a 500-mL flask. The solution was degassed and sealed under 1 atm of hydrogen at −196 °C. After 7 days $(CpMo)_2(\mu\text{-}S)_2(\mu\text{-}S_2)$,[25] $[CpMoSCH_2CH(Ph)S]_2$, and $[CpMoS(\mu\text{-}S)]_2$ were tentatively identified by NMR in relative ratios of 6:16:5, respectively. There were also several minor resonances that could not be identified.

In a separate experiment, a solution of **1** (18 mg, 0.03 mmol) in ca. 0.5 mL of $CDCl_3$ in an NMR tube was degassed and sealed under ca. 0.75 atm of hydrogen at −196 °C. The solution was maintained at ambient temperature. Within 1 week, resonances for $(CpMo)_2(\mu\text{-}S)_2(\mu\text{-}S_2)$, $[CpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$, and $[CpMoS(\mu\text{-}S)]_2$ were evident. The resonance for water became larger and broader as the reaction proceeded. The reaction tube was placed in an oil bath at 50 °C for 3 days. $[CpMoS(\mu\text{-}S)]_2$ and an unidentified complex with a Cp resonance at 5.25 ppm were the major products. The NMR tube was then cracked open, and the volatiles were collected by vacuum distillation into a second NMR tube. Immiscible beads of water were evident in this fraction. ^1H NMR spectral analysis indicated that the major species in this volatile fraction were water, styrene, and ethylbenzene. GC/MS analyses also identified the major organic products as styrene and ethylbenzene, while a minor product was identified as acetophenone. Another minor organic product was formulated to be $C_8H_{10}S$: m/z 138 (P^+), 105 ($P^+ - SH$), 77 (Ph^+). The relative styrene:ethylbenzene:acetophenone:$C_8H_{10}S$ ratio was ca. 6:4:1:2.

(25) However, in the system described here, $(CpMo)_2(\mu\text{-}S)_2(\mu\text{-}S_2)$ might be expected to undergo a further reaction with hydrogen to form $[CpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$.[15]

Acknowledgment. Support by the National Institutes of Health (Grant GM-25122) and, in part, by the Division of Chemical Sciences, Office of Basic Energy Research, Department of Energy, is gratefully acknowledged.

Registry No. **1**, 113777-02-9; **1**, MeCp analogue, 113777-03-0; **2**, 72186-27-7; **2**, MeCp analogue, 113777-04-1; **3**, 113830-00-5; **4**, 113777-05-2; $[CpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$, 75675-64-8; $[MeCpMoO(\mu\text{-}S)]_2$, 107246-78-6; $[(CH_3)_3Si]_2S$, 3385-94-2; $[CpMoS(\mu\text{-}S)]_2$, 51160-11-3; $(NH_4)_2S$, 12135-76-1; $[CpMo(CO)_3]_2$, 12091-64-4; $[CpMoSCH_2CH(Ph)S]_2$, 113777-06-3; PhC≡CH, 536-74-3; $(MeCpMo)_2(\mu\text{-}S)_2(\mu\text{-}S_2)$, 100791-15-9; $(CpMo)_2(\mu\text{-}S)_2(\mu\text{-}S_2)$, 113777-07-4; styrene, 100-42-5.

Supplementary Material Available: For $CpMoO(\mu\text{-}S)_2Mo(SC(Ph)=CHS)Cp$ (**1**), listings of anisotropic temperature factors and H atom coordinates and isotropic temperature factors and a figure showing the ^1H NMR spectrum (2 pages); tables of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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Structures and Reactivities of Cyclopentadienylmolybdenum Complexes with Oxo and Sulfido Ligands

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Received September 11, 1987

Solutions of $[Cp'Mo(\mu\text{-}S)(\mu\text{-}SH)]_2$ (Cp' = C_5H_5, $C_5H_4CH_3$) have been oxidized by air to produce *syn*- and *anti*-$[Cp'MoO(\mu\text{-}S)]_2$. Chromatographic procedures for the isolation of each isomer are reported. The methylcyclopentadienyl derivatives have been characterized by X-ray diffraction studies. The syn isomer crystallizes in space group $C2/c$ with a = 8.214 (2) Å, b = 11.957 (3) Å, c = 14.610 (2) Å, and β = 106.51 (2)°. The Mo_2S_2 unit is bent, and the distance between bridging sulfido atoms is 3.577 Å. *anti*-$[MeCpMoO(\mu\text{-}S)]_2$ crystallizes in space group $P\bar{1}$ with a = 6.939 (1) Å, b = 7.197 (1) Å, c = 7.756 (1) Å, α = 103.73 (1)°, β = 90.16 (1)°, and γ = 107.92 (1)°. Each isomer reacts with $[(CH_3)_3Si]_2S$ in a reaction that exchanges sulfido for terminal oxo ligands and forms $(MeCpMo)_2S_4$ derivatives. Intermediate products *syn*- and *anti*-$(MeCpMo)_2(O)(S)(\mu\text{-}S)_2$ have also been isolated and characterized by spectroscopic methods. *syn*-$(MeCpMo)_2(O)(S)(\mu\text{-}S)_2$ undergoes a disproportionation upon heating to form $(MeCpMo)_2O_2S_2$ and $(MeCpMo)_2S_4$. Intermolecular oxo/sulfido transfer is also involved in the reaction of *syn*-$(MeCpMo)_2(O)(S)(\mu\text{-}S)_2$ with alkynes, which results in products of the formulations $MeCpMo(O)(\mu\text{-}S)_2Mo(SCR{=}C(R)S)(MeCp)$ and $MeCpMo(O)(\mu\text{-}S)_2Mo(OCR{=}C(R)S)(MeCp)$.

Introduction

In the preceding paper we reported that $[CpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$ reacted with oxygen in the presence of alkynes to form a new structural class of dinuclear complexes with terminally chelated alkenedithiolate ligands.[1] This interesting reactivity prompted a further study in which we have isolated and characterized the air-oxidation products of $[CpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$ in the absence of alkyne trapping agents and investigated the stabilities and reactivities of the products. In this paper we report the isolation procedures and characterization data for *syn*- and *anti*-$(MeCpMo)_2(O)(S)(\mu\text{-}S)_2$ and *syn* and *anti*-$[Cp'MoO(\mu\text{-}S)]_2$, where Cp' = C_5H_5 or $CH_3C_5H_4$. Complexes of the general formula $(CpMoX_2)_2$, where X = S, O, or NR, have been known for many years, and several derivatives have been structurally characterized by X-ray diffraction studies.[2-9] However, efficient synthetic routes for these complexes with many of the possible ligand combinations, including those cited above, have not been developed. As a result, the reactivities of these systems have not been investigated. Our studies have defined a reaction chemistry for these complexes that appears to be largely based on their ability to undergo intermolecular transfer of oxo and sulfido ligands.

