)	Mo(3)-S(6)-Mo(4)	64.6 (1)
Mo(1)-S(4)-Mo(2)	68.8 (1)	Mo(3)-S(7)-Mo(4)	68.4 (1)
S(1)-Mo(1)-S(2)	66.4 (1)	S(5)-Mo(3)-S(8)	66.9 (1)
S(1)-Mo(1)-S(3)	115.3 (1)	S(6)-Mo(3)-S(8)	115.3 (1)
S(2)-Mo(1)-S(3)	75.5 (1)	S(5)-Mo(3)-S(6)	75.4 (1)
S(2)-Mo(1)-S(4)	113.2 (1)	S(5)-Mo(3)-S(7)	113.8 (1)
S(1)-Mo(1)-S(4)	75.6 (1)	S(8)-Mo(3)-S(7)	75.6 (1)
S(3)-Mo(1)-S(4)	74.2 (1)	S(6)-Mo(3)-S(7)	74.4 (1)
S(1)-C(13)-S(2)	94.5 (5)	S(8)-C(27)-S(5)	92.2 (5)
C(13)-S(1)-Mo(1)	92.0 (4)	C(27)-S(8)-Mo(3)	94.0 (4)
C(13)-S(1)-Mo(2)	93.3 (4)	C(27)-S(8)-Mo(4)	94.7 (4)
C(14)-S(3)-Mo(1)	114.3 (4)	C(28)-S(6)-Mo(3)	113.4 (4)
C(14)-S(3)-Mo(2)	112.5 (4)	C(28)-S(6)-Mo(4)	112.2 (4)

<sup>a</sup> Estimated standard deviations are given in parentheses in this and on following tables. <sup>b</sup> The numbering scheme for molecule 2 is available as supplementary material. Distances and angles given here correspond to each analogous parameter defined on the same line for molecule 1.

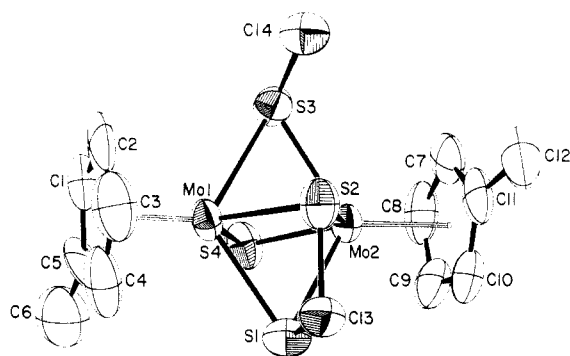


Figure 1. Perspective drawing and numbering scheme for molecule 1 of the cation  $[(\text{CpMo})_2(\mu\text{-S})(\mu\text{-SCH}_3)\text{S}_2\text{CH}_2]^+$  (II). Thermal ellipsoids are drawn at 50% probability.

react similarly; the reaction with methyl fluorosulfate provided crystals of II suitable for single-crystal X-ray analysis. The complex crystallizes in space group  $P2_1/n$  with two formula equivalents in the asymmetric crystal unit. Structurally, both molecules are very similar. A perspective drawing of one of the independent cations is shown in Figure 1. Selected bond distances and angles for both cations are summarized in Table I, and positional parameters are given in Table II. The structure confirms that a sulfido ligand is the site of electrophilic attack. The orientation of the resulting S-Me group has been referred to previously in other thiolate-bridged dimers as an equatorial configuration.<sup>4</sup> The Mo-S distances for the sulfido ligands are approximately 0.13 Å shorter than those of the thiolates. Similar differences have been observed previously<sup>5</sup> and are consistent with the difference in formal charge on the two types of sulfur bridges. The Mo-Mo distances in this cationic derivative are significantly longer,

and the Mo-S-Mo angles are larger than the corresponding values in isoelectronic neutral molybdenum complexes with the  $\text{Mo}_2\text{S}_4$  core.<sup>5,6</sup>

Complex II is a diamagnetic derivative. The proton NMR spectrum in chloroform gives evidence of only one isomer in solution, even at low temperatures, suggesting that the equatorial configuration of the methyl thiolate ligand is significantly more stable than the axial for this cationic dimer. The chemical shift of the protons in the methanedithiolate ligand has been shown previously to be very sensitive to the electronic characteristics of the dimer.<sup>2</sup> The shift of 4.8 ppm observed for II is approximately midway between the shifts observed for the same ligand in I (2.6 ppm) and in neutral Mo(III) dimers (6.2 ppm) and appears to be characteristic of this ligand in a cationic Mo(IV)/Mo(IV) dimer. Protonation of I results in a similar chemical shift for the methanedithiolate group, suggesting that the cation  $[(\text{CpMo})_2\text{S}_2\text{CH}_2(\mu\text{-S})(\mu\text{-SH})]^+$  is formed. However an excess of acid (roughly 10 equiv) is required to shift the resonance in the spectrum to the limiting chemical shift of the completely protonated form.

The cyclic voltammogram of II in acetonitrile is shown in Figure 2. Two reversible one-electron reductions occur for the cation within the accessible potential range, while structurally similar neutral Mo(IV) dimers generally undergo only one reduction. A comparison of the reversible and quasi-reversible waves ( $\Delta E_p = 60\text{-}90$  mV) in an extensive series of molybdenum dimers reveals that the reduction potentials for the formal molybdenum couples V/IV = IV/IV, IV/IV = IV/III, and IV/III = III/III shift significantly as the nature of the bridging ligands and the

(6) McKenna, M.; Haltiwanger, R. C.; Noordik, J.; Rakowski DuBois, M., manuscript in preparation.

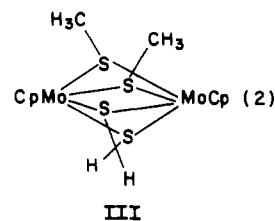
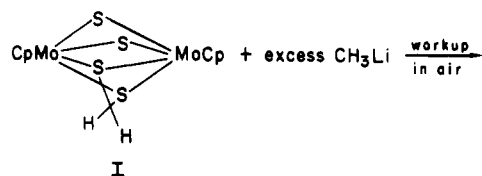
Table II. Atomic Coordinates for  $[\text{CpMo}(\mu\text{-S})(\mu\text{-SCH}_3)_2\text{S}_2\text{CH}_2]\text{HSO}_4$ 

atom	x	y	z	atom	x	y	z
Mo(1)	0.63179 (8)	0.19082 (5)	-0.07794 (4)	H(4)	0.8635 (8)	0.2499 (8)	0.0092 (3)
Mo(2)	0.37715 (8)	0.19178 (5)	-0.07134 (4)	H(61)	0.762 (2)	0.336 (1)	-0.1445 (9)
Mo(3)	0.12720 (8)	0.04791 (5)	0.63338 (4)	H(62)	0.929 (2)	0.351 (1)	-0.1126 (9)
Mo(4)	0.38408 (9)	0.06470 (6)	0.64596 (4)	H(63)	0.799 (2)	0.373 (1)	-0.0702 (9)
S(1)	0.5385 (3)	0.2605 (2)	0.0019 (1)	H(7)	0.1472 (7)	0.0975 (6)	-0.1379 (4)
S(2)	0.5325 (3)	0.1080 (2)	-0.0080 (1)	H(8)	0.1450 (7)	0.2488 (6)	-0.1600 (4)
S(3)	0.4747 (3)	0.1117 (2)	-0.1435 (1)	H(9)	0.1940 (7)	0.3218 (6)	-0.0526 (4)
S(4)	0.4813 (3)	0.2750 (2)	-0.1302 (1)	H(10)	0.2264 (7)	0.2155 (6)	0.0359 (4)
S(5)	0.2630 (3)	0.0448 (2)	0.7331 (1)	H(121)	0.256 (1)	0.0691 (7)	0.0340 (6)
S(6)	0.2338 (3)	0.1732 (2)	0.6436 (1)	H(122)	0.229 (1)	0.0080 (7)	-0.0298 (6)
S(7)	0.2494 (3)	0.0571 (2)	0.5532 (1)	H(123)	0.093 (1)	0.0439 (7)	0.0027 (6)
S(8)	0.2789 (3)	-0.0616 (2)	0.6466 (1)	H(131)	0.661 (1)	0.1774 (6)	0.0780 (5)
S(9)	0.8327 (3)	0.3278 (2)	0.7030 (1)	H(132)	0.490 (1)	0.1780 (6)	0.0841 (5)
O(1)	0.7217 (7)	0.3001 (5)	0.7329 (4)	H(141)	0.529 (1)	-0.0136 (6)	-0.1574 (5)
S(10)	0.4504 (3)	0.3963 (2)	0.6452 (1)	H(142)	0.391 (1)	-0.0220 (6)	-0.1174 (5)
O(8)	0.4879 (7)	0.3624 (5)	0.7059 (3)	H(143)	0.543 (1)	0.0140 (6)	-0.0804 (5)
C(1)	0.8042 (8)	0.1973 (8)	-0.1367 (3)	H(15)	-0.0423 (7)	-0.0690 (4)	0.6876 (4)
C(2)	0.8169 (8)	0.1257 (8)	-0.1062 (3)	H(16)	-0.0550 (7)	-0.0683 (4)	0.5658 (4)
C(3)	0.8428 (8)	0.1402 (8)	-0.0427 (3)	H(18)	-0.0889 (7)	0.0772 (4)	0.5274 (4)
C(4)	0.8460 (8)	0.2207 (8)	-0.0340 (3)	H(19)	-0.0973 (7)	0.1665 (4)	0.6255 (4)
C(5)	0.8221 (8)	0.2560 (8)	-0.0921 (3)	H(201)	-0.019 (1)	0.0391 (9)	0.7639 (6)
C(6)	0.831 (2)	0.334 (1)	-0.1031 (9)	H(202)	-0.176 (1)	0.0842 (9)	0.7542 (6)
C(7)	0.1637 (7)	0.1421 (6)	-0.1041 (4)	H(203)	-0.030 (1)	0.1391 (9)	0.7544 (6)
C(8)	0.1625 (7)	0.2220 (6)	-0.1158 (4)	C(21)	0.594 (2)	0.0225 (7)	0.634 (1)
C(9)	0.1884 (7)	0.2606 (6)	-0.0591 (4)	C(22)	0.593 (2)	0.0416 (7)	0.696 (1)
C(10)	0.2055 (7)	0.2045 (6)	-0.0124 (4)	C(24)	0.573 (2)	0.1218 (7)	0.700 (1)
C(11)	0.1902 (7)	0.1313 (6)	-0.0402 (4)	C(25)	0.562 (2)	0.1523 (7)	0.640 (1)
C(12)	0.191 (1)	0.0567 (7)	-0.0076 (6)	C(23)	0.576 (2)	0.0909 (7)	0.599 (1)
C(13)	0.563 (1)	0.1804 (6)	0.0528 (5)	H(21)	0.608 (2)	-0.0341 (7)	0.616 (1)
C(14)	0.477 (1)	0.0119 (6)	-0.1229 (5)	H(22)	0.605 (2)	0.0021 (7)	0.734 (1)
C(15)	-0.0556 (7)	-0.0192 (4)	0.6586 (4)	H(24)	0.567 (2)	0.1540 (7)	0.741 (1)
C(16)	-0.0622 (7)	-0.0189 (4)	0.5943 (4)	H(25)	0.547 (2)	0.2117 (7)	0.627 (1)
C(18)	-0.0802 (7)	0.0580 (4)	0.5740 (4)	C(26)	0.577 (3)	0.107 (2)	0.536 (1)
C(19)	-0.0846 (7)	0.1051 (4)	0.6258 (4)	H(261)	0.514 (3)	0.120 (2)	0.494 (1)
C(17)	-0.0694 (7)	0.0574 (4)	0.6781 (4)	H(262)	0.578 (3)	0.046 (2)	0.544 (1)
C(20)	-0.077 (1)	0.0851 (9)	0.7413 (6)	H(263)	0.677 (3)	0.127 (2)	0.533 (1)
C(27)	0.283 (1)	-0.0646 (6)	0.7284 (5)	C(212)	0.579 (3)	0.1330 (8)	0.676 (1)
C(28)	0.234 (1)	0.2153 (7)	0.7175 (6)	C(222)	0.588 (3)	0.0653 (8)	0.712 (1)
O(2)	0.9525 (9)	0.3248 (8)	0.7448 (5)	C(232)	0.593 (3)	0.0019 (8)	0.672 (1)
O(3)	0.839 (1)	0.2850 (6)	0.6489 (4)	C(252)	0.586 (3)	0.0305 (8)	0.612 (1)
O(4)	0.802 (1)	0.4083 (4)	0.6876 (5)	C(242)	0.577 (3)	0.1115 (8)	0.614 (1)
O(5)	0.780 (2)	0.351 (2)	0.6414 (6)	H(212)	0.574 (3)	0.1907 (8)	0.693 (1)
O(6)	0.894 (2)	0.392 (1)	0.7359 (9)	H(222)	0.591 (3)	0.0625 (8)	0.761 (1)
O(7)	0.927 (2)	0.266 (1)	0.701 (1)	H(242)	0.600 (3)	-0.0576 (8)	0.685 (1)
O(9)	0.557 (1)	0.4499 (7)	0.6363 (5)	H(252)	0.587 (3)	-0.0035 (8)	0.571 (1)
O(10)	0.450 (1)	0.3360 (6)	0.6007 (4)	C(262)	0.576 (4)	0.160 (2)	0.574 (2)
O(11)	0.326 (1)	0.4331 (8)	0.6412 (6)	H(264)	0.558 (4)	0.170 (2)	0.525 (2)
O(12)	0.374 (2)	0.342 (1)	0.6072 (7)	H(265)	0.657 (4)	0.196 (2)	0.594 (2)
O(13)	0.372 (2)	0.4640 (9)	0.6530 (7)	H(266)	0.487 (4)	0.174 (2)	0.593 (2)
O(14)	0.569 (1)	0.417 (1)	0.6203 (8)	H(271)	0.202 (1)	-0.0966 (6)	0.7432 (5)
H(1)	0.7843 (8)	0.2056 (8)	-0.1853 (3)	H(272)	0.376 (1)	-0.0851 (6)	0.7519 (5)
H(2)	0.8085 (8)	0.0701 (8)	-0.1275 (3)	H(281)	0.277 (1)	0.2603 (7)	0.6930 (6)
H(3)	0.8575 (8)	0.0974 (8)	-0.0073 (3)	H(282)	0.301 (1)	0.2017 (7)	0.7583 (6)
				H(283)	0.140 (1)	0.2342 (7)	0.7296 (6)

charge of the complex are varied, as shown in Table III. Complex II is unique in this series in that it serves as a source of a Mo(III)/Mo(III) dimer with a much more negative potential than is normally achieved by dimers in this oxidation state. This suggested to us that a study of the reactions of the sulfido ligands in reduced forms of II might lead to the development of new reaction patterns for this ligand type. These studies are discussed below.

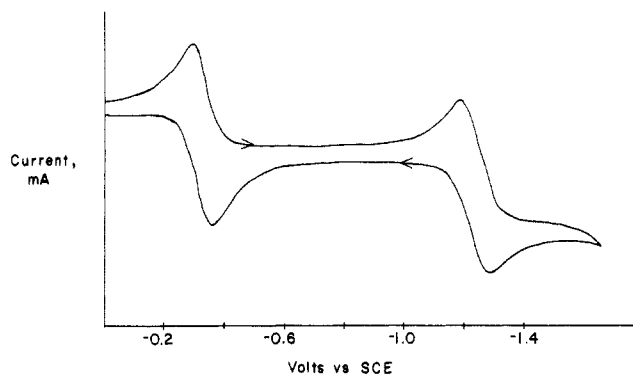
The reactions of  $\mu$ -sulfido ligands with electrophiles, such as that described above for I, is a characteristic reaction consistent with the presence of reactive lone electron pairs on the bridging ligand. However the interactions of the *cis*  $\mu$ -sulfido ligands in these dimers with alkenes and alkynes have been described previously in terms of donation of  $\pi$  electron density from the hydrocarbon to a LUMO with significant sulfur p character,<sup>7</sup> suggesting that

the ligands also have electrophilic properties. The reaction of I with excess methyl lithium (reaction 2) is consistent



(7) DuBois, D. L.; Miller, W. K.; Rakowski DuBois, M. *J. Am. Chem. Soc.* 1981, 103, 5239.

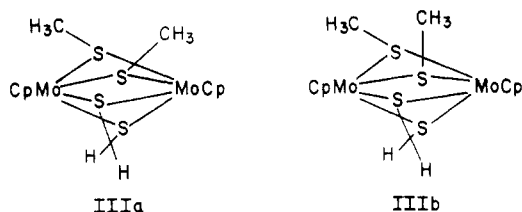
with this proposal. Although anionic intermediates have



**Figure 2.** Cyclic voltammogram for the reductions of a  $10^{-3}$  M solution of  $[(\text{CpMo})_2(\mu\text{-S})(\mu\text{-SCH}_3)\text{S}_2\text{CH}_2]\text{I}$  (II) in acetonitrile (0.1 M  $(n\text{-Bu})_4\text{NBF}_4$ ) at a scan rate of 100 mV/s ( $\Delta E_1 = 70$  mV;  $\Delta E_2 = 80$  mV;  $i_{pc}/i_{pa} = 1$  for both reductions).

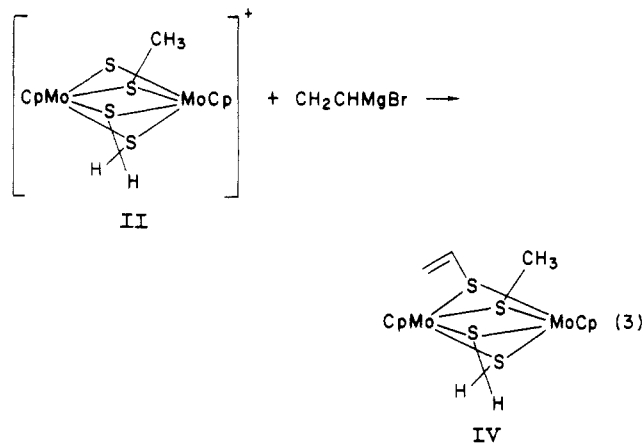
not been characterized, we find that after workup in air, the neutral bis( $\mu$ -methyl thiolate) derivative III is isolated in 74% yield. An alternate synthesis and further characterization of this complex are discussed below.

**Reactions of II with Nucleophiles.** The electrophilic character of the sulfido ligand in the cation II is reflected by its reactivity toward carbanions such as Grignard and alkyllithium reagents. The reaction with methyllithium produces dimer III in 60% yield. The proton NMR spectrum of the air-stable, orange-brown product shows it to be a mixture of two isomers, ee (IIIa) and ea (IIIb).

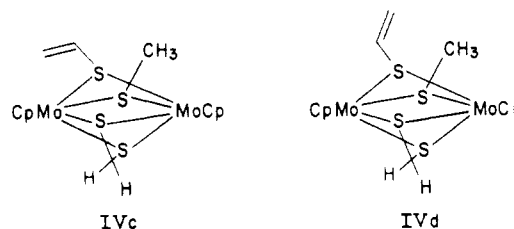


The former isomer has been characterized by an X-ray diffraction study.<sup>2</sup> A mixture enriched in b isomerizes in  $\text{CDCl}_3$  in several hours at room temperature to give an equilibrium mixture of a/b (80%/20%). This isomerization is attributed to inversion at the tricoordinate sulfur atoms. Low activation energies for bridging thiolate isomerizations have been measured for several dimeric complexes,<sup>8</sup> and the proposed trigonal-planar transition state at the sulfur has been modeled recently by a thiolate-bridged copper dimer.<sup>9</sup>

The reaction of II with vinylmagnesium bromide yields IV (reaction 3). The product is an air-stable, orange-brown oil, and attempts to grow crystals for X-ray analysis have not been successful. The proton NMR spectrum of the product is consistent with a mixture of three isomers. In addition to the isomer possibilities that arise from inversion at the sulfur atoms, additional isomers appear to be possible as a result of restricted rotation around the C-S bond of the alkenyl thiolate ligand. Extended Hückel molecular orbital calculations on a related derivative<sup>10</sup> indicate that for the equatorial orientation of this ligand, the energy barrier to rotation about the C-S bond is very



large,<sup>11</sup> with the orientation in IVc being more stable than that in IVd.



Mo(III) derivatives with cis bridging mercapto ligands have been postulated as possible intermediates in hydrogenation reactions,<sup>12</sup> but these have not been isolated or even detected spectrally. Elimination of hydrogen has been proposed as a facile decomposition route for such derivatives.<sup>7</sup> The reaction of II with potential hydride transfer reagents has been investigated as a possible synthetic route to a relatively stable Mo(III) dimer with a single bridging SH ligand (VI). However, such a derivative has proven to be difficult to characterize. II reacts smoothly with  $\text{LiEt}_3\text{H}$  or  $\text{KB}(\text{sec-Bu})_3\text{H}$  in THF in an unexpected boron-to-sulfur alkyl transfer reaction to form  $(\text{CpMo})_2(\mu\text{-SR})(\mu\text{-SCH}_3)\text{S}_2\text{CH}_2$ , R = Et or *sec*-Bu. The products have been isolated and characterized by NMR and mass spectroscopy. A mercury-induced boron-sulfur alkyl transfer has been reported previously.<sup>13</sup> The reaction of II with several other hydridic reagents, such as sodium hydride or  $\text{NaAlH}(\text{O-}t\text{-Bu})_3$ , proceeds in one-electron-transfer steps. The products of these reactions are discussed below. The reduction of II with  $\text{NaBH}_4$  supported on alumina, followed by protonation appears to be the most promising route to a mercapto-bridged derivative. The reaction produces a mixture of products, but the desired complex is evidenced by a resonance at -1.3 ppm in the NMR spectrum and an absorption near  $2400\text{ cm}^{-1}$  in the infrared spectrum. It is of interest to us to characterize both the radical and ionic reactivity of such a derivative, and further work to obtain good yields of the pure product is in progress.