Results and Discussion

Synthesis, Isolation, and Characterization of Complexes. Solutions of $[MeCpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$ reacted in air to initially form $(MeCpMo)_2(\mu\text{-}S)_2(\mu\text{-}S_2)$, which has been characterized previously.[10] This product underwent further oxidation in solution to produce several oxo-containing derivatives. Under dry oxygen, *syn*- and *anti*-$[MeCpMoO(\mu\text{-}S)]_2$ were produced. No reaction occurred under similar conditions when water was substituted for oxygen.[11] In air, the oxidation proceeded more slowly, but in addition to the bis(oxo) products, an intermediate oxidation product, $(MeCpMo)_2(O)(S)(\mu\text{-}S)_2$, was also detected in the NMR spectrum of the crude oxidized material in a relative yield of ca. 25%. Except where noted below, the analogous products with unsubstituted cyclopentadienyl ligands were prepared by com-

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0020-1669/88/1327-1741$01.50/0

Table I. Bond Distances and Selected Bond Angles for *anti*-$(MeCpMo)_2O_2(\mu\text{-}S)_2$

	Distances, Å		
Mo–S	2.312 (1)	Mo–O	1.700 (2)
Mo–C(1)	2.492 (3)	Mo–C(2)	2.460 (3)
Mo–C(3)	2.326 (3)	Mo–C(4)	2.337 (2)
Mo–C(5)	2.364 (2)	Mo–Mo(A)	2.885 (1)
Mo–S(A)	2.313 (1)	S–Mo(A)	2.312 (1)
C(1)–C(2)	1.400 (5)	C(1)–C(5)	1.427 (4)
C(1)–C(6)	1.482 (6)	C(2)–C(3)	1.421 (5)
C(3)–C(4)	1.380 (5)		
C(4)–C(5)	1.398 (5)		
	Angles, deg		
S–Mo–O	103.2 (1)	S–Mo–C(1)	112.1 (1)
O–Mo–C(1)	140.7 (1)	S–Mo–C(2)	85.1 (1)
O–Mo–C(2)	143.0 (1)	S–Mo–C(3)	89.9 (1)
O–Mo–C(3)	108.8 (1)	S–Mo–C(4)	122.9 (1)
O–Mo–C(4)	90.2 (1)	S–Mo–C(5)	141.1 (1)
O–Mo–C(5)	106.7 (1)	S–Mo–Mo(A)	51.4 (1)
O–Mo–Mo(A)	112.4 (1)	O–Mo–S(A)	104.2 (1)
S–Mo–S(A)	102.8 (1)	Mo(A)–Mo–S(A)	51.4 (1)
Mo–S–Mo(A)	77.2 (1)		

Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for *anti*-$(MeCpMo)_2O_2(\mu\text{-}S)_2$

	x/a	*y/b*	*z/c*	U^a
Mo	1302 (1)	2068 (1)	376 (1)	34 (1)
S	−2207 (1)	843 (1)	227 (1)	45 (1)
O	1763 (3)	2917 (3)	−1497 (3)	57 (1)
C(1)	2877 (4)	2646 (4)	3429 (3)	48 (1)
C(2)	1092 (4)	3172 (4)	3604 (3)	53 (1)
C(3)	1282 (5)	4745 (4)	2738 (4)	57 (1)
C(4)	3189 (5)	5251 (4)	2117 (4)	57 (1)
C(5)	4152 (4)	3908 (4)	2439 (4)	49 (1)
C(6)	3380 (8)	1130 (6)	4187 (5)	82 (2)

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

pletely analogous procedures. The products were separated by several chromatographic steps.

Chromatography of the crude air-oxidized product on alumina with dichloromethane resulted in an olive green band, which was further chromatographed on silica gel with a 1:4 mixture of hexane/dichloromethane. The first gold fraction gave orange-gold crystals upon removal of the solvent. The product was found to have the composition $[Cp'MoOS]_2$ on the bases of mass spectral data and elemental analyses. The infrared spectrum showed a medium absorption at 920 cm^{-1}, characteristic of terminal oxo ligands on molybdenum. A weak band at 455 cm^{-1} was assigned to a vibration of a bridging sulfido ligand. A single NMR resonance was observed at 6.08 ppm for the Cp derivative. The NMR spectrum of the methylcyclopentadienyl analogue showed two Cp multiplets. Cyclic voltammetry in acetonitrile revealed a reversible one-electron reduction for the MeCp derivative at −1.56 V vs SCE (ΔE_p = 66 mV).

An X-ray diffraction study was undertaken on $[MeCpMo(O)(\mu\text{-}S)]_2$ to determine whether the terminal oxo ligands were in the syn or anti configuration. Golden brown crystals were grown from a saturated methanol/dichloromethane solution. A perspective drawing of the molecule is shown in Figure 1. Bond distances and selected bond angles are presented in Table I, and positional parameters are given in Table II. The molecule is a centrosymmetric dimer with a planar $Mo_2(\mu\text{-}S)_2$ unit and an anti configuration of both oxo and cyclopentadienyl ligands. The extent of methyl substitution on the cyclopentadienyl ring does not significantly influence the structural features of the molybdenum ions. The Mo–Mo, Mo–S, and Mo–O distances are all very similar to those of the analogous anti isomers of $[C_5H_5Mo(O)\mu\text{-}S]_2$[4] and $[(CH_3)_5C_5Mo(O)\mu\text{-}S]_2$.[8]

The second olive green fraction on the silica gel column was eluted with dichloromethane and isolated as an air-sensitive dark green powder in a relative yield of 25%. Although the unsubstituted cyclopentadienyl derivative was difficult to isolate in pure

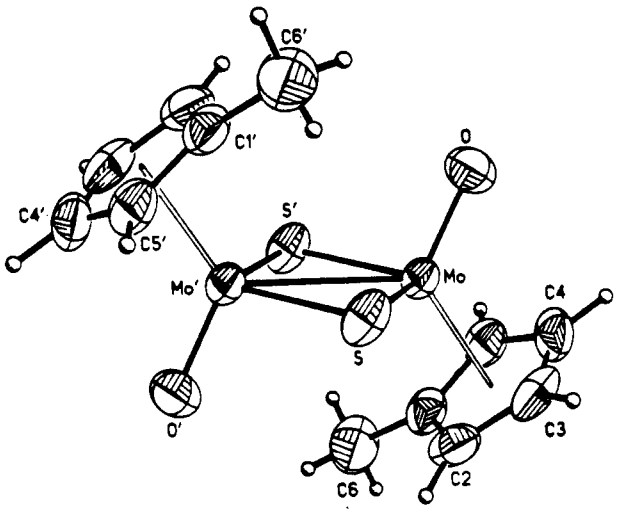

Figure 1. Perspective drawing and numbering scheme for *anti*-$[MeCpMoO(\mu\text{-}S)]_2$. Thermal ellipsoids are drawn at the 50% probability level.

form, the methylcyclopentadienyl derivative was isolated, characterized by elemental analyses and mass spectral data, and found to have the formulation $(MeCpMo)_2OS_3$. In the mass spectrum, a strong parent ion peak was observed, as well as fragments resulting from the loss of oxygen and sulfur atoms. Strong absorptions observed in the infrared spectrum at 900 and 482 cm^{-1} are characteristic of Mo=O and Mo=S bonds, respectively. The ^1H NMR spectrum is consistent with inequivalent molybdenum environments. Four multiplets are observed for the cyclopentadienyl ring protons, and two MeCp singlets are present in the spectrum. Cyclic voltammetry in acetonitrile shows a near-reversible one-electron reduction at −1.18 V vs SCE (ΔE_p = 80 mV). On the basis of the results of an experiment discussed below, the green $(MeCpMo)_2(O)(S)(\mu\text{-}S)_2$ derivative described here is proposed to be the syn isomer. A pentamethylcyclopentadienyl analogue with the Mo_2OS_3 core has been isolated previously.[9]

The third yellow fraction on the silica gel column was found to be composed largely of a second isomer of $[Cp'Mo(O)\mu\text{-}S]_2$. This product was further purified and characterized by elemental analyses and mass spectral data. Strong absorptions observed in the infrared spectrum at 920 and 900 cm^{-1} are characteristic of asymmetric and symmetric Mo=O stretches, respectively. In the ^1H NMR spectrum the chemical shift for the Cp resonance, 6.09 ppm, is similar to that of the anti isomer. However, for the methylcyclopentadienyl derivative, the Cp multiplets and methyl resonance have chemical shifts different from those of the anti isomer (see Experimental Section). Cyclic voltammetric studies established that the methylcyclopentadienyl derivative of this isomer also undergoes a reversible reduction at −1.61 V vs SCE (ΔE_p = 68 mV).