**Synthesis and Reactions of  $(\text{CpMo})_2(\mu\text{-S})(\mu\text{-SCH}_3)\text{S}_2\text{CH}_2$  (V).** As discussed above, II undergoes a reversible one-electron reduction at a potential of -0.34 V vs. SCE in acetonitrile. This reduction product V has been generated by controlled potential electrolysis and also by the addition of 1 equiv of a chemical reducing agent,

(11) The energy barrier was found to be on the order of 12 eV without geometry optimization.

(12) Miller, W. K.; Wright, L. L.; Casewit, C. J.; Rakowski DuBois, M., manuscript in preparation.

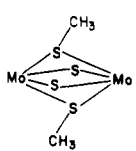
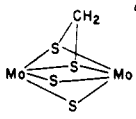
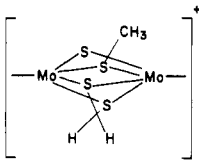
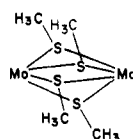
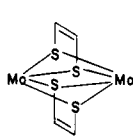
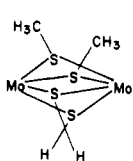
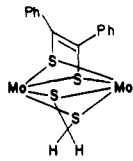
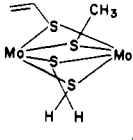
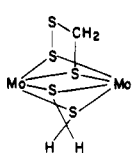
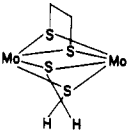
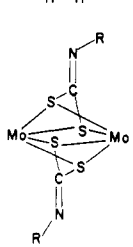
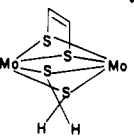
(13) Seyferth, D.; Song L.-C.; Henderson, R. S. *J. Am. Chem. Soc.* 1981, 103, 5103.

(8) (a) Patel, V. D.; Boorman, P. M.; Kerr, K. A.; Moynihan, K. J. *Inorg. Chem.* 1982, 21, 1383 and references cited therein. (b) Benson, I. B.; Knox, S. A. R.; Naish, P. J.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* 1978, 878.

(9) Dance, I. G.; Guernsey, P. J.; Rae, A. D.; Scudder, M. L. *Inorg. Chem.* 1983, 22, 2883.

(10) Calculations were carried out on the analogous simpler molecule  $(\text{C}_5\text{H}_5\text{Mo})_2(\text{S}_2\text{CH}_2)(\mu\text{-SH})(\mu\text{-SC}_2\text{H}_3)$ : Wright, L. L.; DuBois, D. L.; Rakowski DuBois, M., unpublished results.

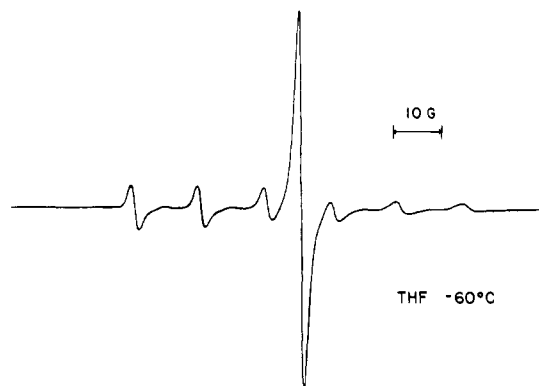
Table III. Reduction Potentials (V vs. SCE) for Cyclopentadienylmolybdenum Dimers<sup>a</sup>

III/III	⇌	III/IV	⇌	IV/IV	⇌	III/III	⇌	III/IV	⇌	IV/IV
			-1.43		+0.57					
			-1.30		+0.27					
	-1.24		-0.34		+1.39 (irrev)					
	-0.15	+0.65			+0.15	+0.64 (irrev)				
	+0.04	+0.76			+0.16	+0.82 <sup>i</sup>				
	+0.12	+0.83			+0.28	+0.84				
	+0.13	+0.79			+0.61	1.1 (irrev)				
	+0.12	+0.51 <sup>h</sup>								

<sup>a</sup> Potentials are reported for the methylcyclopentadienyl derivatives in acetonitrile, 0.1 M  $(n\text{-Bu})_4\text{NBF}_4$  solutions. All cyclic voltammograms are reversible or quasi-reversible with  $\Delta E_p = 60\text{--}100$  mV and  $i_{pc}/i_{pa} = 1$ , unless otherwise noted.

<sup>b</sup> Reference 5. <sup>c</sup> Reference 2. <sup>d</sup> Reference 16. <sup>e</sup> Rakowski DuBois, M.; Haltiwanger, R. C.; Miller, D. J.; Glatzmaier, G. *J. Am. Chem. Soc.* 1979, 101, 5245. <sup>f</sup> Reference 3. <sup>g</sup> Miller, D. J.; Rakowski DuBois, M. *J. Am. Chem. Soc.* 1980, 102, 4925. <sup>h</sup>  $\Delta E_p = 140$  mV. <sup>i</sup>  $\Delta E_p = 190$  mV.

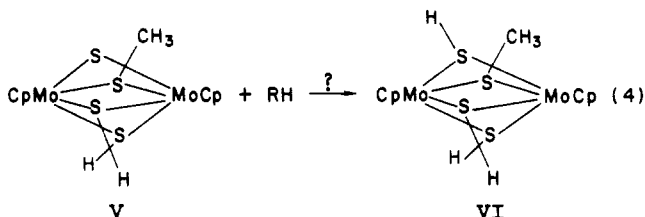
such as sodium hydride or potassium graphite. Characterization of V by cyclic voltammetry shows the expected reversible oxidation and reduction waves at  $-0.34$  and  $-1.24$  V, respectively. The neutral product is formally a mixed-valence Mo(III)/Mo(IV) dimer, which is intense pink in solution and blue as a solid.<sup>14</sup> The radical character of the dimer is confirmed by the EPR spectrum which was recorded at 213 K in THF (Figure 3). The intense signal ( $g = 1.993$ ) is associated with the statistically predominant dimer in which  $I_{\text{Mo1}} = I_{\text{Mo2}} = 0$ . Hyperfine coupling in the

Figure 3. EPR spectrum of  $(\text{CpMo})_2(\mu\text{-S})(\mu\text{-SCH}_3)\text{S}_2\text{CH}_2$  (V).

(14) An electronic absorption is observed at 1360 nm ( $\epsilon 975 \text{ M}^{-1} \text{ cm}^{-1}$ ) in tetrahydrofuran solution. Further discussion of the spectral features of this and related mixed valence dimers will appear elsewhere: Casewit, C. J.; Rakowski DuBois, M., unpublished results.

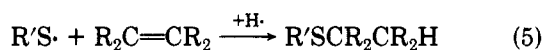
dimer with  $I_{\text{Mo}1} = 0$  and  $I_{\text{Mo}2} = 5/2$  (and vice versa) leads to the lower intensity sextet ( $A = 14$  G). The complex in which  $I_{\text{Mo}1} = I_{\text{Mo}2} = 5/2$  is statistically unlikely, and the resulting 11-line pattern is not observed in this spectrum.<sup>15</sup> The presence of hyperfine coupling with a metal nucleus confirms that the HOMO contains a contribution from metal d orbitals. Although hyperfine coupling was not observed in the spectrum of the previously reported Mo(III)/Mo(IV) dimer  $[\text{CpMo}(\text{SCH}_3)_2]_2^+$ ,<sup>16</sup> the coupling constant for V is smaller than that observed in our laboratory for a related cationic derivative  $[\text{CpMoSC}_2\text{H}_4\text{S}]_2^+$  (38 G). The value is also significantly smaller than those observed for other types of molybdenum dimers<sup>15,17</sup> and for monomeric Mo(III)<sup>18</sup> and Mo(V)<sup>19</sup> complexes, which are generally in the range of 30–70 G.

Because of the relatively small hyperfine coupling constant observed for V, we have attempted to determine whether the electron density might be localized on the bridging sulfido ligand in this complex and whether this ligand might undergo reactions characteristic of sulfur-based radicals. The S–H bond strength of a bridging mercapto ligand such as that in VI (reaction 4) is unknown,



but if we estimate a value similar to those of organic thiols,<sup>20</sup> the abstraction of a hydrogen atom might be expected to proceed with certain activated hydrocarbons (reaction 4), if the sulfido ligand has significant radical character. However, we have not detected the formation of VI resulting from a reaction with the solvent THF ( $D_{\text{C-H}} = 92$  kcal/mol)<sup>21</sup> or with 1,4-cyclohexadiene ( $D_{\text{C-H}} = 76$  kcal/mol)<sup>22</sup> as potential hydrogen sources.

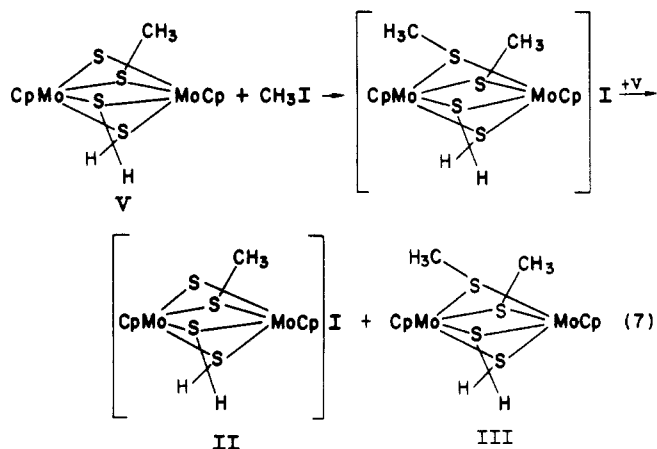
Another reaction characteristic of organic sulfur-based radicals is their attack on alkenes and alkynes (eq 5 and 6).<sup>23</sup> However, no reaction is observed when a solution



of V is stirred with acetylene or ethylene at temperatures ranging from 25 to 60 °C. Phenyl acetylene, which is more reactive toward benzenethiyl radicals than either 1-hexene or 1-hexyne,<sup>24</sup> is also unreactive toward V. We believe

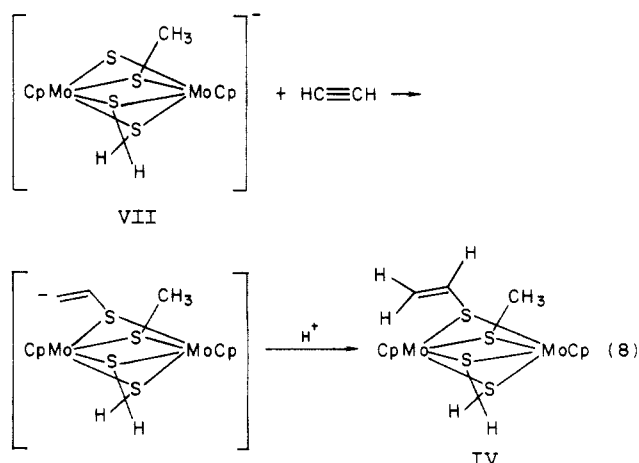
these observations are significant because they suggest that sulfur-based radical reactions are unlikely in the observed hydrogenations of alkynes catalyzed by closely related molybdenum dimers.