The X-ray diffraction study described above, which identified the anti isomer of $[MeCpMo(O)\mu\text{-}S]_2$, allows us to assign the syn configuration to this derivative. No X-ray diffraction studies have been carried out on *syn*-$[CpMoX_2]_2$ derivatives. The pentamethylcyclopentadienyl derivative *syn*-$[Me_5C_5MoS(\mu\text{-}S)]_2$ has been isolated by Wachter and co-workers and has been proposed to have a bridging disulfide ligand.[9] In order to determine the bonding mode of the bridging sulfur ligands in *syn*-$[MeCpMoO(\mu\text{-}S)]_2$, a crystallographic study was carried out. Orange-brown crystals of the complex were grown from a saturated dichloromethane solution. A perspective drawing is shown in Figure 2, and selected bond distances and angles are given in Table III. Positional parameters are presented in Table IV. The molecule has C_{2v} symmetry. Each molybdenum ion contains a pseudotetrahedral coordination environment. The Mo_2S_2 core of the molecule is nonplanar with a dihedral angle between $Mo-S_2$ planes of 154.3°. The metal–metal distance of 2.873 (1) Å and Mo=O distance of 1.696 (2) Å are very similar to those of the anti isomer. The S···S distance of 3.577 (3) Å is close to the expected van der Waals distance and is consistent with the for-

Table III. Bond Distances and Selected Bond Angles for *syn*-$(MeCpMo)_2O_2(\mu\text{-}S)_2$

	Distances, Å		
Mo(1)–S(1)	2.316 (1)	Mo(1)–O(1)	1.696 (2)
Mo(1)–C(1)	2.467 (3)	Mo(1)–C(2)	2.376 (3)
Mo(1)–C(3)	2.392 (4)	Mo(1)–C(4)	2.382 (3)
Mo(1)–C(5)	2.438 (3)	Mo(1)–Mo(1A)	2.873 (1)
Mo(1)–S(1A)	2.316 (1)	S(1)–Mo(1A)	2.317 (1)
C(1)–C(2)	1.437 (4)	C(1)–C(5)	1.397 (4)
C(1)–C(6)	1.483 (5)	C(2)–C(3)	1.416 (5)
C(3)–C(4)	1.395 (4)	C(4)–C(5)	1.435 (5)
O(1)··O(1A)	3.651 (3)	S(1)··S(1A)	3.577 (3)
	Angles, deg		
S(1)–Mo(1)–O(1)	106.5 (1)	O(1)–Mo(1)–C(3)	85.6 (1)
O(1)–Mo(1)–C(1)	141.3 (1)	O(1)–Mo(1)–C(4)	98.0 (1)
O(1)–Mo(1)–C(2)	108.5 (1)	S(1)–Mo(1)–Mo(1A)	51.7 (1)
O(1)–Mo(1)–C(5)	132.5 (1)	O(1)–Mo(1)–S(1A)	106.0 (1)
O(1)–Mo(1)–Mo(1A)	103.3 (1)	Mo(1A)–Mo(1)–S(1A)	51.7 (1)
Mo(1)–S(1)–Mo(1A)	76.6 (1)		

Table IV. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for *syn*-$(MeCpMo)_2O_2(\mu\text{-}S)_2$

	x/a	y/b	z/c	U[a]
Mo(1)	895 (1)	903 (1)	1786 (1)	24 (1)
S(1)	1978 (1)	1177 (1)	3416 (1)	34 (1)
O(1)	1128 (3)	−477 (2)	1588 (2)	43 (1)
C(1)	953 (4)	2752 (2)	1047 (2)	32 (1)
C(2)	602 (4)	1887 (3)	335 (2)	35 (1)
C(3)	2070 (4)	1209 (3)	485 (2)	39 (1)
C(4)	3263 (4)	1578 (3)	1314 (2)	40 (1)
C(5)	2576 (4)	2545 (2)	1654 (2)	35 (1)
C(6)	−174 (6)	3703 (3)	1103 (3)	54 (1)

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

mulation of two μ-sulfido ligands in a molybdenum(V) dimer.

Reactivity of [MeCpMoO(μ-S)]$_2$. Unlike the related $[CpMoS_2]_2$ derivatives,[8] these complexes with two terminal oxo ligands did not react with alkenes or alkynes. Nor was a well-defined reaction with hydrogen observed. When a mixture of *syn*- and *anti*-$[MeCpMoO(\mu\text{-}S)]_2$ in $CDCl_3$ was placed under an atmosphere of hydrogen and monitored by NMR, the relative intensities of the resonances assigned to the anti isomer decreased over a period of 2 weeks, while those of the syn isomer remained relatively constant. Although the formation of a brown solid was noted, no products from this reaction have been identified.

Oxo/Sulfido Exchange Experiments. The syn and anti isomers of $[MeCpMoO(\mu\text{-}S)]_2$ were each reacted with hexamethyldisilthiane in an effort to obtain the corresponding terminal sulfido analogues. Although *anti*-$[MeCpMoS(\mu\text{-}S)]_2$ and, tentatively, the syn isomer have been identified in the NMR spectrum when $(MeCpMo)_2(\mu\text{-}S)_2(\mu\text{-}S_2)$ was heated at 65 °C in $CDCl_3$ under argon (see Experimental Section) or when $(MeCpMo)_2(\mu\text{-}S)_2(\mu\text{-}S_2)$ was photolyzed in an NMR tube,[12] a selective, high-yield synthesis for each of these isomers is not known. Although *anti*-$[MeCpMoS(\mu\text{-}S)]_2$ has been characterized by an X-ray diffraction study, it has been prepared only in a low-yield synthesis.[8] Pure samples of *syn*-$[MeCpMoS(\mu\text{-}S)]_2$ have not been characterized. It has been suggested previously that intramolecular steric interactions between ligands of this isomer may disfavor the syn configuration relative to the anti form.[13]

The reaction of *syn*-$[MeCpMoO(\mu\text{-}S)]_2$ with 2–3 equiv of the disilthiane reagent was monitored by NMR spectroscopy. The intermediate product *syn*-$(MeCpMo)_2(O)(S)(\mu\text{-}S)_2$, which was isolated from a separate synthesis (vide supra), was detected within 1 week. After $2^1/_2$ weeks at room temperature, the major product was identified as $(MeCpMo)_2(\mu\text{-}S)_2(\mu\text{-}S_2)$.[10] The syn isomer of $[(MeCpMoS(\mu\text{-}S)]_2$ was not detected as a product in this reaction. The reaction of *anti*-$[MeCpMoO(\mu\text{-}S)]_2$ with $[(CH_3)_3Si]_2S$ proceeded in a similar fashion. Within 3 days an intermediate was detected in the NMR spectrum, which was assigned as the

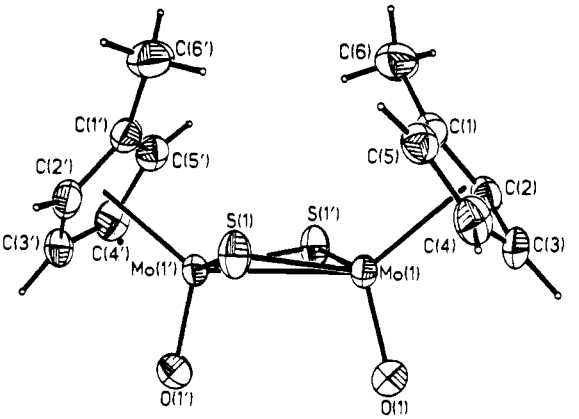

Figure 2. Perspective drawing and numbering scheme for *syn*-$[MeCpMoO(\mu\text{-}S)]_2$. Thermal ellipsoids are drawn at the 50% probability level.

anti isomer of $(MeCpMo)_2(O)(S)(\mu\text{-}S)_2$. Isolation and further characterization of this derivative are discussed below. After the solution was heated at 50 °C for 7 days, the major product of the reaction was again identified as $(MeCpMo)_2(\mu\text{-}S)_2(\mu\text{-}S_2)$. In this case the anti and possibly the syn isomers of $[MeCpMoS(\mu\text{-}S)]_2$ were identified as minor products. However, the formation of the quadruply bridged isomer of the $Cp_2Mo_2S_4$ derivatives appears to be favored in these reactions even at room temperature, and selective syntheses of the syn and anti doubly bridged isomers did not result from these studies.