The sulfido ligand in V does react with  $\text{CH}_3\text{I}$  to form an approximately equimolar mixture of products as shown in eq 7. Initial formation of an ionic mixed-valence derivative and its redox reaction with V is one pathway which is consistent with both the known redox potentials and the observed products.



**Synthesis and Reactions of  $[(\text{CpMo})_2(\mu\text{-S})(\mu\text{-SCH}_3)\text{S}_2\text{CH}_2]^-$  (VII).** The two-electron reduction product of II has been synthesized by means of chemical reducing agents such as excess  $\text{KC}_8$  or  $\text{NaH}$ . The NMR spectrum of the anionic derivative was obtained after the complex was generated in situ in  $\text{THF-d}_8$  in a sealed NMR tube. For these dimers, as well as for previously characterized derivatives,<sup>2,5</sup> the chemical shifts of the cyclopentadienyl protons serve as a useful indication of formal oxidation states of the metal ions; and the multiplet at 5.07 ppm for VII is characteristic of a Mo(III)/Mo(III) dimer. The products of the reaction of VII with electrophiles are consistent with VII being a quadruply bridged anionic dimer with significant electron density located on the  $\mu$ -sulfido ligand. For example, the reaction with ethyl iodide forms  $(\text{CpMo})_2(\mu\text{-SEt})(\mu\text{-SMe})\text{S}_2\text{CH}_2$  in high yields, and the reaction with II is a quantitative route to the neutral dimer V.

We were particularly interested in determining how this anion reacts with unsaturated molecules. In contrast to V, the anion reacts smoothly in THF with alkynes, including unsubstituted acetylene. The sulfido ligand is involved in the nucleophilic attack as shown in reaction 8. Although the anionic intermediate has not been



(15) The magnetic moments of <sup>96</sup>Mo and <sup>97</sup>Mo are very similar, and their hyperfine coupling constants are assumed to be equivalent. Cotton, F. A.; Frenz, B. A.; Pedersen, E.; Webb, T. R. *Inorg. Chem.* **1975**, *14*, 391.

(16) Connelly, N. G.; Dahl, L. F. *J. Am. Chem. Soc.* **1970**, *92*, 7470.

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(18) Averill, B. A.; Silvis, H. C.; Tieckelmann, R. H.; Orme-Johnson, W. H. In "Molybdenum Chemistry of Biological Significance"; Newton, W. E., Otsuka, S., Eds.; Plenum Press: New York, 1980; p 217.

(19) (a) Spence, J. T.; Minelli, M.; Rice, C. A.; Chasteen, N. C.; Scullane, M. ref 18, p 263. (b) Gardner, J.; Pariyadath, N.; Corbin, J. L.; Stiefel, E. I. *Inorg. Chem.* **1978**, *17*, 897. (c) Pariyadath, N.; Newton, W. E.; Stiefel, E. I. *J. Am. Chem. Soc.* **1976**, *98*, 5388.

(20) The S–H bond dissociation energy for thiols is approximately 90 kcal/mol: Block, E. "Reactions of Organosulfur Compounds"; Academic Press: New York, 1978.

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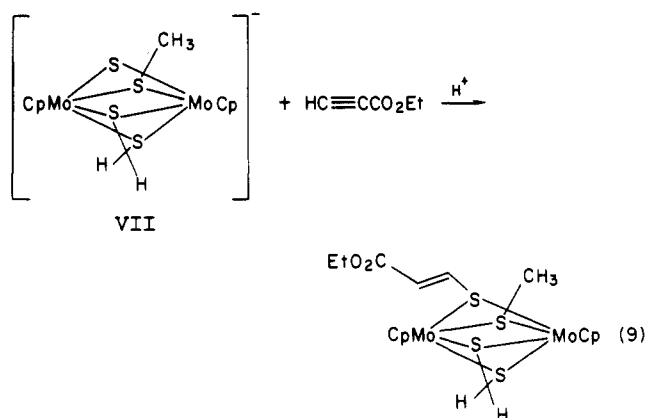
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characterized, the alkenyl thiolate derivative has been isolated in 50–60% yields and identified by comparison of spectral data with those of an authentic sample of IV prepared by reaction 3. The source of the proton was thought to be either a trace of moisture encountered in the solvent or during workup, or the excess acetylene. Two experiments were carried out to investigate these possibilities. Introduction of methyl iodide to the reaction mixture after it had been stirred for 4 days, but prior to workup procedures, did not lead to the formation of a propenyl thiolate derivative suggesting that the vinyl anion had already been protonated. When reaction 8 was carried out with acetylene- $d_2$ , no vinyl proton resonances were observed in the  $^1\text{H}$  NMR spectrum of the vinyl thiolate product. It therefore appears that the excess acetylene serves as the protonating agent in this system.

The reactions of VII with the alkynes diphenylacetylene, ethyl propiolate, and dimethyl acetylenedicarboxylate proceed to form analogous products, which have been identified by NMR and mass spectral data. However the yields are significantly lower for the disubstituted alkynes. In these reactions, protonation presumably occurs during workup. Lower yields may also be a result of unfavorable steric interactions for many of the possible product isomers. Spectral data for the new alkenyl thiolate derivatives are given in the Experimental Section. In the reaction with ethyl propiolate, one major isomer is formed. Analysis of the NMR coupling constants between vinyl protons of the product (15 Hz) indicates that the product is the *trans* isomer resulting from *cis* addition<sup>25</sup> (reaction 9). The

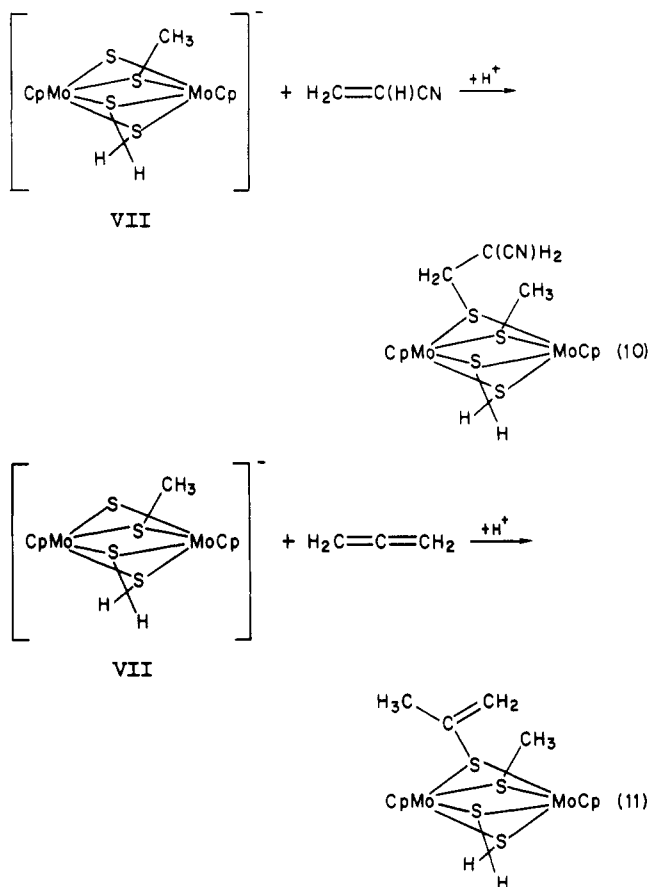


nucleophilic reactivity of the bridging ligand in VII appears to be similar to that of organic thiolates, which are known to react with alkynes to form vinyl sulfides.<sup>26</sup> The latter reactions, however, generally proceed by *trans* addition.<sup>27</sup> It seems likely that the *cis* addition involving the sulfido ligand in VII is dictated by steric interactions between the dimer and the alkyne substituents.

The nucleophilic attack of a coordinated sulfido ligand on an unactivated acetylene has not been reported previously. However, several reactions of activated acetylenes with metal thioanions have been reported. While the formation of alkenyl thiolate ligands has not been observed in these systems, several other modes of reactivity have been identified. For example, the addition of dimethyl acetylenedicarboxylate to  $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]^-$  leads to insertion of the alkyne into a Mo–S bond.<sup>28</sup> The monomeric complex  $\text{Mo}(\text{S})(\text{S}_4)_2^{2-}$  undergoes a complex reaction with

dimethyl acetylenedicarboxylate to form the tris(1,2-dithiolene) complex.<sup>29</sup> In reactions that appear to be quite closely related to those reported here, both 1,2- and 1,1-dithiolate complexes are formed when activated alkynes are added to  $[(\text{CO})_3\text{Fe}(\mu\text{-SH})_2]$  in the presence of base.<sup>30</sup> The sulfido ligand based reactivity described here, which involves a formal electron–proton transfer sequence, may have mechanistic relevance to the reductions of acetylene catalyzed by metal sulfur clusters both in enzymatic<sup>31</sup> and in synthetic systems.<sup>2,32</sup>

The reactivity of VII with other unsaturated molecules has also been investigated. No reaction with ethylene is observed; alkenes are generally less susceptible to nucleophilic attack than alkynes, and a similar difference in reactivity is observed with organic thiolates.<sup>33</sup> The reaction with the activated olefin acrylonitrile is facile at room temperature, and reaction with allene occurs at 60 °C (reactions 10 and 11). Spectral characterization of the



protonated products of each of these reactions suggests that the sulfido atom attacks the  $\beta$ -carbon of acrylonitrile and the central carbon of allene. Similar regioselectivity has been characterized for the nucleophilic attack of organic thiolates on these substrates.<sup>34,35</sup>

Although the relationship between VII and intermediates in the hydrogenation reactions catalyzed by I has not been established, it is interesting to note that the two

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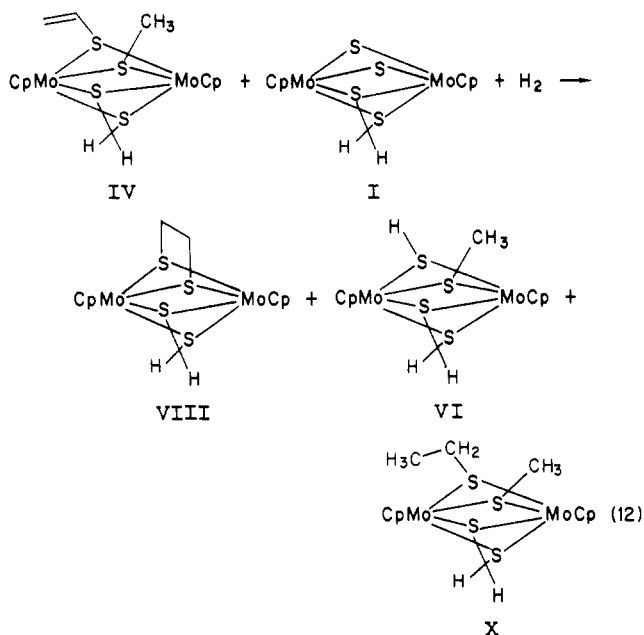
(33) Oae, S.; Ohno, A. In "Organic Chemistry of Sulfur"; Oae, S., Ed.; Plenum Press: New York, 1977; p 119.

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systems share several common characteristics. For example, with catalyst I, ethylene is not reduced, but acrylonitrile is hydrogenated to propionitrile.<sup>36</sup> In the hydrogenation of allene to propene catalyzed by I, a molybdenum dimer with a 2,2-propanedithiolate ligand is formed as a secondary product.<sup>2</sup> This is consistent with attack of the sulfur ligand at the central carbon of allene. In addition, the *cis* addition of the sulfido and proton ions established in reaction 9 may be a model for how the *cis* stereochemistry is preserved in one step of the hydrogenation reaction.

We were interested in establishing under what conditions the alkenyl thiolate ligand in IV could be further reduced to the free alkene. No reaction is observed with hydrogen under conditions used in the hydrogenation reactions, and only traces of C-S hydrogenolysis products are observed after several weeks of heating under hydrogen. This observation is consistent with previous, more general, studies in our laboratory which indicated that Mo(III) dimers with substituents on all four bridging sulfur ligands do not react readily with hydrogen or with unsaturated molecules. The methyl substituent on the sulfur bridge in IV is not present in the hydrogenation catalysts; it may significantly alter the reactivity that is involved in alkene formation in the latter systems. Alternatively, the bridging sulfido ligands in I could play an intermolecular role in the reduction of a vinyl thiolate bridged intermediate in the hydrogenation reactions. In order to investigate this possibility, we have studied the reaction of IV with hydrogen in the presence of 1 mol equiv of I (eq 12).



The reaction proceeds at 60 °C to form a mixture of products. It is significant that the ethylene adduct of complex I, VIII, is a major product when the reaction is carried out in a closed system. NMR data also reveal resonances that are consistent with and tentatively assigned to VI (*vide supra*). The products are consistent with hydrogenolysis of the C-S bond of the alkenyl thiolate ligand in IV. Some hydrogenation of the olefinic bond in the ligand also occurs to form product X, also identified by NMR data. Neither methane nor ethane have been detected, however. The ability of I to promote the reactions of the alkenyl thiolate bridge with hydrogen is at-

tributed to the reactivity of the *cis*  $\mu$ -sulfido ligands. Further studies of such intermolecular interactions are in progress.

**Summary.** Several modes of reactivity have been identified for  $\mu$ -sulfido ligands in cyclopentadienyl dimers of molybdenum. The reactivity depends on the electronic characteristics of the complex as well as on the number and geometric relationship of the ligands. In addition to the initially characterized reaction mode for  $(\text{CpMo}(\mu\text{-S})_2\text{S}_2\text{CH}_2)$ , I, in which the *cis* sulfido ligands comprise a reactive site that forms an adduct with alkenes and alkynes, reactions in which the individual sulfido sites in I show ionic reactivity with electrophiles and nucleophiles have also been characterized. The electrophilic and nucleophilic reactivity at the ligands can be enhanced by synthesizing cationic and anionic derivatives, respectively. The  $\mu$ -sulfido ligand in the anion  $[(\text{CpMo})_2(\mu\text{-S})(\mu\text{-SCH}_3)_2\text{S}_2\text{CH}_2]^-$  appears to have nucleophilic strength similar to that of an organic thiolate anion. A  $\mu$ -sulfido ligand in a mixed-valence Mo(III)/Mo(IV) dimer does not display radical character, and no radical reactions of the bridging ligands in this series of dimers have been identified.

### Experimental Section

**Materials.** Bis[(methylcyclopentadienyl)molybdenum tricarbonyl] was purchased from Alfa or synthesized by a published procedure.<sup>37</sup> Reagent grade alkenes and alkynes were used without further purification. Allene was purchased from Liquid Carbonic, acetylene and ethylene were purchased from Matheson, and acetylene-*d*<sub>2</sub> from Cambridge Isotope Laboratories. Potassium graphite, lithium triethylhydridoborate in THF, methyl lithium in ether, and vinylmagnesium bromide in THF and NaBH<sub>4</sub> supported on Al<sub>2</sub>O<sub>3</sub> were obtained from Alfa. Dry NaH and potassium tri-*sec*-butylborohydride were purchased from Aldrich. Tetrahydrofuran was distilled from LiAlH<sub>4</sub> or CaH<sub>2</sub> prior to use. Acetonitrile used in cyclic voltammetric studies was dried over CaH<sub>2</sub>, filtered, and distilled from P<sub>2</sub>O<sub>5</sub>.

**Physical Measurements.** Routine <sup>1</sup>H NMR spectra were measured at 90 MHz on a Varian 390 spectrometer. High-field <sup>1</sup>H NMR spectra were recorded on a Bruker WM-250 spectrometer. Infrared spectra were obtained on a Perkin-Elmer 337 spectrophotometer. Mass spectra were measured at 70 eV on a Varian MAT CH-5 spectrometer. EPR spectra were recorded on a Varian E-109 X-band spectrometer. Elemental analyses were provided by Spang Laboratories. Cyclic voltammetric studies were carried out with a Princeton Applied Research 174A polarographic analyzer on millimolar solutions of complexes in acetonitrile/0.1 M *n*-Bu<sub>4</sub>NBF<sub>4</sub>. Platinum wires were used as working and auxiliary electrodes. The saturated calomel reference electrode was separated from the test solution by a bridge tube tipped with a Vycor frit.  $\Delta E_p$  for a reversible one-electron oxidation of a standard compound, ferrocene, was found to be 80 mV for this cell system. Controlled potential electrolysis was carried out with a Princeton Applied Research 371 potentiostat-galvanostat and 379 digital coulometer. The working and counterelectrodes were platinum gauze, and the reference electrode was a Ag/AgCl wire.

**X-ray Diffraction Study of  $[(\text{CpMo})_2(\mu\text{-S})(\mu\text{-SCH}_3)_2\text{S}_2\text{CH}_2]\text{HSO}_4$ .** Crystals suitable for X-ray diffraction were obtained by slow evaporation of a wet methanol solution of the fluorosulfate salt of II. During the course of evaporation, hydrolysis of the anion apparently occurred,<sup>38</sup> and crystals were isolated as the HSO<sub>4</sub><sup>-</sup> salt. Details of the crystal data, experimental conditions, and a summary of solution and refinement details are given in Table IV. In the final model with the exception of disordered atoms, all non-hydrogen atoms were refined anisotropically. Hydrogen atoms, held in idealized geometries ( $d(\text{C-H}) = 1.08 \text{ \AA}$ ) with the methyl moieties treated as rigid groups, were refined with two common fixed isotropic thermal parameters, one

(37) King, R. B. "Organometallic Syntheses"; Academic Press: New York, 1965; Vol. 1, p 109.

(38) Fluorosulfates are readily hydrolyzed: Jacke, A. W. *Adv. Inorg. Chem. Radiochem.* 1974, 16, 177.

(36) McKenna, M. Ph.D. Dissertation, University of Colorado, Boulder, CO, 1984.



for methyl hydrogens and one for non-methyl hydrogens. There are three disordered groups in the unit cell, both  $\text{HSO}_4^-$  anions and the methylcyclopentadiene on Mo(4). The sulfur atom and one of the oxygen atoms on each  $\text{HSO}_4^-$  anion appear to be well-defined. The oxygen is held in position by the hydrogen bond that links the two bisulfate anions ( $d(\text{O}(1)-\text{O}(8)) = 2.607 \text{ \AA}$ ). The other three oxygens are found in two orientations corresponding to rotations about the SO bond, both partially stabilized by hydrogen-bonding interactions. The anions were refined with constrained bond distances and isotropic thermal parameters for the disordered atoms. The disordered cyclopentadiene was refined as a rigid group with isotropic thermal parameters. Occupancy factors for all disordered atoms were determined by refinement and then held fixed.

**Syntheses.** Reactions were carried out under a nitrogen atmosphere and products isolated in air unless noted.

**(CpMoS)<sub>2</sub>S<sub>2</sub>CH<sub>2</sub> (I).** The synthesis and characterization of this compound has been reported previously.<sup>2</sup>

**[(CpMo)<sub>2</sub>(μ-S)(μ-SCH<sub>3</sub>)S<sub>2</sub>CH<sub>2</sub>] (II).** (CpMoS)<sub>2</sub>S<sub>2</sub>CH<sub>2</sub> (1.96 g, 4 mmol) was dissolved in 70 mL of THF, and 0.4 mL of CH<sub>3</sub>I (6.4 mmol) was added. The mixture was stirred at 25 °C for 3 h, cooled in an ice/salt bath, and then filtered. The resulting purple powder was washed several times with diethyl ether; yield 1.95 g (77%). The product was further purified by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/ether: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.61 (s, 3, SCH<sub>3</sub>), 2.41 (s, 6, CH<sub>3</sub>Cp), 4.48 (s, 2, S<sub>2</sub>CH<sub>2</sub>), 6.86 (s, 8, Cp); mass spectrum, *m/e* 492 (P - CH<sub>3</sub>), 446 (Cp<sub>2</sub>Mo<sub>2</sub>S<sub>3</sub>), 142 (CH<sub>3</sub>I), 127 (I). Anal. Calcd for Mo<sub>2</sub>S<sub>4</sub>C<sub>14</sub>H<sub>9</sub>I: C, 26.50; H, 3.00; S, 20.19. Found: C, 26.53; H, 3.08; S, 20.21. The alkylation of (CpMoS)<sub>2</sub>S<sub>2</sub>CH<sub>2</sub> with methyl iodide is reversible, and solutions of this salt decompose at 60 °C to some extent to give starting materials. Therefore reactions of II were carried out at room temperature.