Reactivity of *syn*-$(MeCpMo)_2(O)(S)(\mu\text{-}S)_2$. The thermal stability of this complex in solution has been investigated. A chloroform solution of *syn*-$(MeCpMo)_2(O)(S)(\mu\text{-}S)_2$ was heated under argon at 65 °C for 5 days. At this time a black precipitate was apparent in the reaction solution. This material was isolated (ca. 5% yield) and reacted with an atmosphere of hydrogen at 65 °C. The NMR spectrum showed complete conversion to $[MeCpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$ within 4 h. The reaction of a polymeric material $[CpMoS_x]_y$ with hydrogen to form the hydrosulfido-bridged derivative has been characterized previously.[14]

The soluble products in the thermal decomposition of $(MeCpMo)_2(O)(S)(\mu\text{-}S)_2$ were separated by chromatography and identified by NMR spectroscopy. The major products were the syn (30% yield) and anti (20% yield) isomers of $[MeCpMoO(\mu\text{-}S)]_2$. The starting reagent (5%) and its anti isomer (11%) were also present. Approximately 25% of the material did not elute from the column and therefore was not characterized. The nature of the products suggests that $(MeCpMo)_2(O)(S)(\mu\text{-}S)_2$ undergoes a disproportionation upon heating to form $(MeCp)_2Mo_2O_2S_2$ and $(MeCp)_2Mo_2S_4$ derivatives. Although the relative isolated yields of these two product types were not equal, the relative ease of oxidation of one or more of the Mo_2S_4 isomers to the $Mo_2O_2S_2$ complexes under chromatographic conditions could contribute to the higher yields of the latter.

syn-$(MeCpMo)_2(O)(S)(\mu\text{-}S)_2$ was found to react with acetylene at room temperature to form a mixture of several products. The minor product $[MeCpMoO(\mu\text{-}S)]_2$ suggested that some disproportionation of the starting reagent had occurred. A small amount of the other disproportionation product, $MeCp_2Mo_2S_4$, was detected as the acetylene adduct $[MeCpMoSCH{=}CHS]_2$.[14] Additional products provided evidence for intermediates with increased coordination numbers around molybdenum. $MeCpMo(O)(\mu\text{-}S)_2Mo(SCH{=}CHS)(MeCp)$ was isolated in ~15% yield as a mixture of syn and anti isomers. This complex has been prepared previously by other routes[1] and has been found to contain a terminal ethenedithiolate ligand chelated to one molybdenum ion and a terminal oxo ligand coordinated to the second metal ion. The major product, isolated from the reaction in 22% yield, appeared to be structurally related to this derivative and is tentatively formulated as $MeCpMo(O)(\mu\text{-}S)_2Mo(SCH{=}C(H)$-

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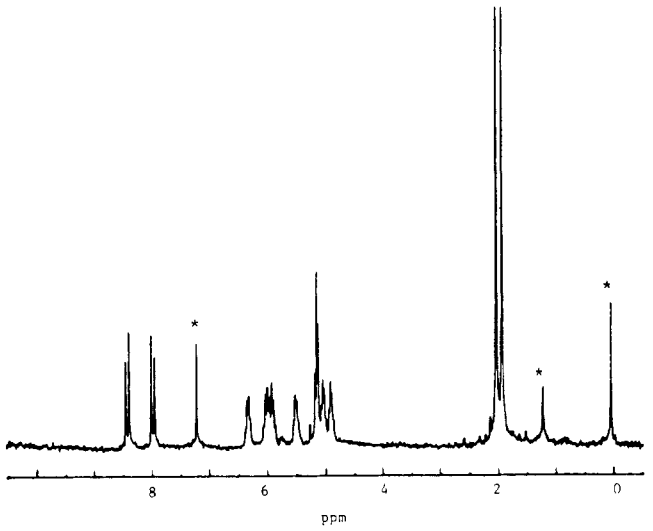

Figure 3. 90-MHz ^1H NMR spectrum of $MeCpMoO(\mu\text{-}S)_2Mo(SC_2H_2O)(MeCp)$. Resonances marked with an asterisk at 0, 1.2, and 7.2 ppm are assigned to TMS, H_2O, and $CHCl_3$, respectively. Other resonances are assigned in the Experimental Section.

O)(MeCp). The mass spectrum of this blue product confirmed the elemental composition. In addition to a strong parent ion peak, fragments corresponding to the loss of SC_2H_2 and SC_2H_2O were also observed. The ^1H NMR spectrum of this product is shown in Figure 3. Complex multiplets in the cyclopentadienyl region (5–6 ppm) and the resonances of the two methyl groups are indicative of a complex of low symmetry with inequivalent cyclopentadienyl ligands. The AB pattern near 8 ppm has a chemical shift characteristic of vinyl protons in a terminally chelated alkenedithiolate ligand. The inequivalence of these vinyl protons, as well as the overall composition of the complex, leads us to propose that this product contains a bidentate thioalkoxide ligand, O–CH=CH–S, rather than a dithiolene chelate. In the reaction of phenylacetylene with $(MeCpMo)_2(O)(S)(\mu\text{-}S)_2$, we isolated an analogous product with the formulation $MeCpMo(O)(\mu\text{-}S)_2Mo(SC_2(H)(Ph)O)(MeCp)$. An X-ray diffraction study on a single crystal of one of these products will be necessary to confirm our tentative spectral assignments. Detailed mechanistic features involved in the formation of these products are not known. However, our studies of the reactivity of $(MeCpMo)_2(O)(S)(\mu\text{-}S)_2$ have revealed a complex chemistry that appears to be based on intermolecular reactions involving oxo- and sulfido-transfer processes.

Since alkynes were able to trap certain intermediates in these intermolecular reactions to form stable products with alkene–dichalcogen ligands, the analogous reactivity of alkenes was also investigated. The reaction of *syn*-$(MeCpMo)_2(O)(S)(\mu\text{-}S)_2$ with ethylene for several days at 55 °C led to the formation of final products resulting from the disproportionation of the starting reagent. The syn and anti isomers of $[MeCpMoO(\mu\text{-}S)]_2$ were identified by NMR spectroscopy. The ethylene adduct of an Mo_2S_4 product, $[MeCpMoSC_2H_4S]_2$, was also formed.[14] No products with terminal alkenedithiolate ligands were detected in this reaction.

When *syn*-$(MeCpMo)_2(O)(S)(\mu\text{-}S)_2$ was heated under ethylene under more dilute conditions, an orange-brown solid was isolated in 34% yield after 5 days and identified by spectroscopic data as an isomer of $(MeCpMo)_2(O)(S)(\mu\text{-}S)_2$. Mass spectral data showed a strong parent peak; strong absorptions observed in the infrared spectrum at 905 and 492 cm^{-1} are characteristic of Mo=O and Mo=S bonds, respectively. This product was also detected as an intermediate in the reaction of *anti*-$[MeCpMoO(\mu\text{-}S)]_2$ with hexamethyldisilthiane (vide supra) and is therefore assigned an anti configuration. This product completes the series of syn and anti isomers of the $Mo_2O_2S_2$ and Mo_2OS_3 complexes. In the experiment described earlier in which *syn*-$(MeCpMo)_2(O)(S)(\mu\text{-}S)_2$ was heated under argon, the anti isomer was also detected (11% yield). It seems likely, therefore, that the increased yields of the isomerization product and the slower formation of disproportionation products in this reaction under ethylene pressure were the result of different reaction concentrations and conditions. However, further studies will be necessary to determine the mechanistic features of the isomerization and disproportionation reactions.