**(CpMo)<sub>2</sub>(μ-SCH<sub>3</sub>)<sub>2</sub>S<sub>2</sub>CH<sub>2</sub> (III).** A 1.9 M solution of methyl lithium in diethyl ether (0.5 mL, 0.95 mmol) was added to a slurry of II (0.29 g, 0.45 mmol) in 50 mL of THF. The brown solution was stirred for 2 h and filtered and the filtrate dried in vacuo. The resulting solid was eluted on an alumina column with CH<sub>2</sub>Cl<sub>2</sub>. The orange-brown fraction was collected and the solvent removed to give 144 mg product: yield 61%; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.35, 1.53 (SCH<sub>3</sub>, ae isomer), 1.37 (SCH<sub>3</sub>, ee isomer), 2.00 (s, 6, CH<sub>3</sub>Cp), 5.39 (s, 10, Cp + SCH<sub>2</sub>). An alternate synthesis and additional characterization data are reported elsewhere.<sup>2</sup>

**(CpMo)<sub>2</sub>(μ-SCHCH<sub>3</sub>)(μ-SCH<sub>3</sub>)S<sub>2</sub>CH<sub>2</sub> (IV).** A 1.3 M solution of vinylmagnesium bromide in THF (1.1 mL, 1.4 mmol) was added to a slurry of II (0.29 g, 0.45 mmol) in 40 mL of THF. The resulting brown solution was stirred for 1 h and filtered and the filtrate dried in vacuo. The crude brown product was eluted on an alumina column with CH<sub>2</sub>Cl<sub>2</sub>. The first orange-brown band was collected and the solvent removed to give 194 mg of orange-brown oil: yield 80%; IR (neat) 1575 cm<sup>-1</sup> (ν<sub>C=C</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>) major isomer δ 1.42 (s, 3, SCH<sub>3</sub>), 1.97 (s, 6, CH<sub>3</sub>Cp), 4.92 (d, 1, CH, *J* = 9 Hz), 5.18 (d, 1, CH, *J* = 16 Hz), 5.56 (m, 1, SCH), 5.38 (d, 10, Cp + S<sub>2</sub>CH<sub>2</sub>); mass spectrum, *m/e* 534 (P), 519 (P - CH<sub>3</sub>), 473 (P - CH<sub>3</sub> - SCH<sub>3</sub>), 446 (Cp<sub>2</sub>Mo<sub>2</sub>S<sub>3</sub>).

**(CpMo)<sub>2</sub>(μ-SCH<sub>2</sub>CH<sub>3</sub>)(μ-SCH<sub>3</sub>)S<sub>2</sub>CH<sub>2</sub> (V).** A 0.95 M solution of LiBHET<sub>3</sub> in THF (1.1 mL, 1.0 mmol) was added to a slurry of II (0.23 g, 0.36 mmol) in 30 mL of THF. After the brown solution was stirred for 1 h, the solvent was evaporated and the crude product was purified by chromatography through an alumina column. Elution with CH<sub>2</sub>Cl<sub>2</sub> produced a brown band that was collected and dried; yield of red-brown oil 150 mg (78%). Two isomers of the product are observed by <sup>1</sup>H NMR in CDCl<sub>3</sub>: isomer A, δ 0.82 (t, 3, CCH<sub>3</sub>, *J* = 8 Hz), 1.37 (s, 3, SCH<sub>3</sub>), 1.69 (q, 2, SCH<sub>2</sub>, *J* = 8 Hz); isomer B, δ 0.83 (t, 3, CCH<sub>3</sub>, *J* = 8 Hz), 1.31 (s, 3, SCH<sub>3</sub>), 2.12 (q, 2, *J* = 8 Hz), 2.02 (s, 6, CH<sub>3</sub>Cp), 5.43 (m, 10, Cp + S<sub>2</sub>CH<sub>2</sub>); mass spectrum, *m/e* 536 (P), 507 (P - CH<sub>2</sub>CH<sub>3</sub>), 461 (P - CH<sub>2</sub>CH<sub>3</sub> - SCH<sub>2</sub>), 446 (Cp<sub>2</sub>Mo<sub>2</sub>S<sub>3</sub>). A similar procedure was used to prepare (CpMo)<sub>2</sub>(μ-S(*sec*-butyl))(μ-SCH<sub>3</sub>)S<sub>2</sub>CH<sub>2</sub> in 54% yield from II and KB(*sec*-butyl)<sub>3</sub>H: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.5–0.9 (m, 9, SCH[(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>3</sub>)]), 1.33 (s, 3, SCH<sub>3</sub>), 1.98 (s, 6, CH<sub>3</sub>Cp), 5.42 (m, 10, Cp + S<sub>2</sub>CH<sub>2</sub>); mass spectrum, *m/e* 564 (P), 507 (P - CH(CH<sub>3</sub>)-CH<sub>2</sub>CH<sub>3</sub>), 461 (P - CH(CH<sub>3</sub>)-CH<sub>2</sub>CH<sub>3</sub> - SCH<sub>2</sub>), 446 (Cp<sub>2</sub>Mo<sub>2</sub>S<sub>3</sub>).

**(CpMo)<sub>2</sub>(μ-S)(μ-SCH<sub>3</sub>)S<sub>2</sub>CH<sub>2</sub> (V).** A solution of [(CpMo)<sub>2</sub>(μ-S)(μ-SCH<sub>3</sub>)S<sub>2</sub>CH<sub>2</sub>]K (see below for synthesis of this dimer) in THF was added to 1.1 equiv of II with stirring. After being stirred for 5 min, the intensely pink solution containing the product was

Table IV. Crystal Data and Details of the Structure Determination for [(CpMo)<sub>2</sub>(μ-S)(μ-SCH<sub>3</sub>)S<sub>2</sub>CH<sub>2</sub>]HSO<sub>4</sub>

		Crystal Data	
formula	Mo <sub>2</sub> S <sub>4</sub> C <sub>14</sub> H <sub>11</sub> <sup>+</sup> HSO <sub>4</sub> <sup>-</sup>	β, deg	97.89 (2)
mol wt	604.49	vol., Å <sup>3</sup>	3903 (2)
space group <sup>a</sup>	P2 <sub>1</sub> /n	Z	8
cryst system	monoclinic	D(calcd),	2.057
a, b, Å	10.155 (2)	g/cm <sup>3</sup>	
b, Å	17.478 (9)	F(000)	2400
c, Å	22.201 (7)	Mμ, cm <sup>-1</sup>	17.87
Data Collection and Reduction			
diffractometer	Syntex P1		
radiation, Å	Mo Kα (0.710 69)		
takeoff angle for graphite monochromator, deg	4.0		
temp, K	294–296		
cryst dimens, mm	0.4 × 0.4 × 0.5		
scan technique	θ–2θ		
2θ min–max, deg	3.0–38.0		
hkl values scanned	+h; +, –k; +, –l		
scan speed, deg/min	3.5		
scan range, deg below Kα <sub>1</sub> and above Kα <sub>2</sub>	0.725, 0.725		
bkgd	stationary		
	crystal–stationary counter;		
	bkgd time = scan time		
check reflctns	(7, –5, 2), (1, 8, 0)		
freq	every 75 measurements		
variati	random, net 0% decay		
no. of reflctns measd	6669		
no. of unique reflctns	3170		
agreement factor	0.037		
during averaging			
no. of obsd reflctns	2695		
σ criterion	F > 6σ(F)		
abs correctn	none		
Structure Determination and Refinement			
method of phase determinatn	direct methods, DIRDIF <sup>c</sup>		
programs	SHELX, <sup>d</sup> PLATO, <sup>e</sup> and others <sup>f</sup>		
scattering factors	neutral atoms <sup>g</sup>		
R <sub>1</sub> and R <sub>2</sub> <sup>h</sup>	0.040, 0.055		
weight	2.15/(σ <sup>2</sup> F + 0.0004F <sup>2</sup> )		
no. of parameters	444		
ratio of observns to parameters	6/1		
residual electron density, e/Å <sup>3</sup>	0.9		

<sup>a</sup> This nonstandard setting was chosen to minimize the β angle (98 vs. 108°). The systematic absence are *h*0*l*, *h* + *l* = 2*n* + 1, and 0*h*0, *k* = 2*n* + 1. The equivalent positions are *x*, *y*, *z*, –*x*, –*y*, –*z*, 1/2 – *x*, 1/2 + *y*, 1/2 – *z*, and 1/2 + *x*, 1/2 – *y*, 1/2 + *z*.

<sup>b</sup> Cell dimensions were determined by least-squares fit of the setting angles of 15 reflections with 2θ in the range 25–32. <sup>c</sup> Main, P. MULTAN 78, A system of Computer Programs for the Automatic Solution of Crystal Structures; Department of Physics, University of York: York, England, 1978. Beurskens, P. T.; Bosman, W. P.; Doesburg, H. M.; Gould, R. O.; van den Hark, Th. E. M.; Prick, P. A.; Noordik, J. H.; Buerkens, G.; Parthasarathi, V.; Bruinsslot, H. J.; Haltiwanger, R. C. DIRDIF, Technical Report 1983/1; Crystallography Laboratory, Toernooiveld: 6525 ED Nijmegen, The Netherlands. <sup>d</sup> Sheldrick, G. M. SHELX76, A Program for Crystal Structure Determination; University of Cambridge: Cambridge, England. <sup>e</sup> Spek, A. L. "Computational Crystallography"; Sayre, D., Ed.; Clarendon Press: Oxford, 1982; p 528. <sup>f</sup> The data reduction program was written in this laboratory. Other programs were contained in or derived from the Northwestern Crystallographic Computing Library of Dr. J. A. Ibers. <sup>g</sup> "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4. <sup>h</sup> The quantity minimized in the least squares procedures is  $\sum \{w(|F_o| - |F_c|)^2\}$ ,  $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$ , and  $R_2 = \sum \{w(|F_o| - |F_c|)^2\} / \sum (F_o)^2$ .

passed through a glass wool plug and the solvent removed in vacuo. The resulting solid was redissolved in diethyl ether and filtered. The solvent was removed, and the blue solid was washed with pentane and dried in vacuo. Anal. Calcd for  $\text{Mo}_2\text{S}_4\text{C}_{14}\text{H}_{19}$ : C, 33.14 H, 3.77; S, 25.27. Found: C, 33.08; H, 3.93; S, 25.30.