Summary and Conclusions. The lability of the metal–ligand bond and the resulting reactivity in this series of $Cp'_2Mo_2X_4$ complexes appear to increase with an increasing substitution of sulfur for oxygen atoms. $(Cp'Mo)_2(\mu\text{-}S)_2(\mu\text{-}S_2)$ rearranges to form two additional isomers under thermal conditions. No information is available on whether these isomerizations involve intra- or intermolecular sulfur transfers. The isomers react under mild conditions with molecular hydrogen and with alkenes and alkynes to form dinuclear complexes with hydrosulfido and dithiolate ligands, respectively. Partial oxidation of $(Cp'Mo)_2(\mu\text{-}S)_2(\mu\text{-}S_2)$ produces *syn*-$(Cp'Mo)_2(O)(S)(\mu\text{-}S)_2$, which isomerizes to the anti form upon heating. A significant reactivity feature of $(Cp'Mo)_2(O)(S)(\mu\text{-}S)_2$ is its tendency to undergo a disproportionation to form $(Cp'Mo)_2O_2S_2$ and $(Cp'Mo)_2S_4$. The ability to undergo intermolecular sulfido/oxo transfer also appears to be important in the reactions of $(Cp'Mo)_2(O)(S)(\mu\text{-}S)_2$ with alkynes, since products trapped by the alkyne reagents contain five chalcogen atoms. These dinuclear products are coordinated by terminally chelated alkene–dichalcogen ligands as well as a terminal and two bridging chalcogens. The complexes of formula $(Cp'Mo)_2O_2S_2$ are the final oxidation products obtained under aerobic conditions. These complexes show no evidence for intermolecular oxo/sulfido exchange or for isomerization in the nonaqueous solvents studied here. However, the external sulfide donor hexamethyldisilthiane does react with $(Cp'Mo)_2O_2S_2$ to displace the terminal oxo ligands.

Experimental Section

Materials and Instrumentation. $[CpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$, $[MeCpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$, and $(MeCpMo)_2(\mu\text{-}S)_2(\mu\text{-}S_2)$ were prepared by published procedures.[10,14] Hexamethyldisilthiane, $[(CH_3)_3Si]_2S$, was purchased from Aldrich. Reagent grade chloroform was passed through neutral alumina or dried over 4-Å molecular sieves. ^1H NMR spectra were recorded at 90 MHz on a JEOL FX-90Q or a Varian EM-390 spectrometer. Chemical shifts were reported relative to internal tetramethylsilane or to residual chloroform (7.24 ppm). Infrared spectra were recorded on either a Perkin-Elmer 337 or a Beckman IR 4250 spectrophotometer. Samples were analyzed as Nujol mulls between potassium bromide plates or as dichloromethane solutions in sodium chloride solution cells.

Cyclic voltammetry was carried out with a Bioanalytical Systems BAS-100 electrochemical analyzer. Platinum wires were used as the working and auxiliary electrodes with a $Ag/AgNO_3/CH_3CN$ reference electrode. Samples were analyzed under nitrogen in CH_3CN/0.10 M $n\text{-}Bu_4NBF_4$ at a scan rate of 100 mV/s. Ferrocene was used as an external standard ($E_{1/2}$ = 0.42 V vs SCE; ΔE_p = 68 mV).

Electron impact mass spectra were recorded at 70 eV on a VG Analytical 7070 EQ-HF or a Varian MAT CH-5 mass spectrometer. Elemental analyses were performed by Spang Microanalytical Laboratories.

X-ray Diffraction Studies. Details of the crystal data, experimental conditions, and a summary of solution and refinement details are given in Table V. In the models used for the final block-cascade least-squares refinements, all non-hydrogen atoms were refined independently with anisotropic thermal parameters. Hydrogen atoms were included in riding idealized positions with isotropic thermal parameters set to 1.2 times the thermal parameters of the atoms to which they were attached.

Synthesis and Isolation of Complexes. $[CpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$ (2.0–5.0 g, 4.0–11.0 mmol) was stirred in dichloromethane under air at room temperature for 1–3 weeks. The solvent was removed, and the crude solid was chromatographed on alumina. The first minor gold fraction, eluted with 1:4 hexane/dichloromethane, was not characterized. The major olive green fraction was eluted with dichloromethane. The green solid obtained upon removal of solvent was further purified by chromatography on silica gel.

Silica gel chromatography: The first gold fraction, eluted with 1:4 hexane/dichloromethane, gave orange-gold crystals upon removal of the solvent. The complex was recrystallized from dichloromethane. The product was identified as *anti*-$[CpMoO(\mu\text{-}S)]_2$. Yield: 15–20%. Mass spectrum, m/z: 418 (P^+), 402 (P – O), 386 (P – S), 370 (P – SO). IR (Nujol), cm^{-1}: 920 m ($\nu_{Mo=O}$); 455 w ($\nu_{Mo\text{-}S\text{-}Mo}$). ^1H NMR ($CDCl_3$), δ: 6.08 (s, Cp). Anal. Calcd for $C_{10}H_{10}Mo_2O_2S_2$: C, 28.72; H, 2.45;

Table V. Crystal Data and Details of the Structure Determinations for *anti*- and *syn*-$[MeCpMoO(\mu\text{-}S)]_2$

	anti-$Mo_2S_2O_2C_{12}H_{14}$	*syn*-$Mo_2S_2O_2C_{12}H_{14}$
Crystal Data		
mol wt	446.25	446.25
space group[a]	$P\bar{1}$	$C2/c$
cryst syst	triclinic	monoclinic
a, Å[b]	6.939 (1)	8.214 (2)
b, Å	7.197 (1)	11.957 (3)
c, Å	7.756 (1)	14.610 (2)
α, deg	103.74 (1)	90
β, deg	90.16 (1)	106.51 (2)
γ, deg	107.92 (1)	90
vol, Å^3	356.7 (1)	1375.7 (5)
Z	1	4
calcd density, g/cm^3	2.07	2.15
$F(000)$	218	872
μ, cm^{-1}	19.9	20.7
Data Collection and Reduction		
diffractometer	Syntex P3/F Upgrade	Nicolet P3/F
radiation (λ, Å)	Cu Kα (1.5418)	Mo Kα (0.71069)
takeoff angle for graphite monochromator, deg	4.0	4.0
temp, K	294–297	294–297
cryst habit (needles, plates, etc.)	parallepiped	plate
cryst color	golden-brown	golden-orange-brown
crystal dimens, mm	0.2 × 0.27 × 0.5	0.54 × 0.56 × 0.09
scan technique	θ–2θ	θ–2θ
2θ, deg: min–max	3.0–65.0	3.0–65.0
hkl values scanned	$\pm 11h, \pm 11k, \pm 12l$	$\pm 13h, \pm 19k, \pm 23l$
scan speed, deg/min	4.0–60.0	4.0–60.0
scan range, deg	0.9 below Kα_1 to 1.1 above Kα_2	
bkgd	stationary cryst–stationary counter; bkgd time = 0.5 scan time	
check reflcns (4)	(208), (0,4,–8), (7,–5,0), (–5,6,–5)	(0,6,–6), (171), (4,2,–9), (–3,–5,2)
freq variation	every 96 measmts statistically random	
no. of reflcns	5193	9620
no. of unique reflcns	2598	2492
agreement factor during averaging[c]	0.017	0.0342
no. of obsd. reflcns	2411	2306
σ criterion	$F > 6\sigma(F)$	$F > 6\sigma(F)$
abs cor	none	analytical
Structure Determination and Refinement		
method of phase determination	Patterson	Patterson
programs	SHELXTL[d]	SHELXTL[d]
scattering factors	neutral atoms[e]	neutral atoms[e]
R, R_w[f] for obsd data	0.026, 0.038	0.038, 0.052
for all data	0.028, 0.039	0.042, 0.061
weight	$1.0/(\sigma^2(F) + 0.0003F^2)$	$1.0/(\sigma^2(F) + 0.0005F^2)$
no. of params	82	82
ratio of observns to params	29:1	28:1
esd of observn of unit wt	1.615	1.842
av shift/error	0.001	0.00
max shift/error	0.005	0.003
obsd for	y/a for Mo(1)	y/b for Mo(1)
residual electron density, e/Å^3	0.9 (0.8 Å from Mo(1))	1.3 (0.8 Å from Mo(1))

[a] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1965; Vol. 1. [b] Cell dimensions were determined by least-squares fit of the setting angles of 25 reflections with 2θ in the range 45–50° for the anti isomer and 50–61° for the syn isomer. [c] $R_{merge} = [\sum N(\sum w(F_{mean} - F)^2)/\sum((N-1)\sum wF^2)]^{1/2}$. [d] Sheldrick, G. M. "SHELXTL, A Program for Crystal Structure Determination, Version 5.1"; Nicolet Analytical Instruments: Madison, WI, 1985. [e] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4. [f] The quantity minimized in the least-squares procedures is $\sum w(|F_o| - |F_c|)^2$. $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = \sum w(|F_o| - |F_c|)^2/\sum[w(F_o)^2]$.

S, 15.33. Found: C, 28.72; H, 2.39; S, 15.23. The same procedure was followed to obtain *anti*-$[MeCpMoO(\mu\text{-}S)]_2$. ^{1}H NMR ($CDCl_3$), δ: 6.00, 5.77 (2 m, 8, Cp); 2.05 (s, 6, Me). $E_{1/2}$, V vs SCE: –1.56 (ΔE_p = 66 mV; i_{pc}/i_{pa} = 1.19).

For the methylcyclopentadienyl system, the second olive green fraction, eluted with dichloromethane, gave a dark green powder upon removal of solvent. The product was identified as *syn*-$(MeCpMo)_2(O)(S)(\mu\text{-}S)_2$. Yield: 15–20%. Mass spectrum, m/z: 462 (P^+), 446 (P – O), 430 (P – S), 414 (P – SO). ^{1}H NMR ($CDCl_3$), δ: 6.22, 5.72, 5.55, 5.34 (4 m, 8, Cp); 2.23, 2.16 (2 s, 6, Me). IR (Nujol), cm^{-1}: 900 m, 898 m ($\nu_{Mo=O}$); 482 m (ν_{Mo-S}); 455 w ($\nu_{Mo-S-Mo}$). $E_{1/2}$, V vs SCE: –1.18 (ΔE_p = 80 mV; i_{pc}/i_{pa} = 0.96). Anal. Calcd for $C_{12}H_{14}Mo_2S_3O$: C, 31.18; H, 3.05; S, 20.81. Found: C, 31.28; H, 3.10; S, 20.63.

The analogous derivative for the unsubstituted cyclopentadienyl ligand was observed in a similar procedure but was never isolated cleanly: ^{1}H NMR ($CDCl_3$), δ: 6.12, 5.88 (2 s, Cp).

The third yellow fraction, eluted with acetonitrile, gave orange crystals upon removal of solvent. The ^{1}H NMR spectrum indicated a mixture of isomers were present. These were separated by chromatography on alumina. The first gold fraction, eluted from the alumina with dichloromethane, was identified as *anti*-$[CpMoO(\mu\text{-}S)]_2$. The second orange fraction on the alumina column was eluted with acetonitrile. The solvent was removed, and the complex was recrystallized from 2:3 acetonitrile/dichloromethane. The product was identified as *syn*-$[CpMoO(\mu\text{-}S)]_2$. Yield: ~40%. Mass spectrum: same pattern as observed for the anti isomer. ^{1}H NMR ($CDCl_3$), δ: 6.09 (s, Cp). Anal. Calcd for $C_{10}H_{10}Mo_2O_2S_2$: C, 28.72; H, 2.41; S, 15.33. Found: C, 28.87; H, 2.39; S, 15.49.

The same procedure was followed to obtain *syn*-$[MeCpMoO(\mu\text{-}S)]_2$. ^{1}H NMR ($CDCl_3$), δ: 6.16, 5.46 (2 m, 8, Cp); 2.15 (s, 6, Me). IR (Nujol), cm^{-1}: 920 m, 900 m ($\nu_{Mo=O}$); 455 w ($\nu_{Mo-S-Mo}$). $E_{1/2}$, V vs SCE: –1.61 (ΔE_p = 66 mV; i_{pc}/i_{pa} = 1.23).

Source of Oxo Ligands in the Formation of $[MeCpMoO(\mu\text{-}S)]_2$. $(MeCpMo)_2(\mu\text{-}S)_2(\mu\text{-}S_2)$ (0.020 g, 0.044 mmol) was dissolved in dry CD_2Cl_2, and the solution was placed in an NMR tube that was sealed under nitrogen with a septum. Ultradry oxygen (<10 ppm of water) (2 mL, 0.082 mmol) was added via a gastight syringe. Reactions were followed by NMR spectral analysis; after 2 days significant changes had occurred in the spectrum. After 6 days the final products were *syn*- and *anti*-$[CpMoO(\mu\text{-}S)]_2$ and a third product that was tentatively formulated as $[MeCpMoS_2]_2^{n+}$ (^{1}H NMR ($CDCl_3$), δ: 6.65 (Cp); 2.45 (Me)).[15] In the mass spectrum of the product mixture, a parent ion and fragmentation pattern for $[MeCpMoO(\mu\text{-}S)]_2$ were observed, but no evidence for $[MeCpMoO_2]_2$ or for S_8 was observed.

A second reaction was carried out by using $(MeCpMo)_2(\mu\text{-}S)_2(\mu\text{-}S_2)$ (0.015 g, 0.040 mmol) in $CDCl_3$ with ca. 6 equiv of H_2O. The solution was freeze–pump–thaw degassed three times, and the flask was sealed with a Teflon high-vacuum stopcock. The solution was stirred at room temperature for 7 days. The ^{1}H NMR spectrum showed that only starting material was present. The same result was observed for the reaction of $[CpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$ in THF with excess water under vacuum.

Reaction of *anti*-/*syn*-$[MeCpMoO(\mu\text{-}S)]_2$ with Hydrogen. A mixture of 1:1 *anti*-/*syn*-$[MeCpMoO(\mu\text{-}S)]_2$ (12 mg, 0.027 mmol) was dissolved in ca. 0.5 mL of $CDCl_3$, and the solution was transferred to an NMR tube. The solution was degassed and sealed under ca. 0.75 atm of hydrogen. The tube was placed in an oil bath at 70 °C. The course of the reaction was monitored by ^{1}H NMR spectral analysis. After 6 days the resonances of the syn isomer were unchanged, but those of the anti isomer had decreased in intensity by 66%. No new resonances were observed. A brown solid was present in the reaction tube.

Thermal Isomerization of $[(MeCpMo)_2(\mu\text{-}S)_2(\mu\text{-}S_2)]$. The molybdenum complex (17 mg, 0.036 mmol) was dissolved in ca. 0.5 mL of $CDCl_3$ in an NMR tube. The solution was degassed and sealed under ca. 0.75 atm of argon at ambient temperature. The tube was maintained at ambient temperature for 3 months, during which time very little change was observed in the ^{1}H NMR spectrum. The tube was then placed in an oil bath at 60 °C. After 1 day, the NMR spectrum showed the presence of two additional isomers, *anti*-$[MeCpMoS(\mu\text{-}S)]_2$[8] and probably the syn isomer. ^{1}H NMR data ($CDCl_3$), δ, are as follows. Anti isomer: 6.04, 5.57 (2 m, 8, Cp); 2.03 (s, 6, Me). Syn isomer: ca. 6.30, 5.90 (2 m, 8, Cp); 2.11 (s, 6, Me). $(MeCpMo)_2(\mu\text{-}S_2)(\mu\text{-}S)_2$: 6.24, 6.19 (2 m, 8, Cp); 2.32 (s, 6, Me). The ratio of the starting complex to anti to syn isomer was ca. 5:2:4. No change was observed upon further heating.