**Reaction of V with Air.** A THF solution of V was exposed to air at room temperature. After the solvent was removed, the crude product was chromatographed on alumina with  $\text{CH}_2\text{Cl}_2$  to produce an orange-pink (I) and a purple-pink (II) fraction.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): fraction I,  $\delta$  0.91 (s, 3,  $\text{SCH}_3$ ), 1.30 (s, 3,  $\text{SCH}_3$ ), 1.45 (s, 1), 1.70 (s, 2), 1.93 (s, 6,  $\text{CH}_3\text{Cp}$ ), 2.26 (s, 6,  $\text{CH}_3\text{Cp}$ ), 5.35 (m, 10,  $\text{Cp} + \text{S}_2\text{CH}_2$ ), 6.23 (m, 8,  $\text{Cp}$ ); fraction II,  $\delta$  1.06 (s, 3,  $\text{SCH}_3$ ), 1.29 (s, 3,  $\text{SCH}_3$ ), 1.51 (s, 1), 1.74 (s, 2), 1.93 (s, 6,  $\text{CH}_3\text{Cp}$ ), 2.26 (s, 6,  $\text{CH}_3\text{Cp}$ ), 5.35 (m, 10,  $\text{Cp} + \text{S}_2\text{CH}_2$ ), 6.18 (s, 8,  $\text{Cp}$ ). Although structures have not yet been established, the spectral data are included here because the products appear to be specific to air oxidation of V. Their presence in oxidized reaction mixtures has been taken as evidence for lack of reactivity of V with other reagents.

**Attempted Reaction of V with Acetylenes or Ethylene.** A THF solution of V (0.16 mmol) was degassed in one freeze-pump-thaw cycle, and 1 atm of acetylene or ethylene was added at room temperature. The solution was heated at 60 °C for 3–5 days. Removal of the solvent in air provided only high yields of the product characteristic of air oxidation of V. Reaction of V in THF with 1.1 equiv of phenylacetylene at 60 °C for 4 days also resulted in no reaction.

**Attempted Reaction of V with 1,4-Cyclohexadiene.** A solution of V (0.16 mmol) was added to 3.3 equiv of 1,4-cyclohexadiene in 5 mL of THF. The solution was degassed in one freeze-pump-thaw cycle and stirred at 60 °C for 2 days. After removal of the solvent in air, only the product characteristic of air oxidation of V was detected.

**Reaction of V with Methyl Iodide.** A solution of V (0.16 mmol) was added to 50  $\mu\text{L}$  of  $\text{CH}_3\text{I}$  (0.80 mmol). The solution was degassed in one freeze-pump-thaw cycle. As soon as the solution thawed, dark solids began to precipitate and the solution turned brown. Stirring was continued for another 2 days at 25 °C. The mixture was filtered to give a purple solid and orange-brown filtrate. The solvent was removed from the filtrate; the product was characterized spectrally and identified as III (yield 38%). The purple solid was purified by recrystallization from  $\text{CH}_2\text{Cl}_2$ /diethyl ether and identified spectrally as II (yield 33%). A similar reaction of V (0.16 mmol) with ethyl iodide gave  $(\text{CpMo})_2(\mu\text{-SCH}_3)(\mu\text{-SCH}_2\text{CH}_3)\text{S}_2\text{CH}_2$  (yield 50%) and II (yield 38%).

**$(\text{CpMo})_2(\mu\text{-S})(\mu\text{-SCH}_3)\text{S}_2\text{CH}_2$  (VII).** NaH (0.2 g, 0.75 mmol) was added to a slurry of II (0.10 g, 0.16 mmol) in 20 mL of THF. The mixture was degassed in three freeze-pump-thaw cycles and stirred at 25 °C. After about 3 days a yellow-brown solution of the product was obtained. Alternatively, the product could be prepared by stirring an excess of  $\text{KC}_8$  with a slurry of II in THF under  $\text{N}_2$  for 10 min. Solutions of VII prepared from NaH or  $\text{KC}_8$  were filtered by passing through a glass wool plug. All manipulations of these solutions were carried out under a nitrogen atmosphere or vacuum:  $^1\text{H}$  NMR ( $\text{THF-}d_6$ )  $\delta$  1.36 (s, 3,  $\text{SCH}_3$ ), 1.90 (s, 6,  $\text{CH}_3\text{Cp}$ ), 5.07 (m, 10,  $\text{Cp} + \text{S}_2\text{CH}_2$ ).

**Reaction of VII with Ethyl Iodide.** A THF solution of VII (0.16 mmol) was added to 50  $\mu\text{L}$  of ethyl iodide (0.63 mmol). The solution was degassed in one freeze-pump-thaw cycle and stirred at 25 °C for 3 days. The crude product was eluted in air on an alumina column with  $\text{CH}_2\text{Cl}_2$ . The orange-brown band was collected and the solvent removed to give 59 mg of  $(\text{CpMo})_2(\mu\text{-SCH}_2\text{CH}_3)(\mu\text{-SCH}_3)\text{S}_2\text{CH}_2$ ; yield 69%.

**Reaction of VII with Acetylene.** A THF solution of VII (0.16 mmol) was degassed in two freeze-pump-thaw cycles and 1 atm of acetylene added at 25 °C. The solution was protected from light and stirred at 60 °C for 3 days. The solvent was removed in vacuo and the crude product chromatographed in air on an alumina column. Elution with  $\text{CH}_2\text{Cl}_2$  produced an orange-brown band. The solvent was removed and the product was identified as IV by spectral data; yield 64%.

**Attempted Trapping of  $(\text{CpMo})_2(\mu\text{-SCHCH})(\mu\text{-SCH}_3)\text{S}_2\text{CH}_2$ .** Acetylene was added to VII (0.16 mmol) as described above. The solution was stirred at 25 °C in the absence of light. After 4 days the solution was degassed in one freeze-pump cycle and 100  $\mu\text{L}$  of  $\text{CH}_3\text{I}$  (1.6 mmol) was condensed in.

The thawed solution was stirred for 5 min, and then the solvent was removed. The crude product was eluted on an alumina column with  $\text{CH}_2\text{Cl}_2$ . The orange-brown band was collected to give 76 mg of product.  $^1\text{H}$  NMR and mass spectral data of the product are consistent with a 50:50 mixture of III and IV.

**$(\text{CpMo})_2(\mu\text{-SC}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5))(\mu\text{-SCH}_3)\text{S}_2\text{CH}_2$ .** A THF solution of VII (0.16 mmol) was added to diphenylacetylene (1.14 g, 6.4 mmol). The yellow-brown solution was degassed in two freeze-pump-thaw cycles and stirred at 60 °C for 7 days. The solvent was removed, and chromatography on an alumina column with pentane/ $\text{CH}_2\text{Cl}_2$  provided a yellow fraction. Removal of the solvent followed by hexane extraction and chromatography on alumina with hexane/chloroform gave a yellow oil in very low yield (<5%): 250-MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.43 (s, 3,  $\text{SCH}_3$ ), 2.08 (s, 6,  $\text{CH}_3\text{Cp}$ ), 5.35 (d, 10,  $\text{Cp} + \text{S}_2\text{CH}_2$ ), 6.31 (s, 1,  $\text{C}=\text{CH}$ ), 6.7–7.2 (m, 10,  $\text{C}_6\text{H}_5$ ); mass spectrum,  $m/e$  686 (P), 671 (P -  $\text{CH}_3$ ), 507 (P -  $(\text{C}_6\text{H}_5)_2\text{C}_2\text{H}$ ), 461 (P -  $(\text{C}_6\text{H}_5)_2\text{C}_2\text{H}-\text{SCH}_2$ ), 446 ( $\text{Cp}_2\text{Mo}_2\text{S}_3$ ).

**$(\text{CpMo})_2(\mu\text{-SCHCH}(\text{CO}_2\text{CH}_2\text{CH}_3))(\mu\text{-SCH}_3)\text{S}_2\text{CH}_2$ .** A THF solution of VII (0.16 mmol) was added to 20  $\mu\text{L}$  of ethyl propiolate (0.2 mmol) in 5 mL of THF. The resulting orange-brown solution was degassed in two freeze-pump-thaw cycles and stirred at 25 °C in the absence of light. After 6 days the solvent was removed and the products were eluted on an alumina column with  $\text{CH}_2\text{Cl}_2$ /diethyl ether. The first orange brown fraction contained the desired product, but it was contaminated with traces of the air oxidation product of V: 250-MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.19 (t, 3,  $\text{CH}_3$ ,  $J = 7$  Hz), 1.52 (s, 3,  $\text{SCH}_3$ ), 2.02 (s, 6,  $\text{CH}_3\text{Cp}$ ), 4.05 (q, 2,  $\text{OCH}_2$ ,  $J = 7$  Hz), 5.49 (m, 10,  $\text{SCH}_2 + \text{Cp}$ ), 5.84 (d, 1,  $\text{CH}$ ,  $J = 15$  Hz), 6.65 (d, 1,  $\text{CH}$ ,  $J = 15$  Hz); mass spectrum,  $m/e$  606 (P), 591 (P -  $\text{CH}_3$ ), 542 (P -  $\text{CH}_3 - \text{SCH}_2$ ), 446 ( $\text{Cp}_2\text{Mo}_2\text{S}_3$ ).

**Attempted Reaction of VII with Ethylene.** The reaction was carried out under conditions identical with those described above for the reaction of VII with acetylene. No  $(\text{CpMo})_2(\mu\text{-SCH}_2\text{CH}_3)(\mu\text{-SCH}_3)\text{S}_2\text{CH}_2$  was observed by  $^1\text{H}$  NMR of the crude or chromatographed products.

**$(\text{CpMo})_2(\mu\text{-SCH}_2\text{CH}_2\text{CN})(\mu\text{-SCH}_3)\text{S}_2\text{CH}_2$ .** A THF solution of VII (0.16 mmol) was added to 42  $\mu\text{L}$  (0.64 mmol) of acrylonitrile in 15 mL of THF. The resulting orange-brown solution was degassed in two freeze-pump-thaw cycles and stirred at 25 °C in the dark. After 3 days the solvent was removed and the products chromatographed on an alumina column. Elution with  $\text{CH}_2\text{Cl}_2$  produced an orange band containing the pure product as an orange brown oil in 32% yield: 250-MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 1.40 (s, 3,  $\text{SCH}_3$ ), 1.92 (t, 2,  $\text{CH}_2$ ,  $J = 7$  Hz), 2.08 (s, 6,  $\text{CH}_3\text{Cp}$ ), 2.20 (t, 2,  $\text{CH}_2$ ,  $J = 7$  Hz), 5.55 (m, 10,  $\text{Cp} + \text{S}_2\text{CH}_2$ ); mass spectrum,  $m/e$  561 (P), 507 (P -  $\text{CH}_2\text{CH}_2\text{CN}$ ), 461 (P -  $\text{CH}_2\text{C}-\text{H}_2\text{CN} - \text{SCH}_2$ ), 446 ( $\text{Cp}_2\text{Mo}_2\text{S}_3$ ).