Reaction of *anti*-$[MeCpMoO(\mu\text{-}S)]_2$ with $[(CH_3)_3Si]_2S$. The complex (10.9 mg, 0.023 mmol) was dissolved in ca. 0.5 mL of $CDCl_3$ in an NMR tube. $[(CH_3)_3Si]_2S$ (13 μL, 0.062 mmol) was syringed into the solution, and the mixture was then degassed and sealed under vacuum. The solution was maintained at ambient temperature. The course of the reaction was monitored by ^{1}H NMR spectral analysis. The resonances

(15) A product with similar chemical shifts is obtained when $(MeCpMo)_2(\mu\text{-}S)_2(\mu\text{-}S_2)$ is reacted with I_2.

for the red-brown (anti) isomer of $(MeCpMo)_2(O)(S)(\mu\text{-}S)_2$ began to appear within 3 days. After 2 days of heating at 50 °C, the ratio of the starting reagent to the $MoOS_3$ product was ca. 2:1. After 7 days of heating, resonances for $(MeCpMo)_2(\mu\text{-}S)_2(\mu\text{-}S_2)$ (65–70%) had appeared, in addition to minor resonances for *anti*-$[MeCpMoS(\mu\text{-}S)]_2$ (ca. 25%) and the syn isomer (ca. 5%). This mixture is somewhat enriched in percentage of anti isomer relative to that obtained from thermal isomerization of $(MeCpMo)_2(\mu\text{-}S)_2(\mu\text{-}S_2)$ at 60 °C.

The NMR tube was cracked open after 1 month, and the products were resealed under ca. 0.75 atm of hydrogen. Within 5 min at ambient temperature, $MeCpMo(\mu\text{-}S)_2(\mu\text{-}S)_2$ had been converted to $[MeCpMo(\mu\text{-}S)_2(\mu\text{-}SH)]_2$.[10] By the end of 6 days *anti*-$[MeCpMoS(\mu\text{-}S)]_2$ had also reacted to form the hydrosulfido complex.[8]

Reaction of *syn*-$[MeCpMoO(\mu\text{-}S)]_2$ with $[(CH_3)_3Si]_2S$. The complex (15 mg, 0.034 mmol) was dissolved in ca. 0.5 mL of $CDCl_3$ in an NMR tube. $[(CH_3)_3Si]_2S$ (21.0 μL, 0.10 mmol) was syringed into the solution, and the mixture was then degassed and sealed under vacuum. The solution was maintained at ambient temperature. The course of the reaction was monitored by ^1H NMR spectral analysis. Within 1 week resonances for the green (syn) isomer of $(MeCpMo)_2(O)(S)(\mu\text{-}S)_2$ were observed in the spectrum. Within 2 weeks the ratio was 1:1. After $2^1/_2$ weeks, resonances for $[MeCpMo]_2(\mu\text{-}S)_2(\mu\text{-}S_2)$ had become evident. This was the major product after 4 weeks.

Result of Heating $(MeCpMo)_2(O)(S)(\mu\text{-}S)_2$. The syn isomer (28 mg, 0.060 mmol) was dissolved in ca. 0.5 mL of $CDCl_3$, and the mixture was transferred to an NMR tube. The solution was degassed and sealed under ca. 0.75 atm of argon at ambient temperature. The tube was placed in an oil bath at 65 °C for 5 days. It was then cracked open, and a small amount (<2 mg) of black precipitate was isolated by filtration. This black precipitate and ca. 0.5 mL of $CDCl_3$ were added to an NMR tube. The mixture was degassed and sealed under ca. 0.75 atm of hydrogen at −196 °C, and the tube was placed in an oil bath at 65 °C. The solution turned purple within 4 h. The purple product was identified as $[MeCpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$ by its ^1H NMR spectrum; however, there was only one broad SH resonance at −1.59 ppm instead of the two sharp resonances usually observed.[14]

The solvent was evaporated from the original filtrate to give a green-brown solid, and the products were separated by chromatography on alumina. The first yellow fraction, eluted with 3:1 dichloromethane/hexane, gave a yellow solid upon evaporation of solvent. ^1H NMR spectral analysis identified the products as *anti*-$[MeCpMoO(\mu\text{-}S)]_2$ (yield 11%) and the red-brown isomer of the starting reagent (yield 11%). The second yellow-green fraction, eluted with 4:1 dichloromethane/hexane, contained the starting reagent and the anti bis(oxo) compound in yields of ca. 5 and 9%, respectively. The third red-brown fraction, eluted with 5:1 dichloromethane/acetonitrile, gave red-orange crystals of *syn*-$[MeCpMoO(\mu\text{-}S)]_2$ upon evaporation of solvent. Crude yield: 30%. Approximately 25% of the mass of the original reagent did not elute from the column.

Reaction of $(MeCpMo)_2(O)(S)(\mu\text{-}S)_2$ with Acetylene. The syn isomer (0.049 g, 0.11 mmol) was dissolved in ca. 6 mL of dichloromethane in a 500-mL pressure flask. The solution was degassed and sealed under 1 atm of acetylene at ambient temperature. The solution was maintained at ambient temperature for 5 days, and then the flask was placed in an oil bath at 50 °C for 3 days. After this time, the solvent was removed and the products were separated by chromatography on alumina. The first yellow-purple fraction, eluted with 1:1 dichloromethane/hexane, gave a yellow powder upon removal of solvent. The product was identified as $[MeCpMoS(CH{=}CH)S]_2$[14] by mass spectral data. Crude yield: 9%.

The second green fraction, eluted with 4:1 dichloromethane/hexane, gave upon evaporation of solvent a green solid, which was identified as $[MeCpMoO(\mu\text{-}S)_2Mo(SCH{=}CHS)CpMe]$. Crude yield: 11%. ^1H NMR ($CDCl_3$), δ: 8.39 (s, 2, HC=CH); 6.22, 5.45, 5.14, 4.76 (4 m, 8, Cp); 2.16, 2.03 (2 s, 6, Me). MS(FAB), *m/z*: 520 (P^+), 506 (P^+ − O), 478 ($MeCp_2Mo_2S_4^+$), 464 ($MeCp_2Mo_2S_3O^+$).

The third blue fraction, eluted with dichloromethane, gave a blue solid upon removal of solvent. The product was formulated as $MeCpMoO(\mu\text{-}S)_2Mo(SC_2H_2O)(MeCp)$. Crude yield: 21.6%. MS(EI), *m/z*: 504 (P^+), 446 ($P^+ - SC_2H_2$), 430 ($P^+ - OSC_2H_2$), 414 ($(MeCpMo)_2S_2^+$), 398 ($(MeCpMo)_2OS^+$), 382 ($(MeCpMo)_2S^+$), 368 ($(MeCpMo)_2O^+$). ^1H NMR ($CDCl_3$), δ: 8.44, 8.00 (2 d (AB pattern), 2, J = 5.3 Hz, HC=CH); 6.34 (1), 6.02 (1), 5.94 (1), 5.54 (1), 5.17 (2), 5.06 (1), 4.93 (1) (7 m, 8, Cp); 2.04, 1.95 (2 s, 6, Me). IR (cm^{-1}): 909 w ($\nu_{M=O}$) was only observed in the most concentrated Nujol mulls.

The fourth purple fraction, eluted with 5:1 dichloromethane/acetonitrile, gave a purple-brown solid upon evaporation of solvent. ^1H NMR and MS(EI) data identified one of the major products as *syn*-$[MeCpMoO(\mu\text{-}S)]_2$. In addition, the ^1H NMR spectrum suggested that the purple (syn) isomer of $MeCpMoO(\mu\text{-}S)_2Mo(SCH{=}CHS)(MeCp)$ was present. ^1H NMR ($CDCl_3$), δ: 8.39 (s, 2, HC=CH); 6.12, 6.45, 5.02, 4.48 (4 m, 8, Cp); 2.16, 2.05 (2 s, 6, Me).

Reaction of $(MeCpMo)_2(O)(S)(\mu\text{-}S)_2$ with Phenylacetylene. The complex (0.060 g, 0.13 mmol) was dissolved in ca. 20 mL of dichloromethane in a 500-mL pressure flask. Phenylacetylene (50 μL, 0.46 mmol) was syringed into the solution, which was then degassed and sealed under 1 atm of nitrogen at −196 °C. The green solution, which was maintained at ambient temperature, turned bright blue after 2 days. The solvent was removed, and the products were separated by chromatography on alumina. The first yellow fraction, eluted with 1:3 hexane/dichloromethane, was not characterized.

The second blue fraction, eluted with dichloromethane, gave a blue solid upon removal of solvent. The ^1H NMR spectrum indicated the presence of more than one product. A minor product was $MeCpMoO(\mu\text{-}S)_2Mo(SC(Ph){=}CHS)(MeCp)$,[1] and a major product was *anti*-$[MeCpMoO(\mu\text{-}S)]_2$. Another product, present as two isomers, was formulated to be $(MeCpMo)O(\mu\text{-}S)_2Mo(SCH{=}C(Ph)O)(MeCp)$ and $(MeCpMo)O(\mu\text{-}S)_2Mo(OCH{=}C(Ph)S)(MeCp)$. ^1H NMR ($CDCl_3$), δ: 8.76, 8.36 (2 s, 1, HC=C); 7.78, 7.36 (2 m, 5, Ph); 6.34 (1), 6.02 (1), 5.94 (1), 5.54 (1), 5.17 (2), 5.06 (1), 4.93 (1) (7 m, 8, Cp); 2.04, 1.95 (2 s, 6, Me). MS(EI), *m/z*: 580 (P^+), 446 (P^+ − SC(Ph)=CH), 430 (P^+ − OSC(Ph)=CH), 414 ($MeCp_2Mo_2S_2^+$), 398 ($(MeCp)_2Mo_2SO^+$), 382 ($MeCp_2Mo_2O^+$).

The third dark blue fraction, eluted with 1:1 acetonitrile/dichloromethane, gave a blue-green powder upon evaporation of solvent. The two major products were *syn*-$[MeCpMoO(\mu\text{-}S)]_2$ and the purple isomer of $MeCpMoO(\mu\text{-}S)_2Mo(SC(Ph){=}CHS)(MeCp)$.[1]

Attempted Reaction of *syn*-$(MeCpMo)(O)(S)(\mu\text{-}S)_2$ with Ethylene: Isolation of *anti*-$(MeCpMo)_2(O)(S)(\mu\text{-}S)_2$. The syn isomer (ca. 0.040 g, 0.09 mmol) was dissolved in ca. 6 mL of $CDCl_3$ in a 500-mL pressure flask. The solution was degassed and sealed under ca. 0.75 atm of ethylene at −196 °C. The flask was placed in an oil bath at 65 °C. The solution became browner as the reaction proceeded. After 5 days the solvent was removed and the products were separated by chromatography on alumina. The first orange-brown fraction, eluted with 3:1 dichloromethane/hexane, gave an orange-brown powder upon evaporation of the solvent. The product was identified as the anti isomer of the starting reagent. Yield: 17 mg, 34%. ^1H NMR ($CDCl_3$), δ: 6.15, 6.00, 5.80, 5.44 (4 m, 8, Cp); 2.10, 1.95 (2 s, 6, Me). MS(EI), *m/z*: 462 (P^+), 446 (P^+ − O), 430 (P^+ − S), 414 (P^+ − SO). IR (cm^{-1}): 905 m ($\nu_{Mo=O}$); 492 m ($\nu_{Mo=S}$); 450 w ($\nu_{Mo\text{-}S\text{-}Mo}$).

NMR experiment: *syn*-$(MeCpMo)_2(O)(S)(\mu\text{-}S)_2$ (ca 0.015 g, 0.03 mmol) was dissolved in ca. 0.5 mL of $CDCl_3$ in an NMR tube. The solution was degassed and sealed under ca. 0.75 atm of ethylene at ambient temperature. After 11 days of heating at 55 °C, the anti and syn isomers of $[MeCpMoO(\mu\text{-}S)]_2$ were major products. A small amount of $[MeCpMoSCH_2CH_2S]_2$[14] was also present. A parent ion was observed for the latter complex in the MS(FAB) spectrum of the crude product.

Acknowledgment. Support of this work by the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, Department of Energy, and, in part, by the National Institutes of Health is gratefully acknowledged. Purchase of the X-ray diffraction equipment was made possible by the National Science Foundation (Grant CHE 84-12182).

Registry No. $[CpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$, 75675-64-8; *anti*-$[CpMoO(\mu\text{-}S)]_2$, 64726-45-0; *anti*-$[MeCpMoO(\mu\text{-}S)]_2$, 107870-61-1; $[MeCpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$, 75675-65-9; *syn*-$(MeCpMo)_2(O)(S)(\mu\text{-}S)_2$, 113830-26-5; *syn*-$(CpMo)_2(O)(S)(\mu\text{-}S)_2$, 113779-11-6; *syn*-$[CpMoO(\mu\text{-}S)]_2$, 96393-76-9; *syn*-$[MeCpMoO(\mu\text{-}S)]_2$, 107870-62-2; $(MeCpMo)_2(\mu\text{-}S)_2(\mu\text{-}S_2)$, 100791-15-9; *anti*-$[MeCpMoS(\mu\text{-}S)]_2$, 78018-24-3; *syn*-$[MeCpMoS(\mu\text{-}S)]_2$, 113830-27-6; $[MeCpMoS(CH{=}CH)S]_2$, 75675-70-6; $[MeCpMoO(\mu\text{-}S)_2Mo(SCH{=}CHS)(MeCp)]$, 113779-12-7; $[MeCpMoO(\mu\text{-}S)_2Mo(SC_2H_2O)(MeCp)]$, 113779-13-8; *syn*-$[MeCpMoO(\mu\text{-}S)_2Mo(SCH{=}CHS)(MeCp)]$, 113830-28-7; $[MeCpMoO(\mu\text{-}S)_2Mo(SC(Ph){=}CHS)(MeCp)]$, 113830-29-8; $(MeCpMo)O(\mu\text{-}S)_2Mo(SCH{=}C(Ph)O)(MeCp)$, 113779-14-9; $(MeCpMo)O(\mu\text{-}S)_2Mo(OCH{=}C(Ph)S)(MeCp)$, 113779-15-0; *syn*-$[MeCpMoO(\mu\text{-}S)_2Mo(SC(Ph){=}CHS)(MeCp)]$, 113830-30-1; *anti*-$(MeCpMo)_2(O)(S)(\mu\text{-}S)_2$, 113830-31-2; $[MeCpMoS_2]_2$, 100791-15-9; $[MeCpMoSCH_2CH_2S]_2$, 75675-69-3; $[(CH_3)_3Si]_2S$, 3385-94-2; acetylene, 74-86-2; phenylacetylene, 536-74-3; ethylene, 74-85-1.

Supplementary Material Available: Complete tables of bond angles, anisotropic temperature factors, H atom coordinates, and isotropic temperature factors for *anti*- and *syn*-$[MeCpMoO(\mu\text{-}S)]_2$ (4 pages); tables of observed and calculated structure factors for the above structures (31 pages). Ordering information is given on any current masthead page.