**$(\text{CpMo})_2(\mu\text{-SC}(\text{CH}_3)\text{CH}_2)(\mu\text{-SCH}_3)\text{S}_2\text{CH}_2$ .** A THF solution of VII was degassed in two freeze-pump-thaw cycles and 1 atm of allene added at 25 °C. The solution was stirred at 60 °C in the dark. After 10 days the solvent was removed and the products were chromatographed on an alumina column. Elution with  $\text{CH}_2\text{Cl}_2$  provided a yellow band that was collected and dried in vacuo:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.45 (s, 3,  $\text{SCH}_3$ ), 1.63 (br s, 3,  $\text{SC}(\text{CH}_3)$ ), 2.09 (s, 6,  $\text{CH}_3\text{Cp}$ ), 4.44 (br s, 1,  $\text{CH}$ ), 4.97 (m, 1,  $\text{CH}$ ), 5.53 (m, 10,  $\text{Cp} + \text{S}_2\text{CH}_2$ ); mass spectrum,  $m/e$  548 (P). NMR resonances for  $(\text{CpMo})_2(\text{SCH}_2\text{CCH}_2\text{S})\text{S}_2\text{CH}_2^2$  (25%) were also observed.

**$(\text{CpMo})_2(\mu\text{-SC}(\text{CO}_2\text{CH}_3)\text{CH}(\text{CO}_2\text{CH}_3))(\mu\text{-SCH}_3)\text{S}_2\text{CH}_2$ .** A THF solution of VII (0.16 mmol) was added to 20  $\mu\text{L}$  of dimethyl acetylenedicarboxylate (0.16 mmol) in 15 mL of THF. The solution was degassed in two freeze-pump-thaw cycles, protected from light, and stirred at 60 °C for 3 days. The solvent was removed in vacuo and the crude product eluted on an alumina column with  $\text{CH}_2\text{Cl}_2$ . The second pink-brown fraction contained  $(\text{CpMo})_2(\mu\text{-SC}(\text{CO}_2\text{CH}_3)\text{CH}(\text{CO}_2\text{CH}_3))(\mu\text{-SCH}_3)\text{S}_2\text{CH}_2$  and the material characteristic of exposure of V to air:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.48 (s, 3,  $\text{SCH}_3$ ), 2.10 (s, 6,  $\text{CH}_3\text{Cp}$ ), 3.58 (s, 3,  $\text{CH}_3\text{O}$ ), 3.75 (s, 3,  $\text{CH}_3\text{O}$ ), 5.49 (m, 10,  $\text{Cp} + \text{S}_2\text{CH}_2$ ); mass spectrum,  $m/e$  650 (P), 635 (P -  $\text{CH}_3$ ), 589 (P -  $\text{CH}_3 - \text{SCH}_2$ ), 530 (P -  $\text{CH}_3 - \text{SCH}_2 - \text{CO}_2\text{CH}_3$ ), 461 (P -  $(\text{CH}_3\text{O}_2\text{C})_2\text{C}_2\text{H} - \text{SCH}_2$ ), 446 ( $\text{Cp}_2\text{Mo}_2\text{S}_3$ ).

**Attempted Hydrogenolysis of  $(\text{CpMo})_2(\mu\text{-SCHCH}_2)(\mu\text{-SCH}_3)\text{S}_2\text{CH}_2$ .** A 10-mg sample of IV was dissolved in  $\text{CDCl}_3$  in an NMR tube. The solution was degassed in three freeze-pump-thaw cycles. Slightly less than 1 atm of  $\text{H}_2$  was added at -196 °C, and the tube was then sealed at this temperature. A

sealed NMR tube containing 11 mg of  $(\text{CpMo})_2(\text{SCHCHS})\text{S}_2\text{CH}_2$ ,  $\text{H}_2$ , and  $\text{CDCl}_3$  was prepared in the same way. Both NMR tubes were heated at  $60^\circ\text{C}$  and the NMR spectra monitored periodically. After about 20 h the hydrogenation of  $(\text{CpMo})_2(\text{SCHCHS})\text{S}_2\text{CH}_2$  to  $(\text{CpMo})_2(\text{SCH}_2\text{CH}_2\text{S})\text{S}_2\text{CH}_2$  was complete. Only starting material was observed in the reaction of  $\text{H}_2$  with IV, even after 7 days of heating. The reaction of IV with  $\text{H}_2$  was repeated as described above, with the addition of 1 equiv of I. The products, described in the Discussion, were identified by NMR.

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**Registry No.** I, 86163-42-0; II, 93111-39-8; IIIa, 93219-80-8; IIIb, 93111-40-1; IV, 93111-41-2; V, 93111-42-3; VII, 93111-43-4; VIII, 93134-26-0; X, 93111-49-0;  $(\text{CpMo})_2(\mu\text{-SC}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)(\mu\text{-SCH}_3)\text{S}_2\text{CH}_2$ , 93111-44-5;  $(\text{CpMo})_2(\mu\text{-SCHCH}(\text{CO}_2\text{CH}_2\text{CH}_3)(\mu\text{-SCH}_3)\text{S}_2\text{CH}_2$ , 93111-45-6;  $(\text{CpMo})_2(\mu\text{-SCH}_2\text{CH}_2\text{CN})(\mu\text{-SCH}_3)\text{S}_2\text{CH}_2$ , 93111-46-7;  $(\text{CpMo})_2(\mu\text{-SC}(\text{CH}_3)\text{CH}_2)(\mu\text{-SCH}_3)\text{S}_2\text{CH}_2$ , 93111-47-8;  $(\text{CpMo})_2(\mu\text{-SC}(\text{CO}_2\text{CH}_3)\text{CH}(\text{CO}_2\text{CH}_3))(\mu\text{-SCH}_3)\text{S}_2\text{CH}_2$ , 93111-48-9;  $[(\text{CpMo})_2(\mu\text{-S})(\mu\text{-SCH}_3)(\text{S}_2\text{CH}_2)]\text{HSO}_4$ , 93219-82-0;  $(\text{CpMo})_2(\mu\text{-S}(\text{B})(\mu\text{-SCH}_3)\text{S}_2\text{CH}_2$  (B = *sec*-butyl), 93111-50-3;  $[(\text{CpMo})_2(\mu\text{-S})(\mu\text{-SCH}_3)\text{S}_2\text{CH}_2]\text{K}$ , 93111-51-4;  $(\text{CpMo})_2(\text{SCHCHS})\text{S}_2\text{CH}_2$ , 86163-46-4;  $\text{CH}_3\text{I}$ , 74-88-4;  $\text{CH}_3\text{Li}$ , 917-54-4;  $\text{LiBHET}_3$ , 22560-16-3;  $\text{KB}(\text{R})_3\text{H}$  (R = *sec*-butyl), 54575-49-4;  $\text{HC}\equiv\text{CH}$ , 74-86-2;  $\text{PhC}\equiv\text{CH}$ , 536-74-3;  $\text{C}_2\text{H}_2$ , 74-85-1;  $\text{KC}_8$ , 12081-88-8;  $\text{PhC}\equiv\text{CPh}$ , 501-65-5;  $\text{HC}\equiv\text{CCO}_2\text{Et}$ , 105-37-3;  $\text{H}_2\text{C}=\text{C}(\text{H})\text{CN}$ , 107-13-1;  $\text{H}_2\text{C}=\text{C}=\text{CH}_2$ , 463-49-0; vinyl bromide, 593-60-2; 1,4-cyclohexadiene, 628-41-1; ethyl iodide, 75-03-6; dimethyl acetylenedicarboxylate, 762-42-5.

**Supplementary Material Available:** A perspective drawing of cation II of  $[(\text{CpMo})_2(\mu\text{-S})(\mu\text{-SCH}_3)\text{S}_2\text{CH}_2]^+$  and tables of observed and calculated structure factors and of atomic thermal parameters (16 pages). Ordering information is given on any current masthead page.

## Synthesis, Molecular Structure, and Thermal Chemistry of $(\eta^5\text{-Cyclopentadienyl})\text{dicarbonylrhenacyclopentane}^\dagger$

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Alkylation of  $\text{CpRe}(\text{CO})_2\text{H}_2$  with 1,4-diiodobutane in the presence of the amine base DBU yields the five-membered rhenacyclopentane 1. The crystal structure of 1 was determined by X-ray diffraction using 767 reflections that were refined to a final  $R$  value of 1.90%. The crystals were orthorhombic (space group  $P2_12_12_1$ ) with unit cell parameters  $a = 8.0041$ ,  $b = 8.0139$ , and  $c = 16.6549$  Å. The molecule is disordered at the two  $\beta$ -carbons of the metallacycle ring that each occupy two nearly equivalent positions. Thermolysis of 1 at  $100^\circ\text{C}$  with either  $\text{PMe}_3$  or  $\text{PPh}_3$  leads quantitatively to methylcyclopropane and  $\text{CpRe}(\text{CO})_2\text{PR}_3$ . A kinetic study showed that this reaction was first order in 1 and independent of both phosphine structure and concentration with an average  $k_{\text{obsd}} = 6.88 \times 10^{-4} \text{ s}^{-1}$ . Deuterium labeling studies demonstrated that methylcyclopropane formation proceeds by net  $\beta$  to  $\alpha$  hydrogen migration followed by formation of a bond between the  $\beta$ - and the other  $\alpha$ -carbon. A  $^{13}\text{C}$ O crossover experiment shows that CO dissociation is not occurring on the path to product, suggesting that  $\eta^5 \rightleftharpoons \eta^3$  cyclopentadienyl ring slip is occurring to open a vacant coordination site.

### Introduction

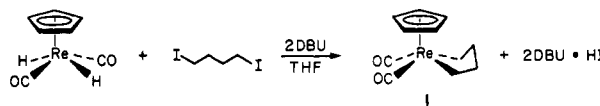
Metallacyclopentanes have been the center of much experimental and theoretical work, particularly regarding their role in olefin dimerization processes.<sup>1-3</sup> The thermal chemistry of metallacyclopentanes consists of  $\beta$ -elimination and reductive elimination processes yielding cyclopentanone, cyclobutane, butenes, or loss of ethylene in 2 + 2 cycloreversion processes.<sup>3,4</sup>

We recently reported the preparation of a new rhenacyclopentane complex (1; Scheme I) from  $\text{CpRe}(\text{CO})_2\text{H}_2$  and its thermolysis to methylcyclopropane via a novel ring contraction process.<sup>5</sup> In this paper we describe the detailed synthesis and characterization of this material as well as mechanistic evidence for transient  $\eta^5 \rightleftharpoons \eta^3$  isomerization ("ring slip") of the cyclopentadienyl ring induced by  $\beta$ -elimination.

### Results

**Synthesis and Structure Determination.** When an excess of 1,4-diiodobutane was added to a stirred solution of  $\text{CpRe}(\text{CO})_2\text{H}_2$  and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in THF (Scheme I), the solution quickly turned

Scheme I



yellow and a white precipitate appeared after several minutes. At this point the infrared spectrum of this

<sup>†</sup>Dedicated to the memory of Earl Muetterties, for the guidance, intellectual stimulation, and leadership he provided at Berkeley.

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