of the solvent dependence of the fragmentation yield,[22] the smaller yield found on PVG must reflect a more efficient nonradiative relaxation of the excited complex and/or a less efficient formation of the isomeric form possessing a coordinatively unsaturated metal center.

The calculated number of silanol groups must be regarded as an approximation, but a reaction controlled only by the silanol number would be expected to produce a mixture of monomeric and cluster reaction products. Since UV photolysis of $Ru_3(CO)_{12}$ physisorbed onto partially dehydroxylated silica (Carbosil) is reported to yield monomeric $Ru(CO)_4\text{–OSi}_{surf}$ complexes,[24] in those regions where the density of silanol groups is sufficient, fragmentation to monomeric products would occur, whereas in regions of lower silanol number, oxidative addition of a single group may occur. The result would be a mixture of reaction products that is inconsistent with the observed specificity of reaction 1. In a sense, formation of the oxidative-addition product is similar to the steps leading to fragmentation in fluid solution. Yet, relative to fluid solution where fragmentation occurs with even less than a stoichiometric amount of a scavenger,[22] the absence of photofragmentation on PVG is not due to an inability to form the precursor complex or a lack of potential two-electron donors.

Wrighton and co-workers attribute the absence of a fragmentation pathway in the photochemistry of $Ru_3(CO)_9L_3$, where L represents a coordinated phosphine functionality anchored to silica gel, to constraints imposed by the functionalized support.[25] Since $Ru_3(CO)_{12}$ is physisorbed onto PVG, the constraints imposed on the complex arise from the support per se, rather than from a distinct chemical interaction. Turro has shown, in the case of dibenzyl ketones on zeolites, that the topology of the adsorbent surface affects photochemical reactivity.[30] In our opinion, it is the rigidity and topology[26-29,70] of the PVG surface, as opposed to the fluidity of a solvent cage, that limits the reaction to the oxidative addition of a single silanol group, and curtails the ability of the primary photoproduct to fragment to monomeric products. While rigidity and topology offer a rationale for the inability to model reaction 1 in fluid solution, it is not immediately apparent that they account for the differences in reactivity on Carbosil and PVG. Clearly, additional quantitative data on the photochemistry of molecules adsorbed onto chemically similar surfaces of characterized dimensionality are necessary to understand, and perhaps distinguish, the role of surface topology.

Conclusion

UV photolysis of Ru_3CO_{12} physisorbed onto porous Vycor glass leads to oxidative addition of a surface silanol group and quantitative formation of $(\mu\text{-H})Ru_3CO_{10}(\mu\text{-OSi}_{surf})$. Relative to fluid solution, the specificity of the reaction on PVG is a consequence of the rigidity and topology of the glass surface.

Acknowledgment. Support of this research by the Research Foundation of the City University of New York, the Dow Chemical Co. Technology Acquisition Program, and the National Science Foundation (Grant CHE-8511727) is gratefully acknowledged. H.D.G. thanks the Andrew W. Mellon Foundation for a fellowship during 1984, Queens College for a Presidential Research Award during 1987, and the Corning Glass Works for samples of porous Vycor glass.

Registry No. $Ru_3(CO)_{12}$, 15243-33-1; $Ru(CO)_4(PPh_3)$, 21192-23-4; $Ru(CO)_3(PPh_3)_2$, 14741-36-7; $Ru(CO)_4(P(t\text{-Bu})_3)$, 69661-89-8; $Ru_3(CO)_{11}(PPh_3)$, 38686-52-1; PPh_3, 603-35-0; $P(t\text{-Bu})_3$, 13716-12-6; CO, 630-08-0; 1-pentene, 109-67-1.

Supplementary Material Available: Figure 1S (infrared spectra recorded during 350-nm photolysis of a deaerated *n*-pentane solution containing 10^{-4} M $Ru_3(CO)_{12}$ and 10^{-3} M PPh_3), Figure 2S (dependencies of the quantum yield of declustrification on the concentration of PPh_3, 1-pentene, and $P(t\text{-Bu})_3$), and Figure 3S (diffuse reflectance FTIR spectrum of PVG calcined at 550 °C) (3 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry and Biochemistry,
University of Colorado, Boulder, Colorado 80309

Synthesis and Reactivity of an Unusual Oxidation Product of $[C_5H_5Mo(\mu\text{-S})(\mu\text{-SH})]_2$

L. D. Tanner, R. C. Haltiwanger, J. Noordik, and M. Rakowski DuBois*

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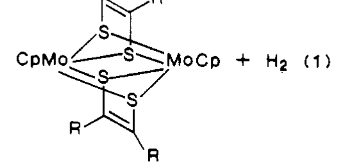
The reaction of a dilute solution of $[CpMo(\mu\text{-S})(\mu\text{-SH})]_2$ (Cp = C_5H_5) with 1 equiv of phenylacetylene under air leads to the formation of *anti*-$CpMo(O)(\mu\text{-S})_2Mo(SCH{=}C(Ph)S)Cp$ (**1**) in 20% yield. Both syn and anti isomers of **1** can be synthesized by the reaction of $[CpMo(SCH{=}C(Ph)S)]_2$ with trifluoroacetic acid under air. The anti isomer has been characterized by an X-ray diffraction study. The complex crystallizes in space group $Pna2_1$, with a = 10.284 (6) Å, b = 15.175 (8) Å, c = 12.018 (7) Å, and V = 1875 (2) Å^3. The dinuclear complex contains two μ-sulfido ligands in a nonplanar Mo_2S_2 core, a terminal oxo ligand on one CpMo site, and a bidentate styrenedithiolate ligand coordinated to the second CpMo site. The cyclopentadienyl ligands are anti with respect to the metal–metal vector. The terminal oxo ligand in **1** is displaced by sulfide in the reaction with hexamethyldisilthiane. Complex **1** reacts with hydrogen to form water, $(CpMo)_2S_4$ derivatives, and organic products that result from hydrogenation and hydrolysis of the styrenedithiolate ligand.

Introduction

During the course of our studies of cyclopentadienylmolybdenum complexes with bridging sulfido ligands, we have reported that these systems react with alkynes to form complexes with alkenedithiolate ligands, e.g., eq 1.[1-3] Although $[CpMo(\mu\text{-S})(\mu\text{-SH})]_2$ is slightly air sensitive, reaction 1 generally proceeds to give the indicated products even in the presence of air. However, when the hydrosulfido complex was reacted with only 1 equiv of an alkyne in the presence of air, we isolated an additional unusual product that had added both an oxygen atom and an alkyne molecule to the $Cp_2Mo_2S_4$ core. In this paper we report the synthesis, spectroscopic characterization, and an X-ray diffraction study of one of these products of composition $Cp_2Mo_2S_4O$-



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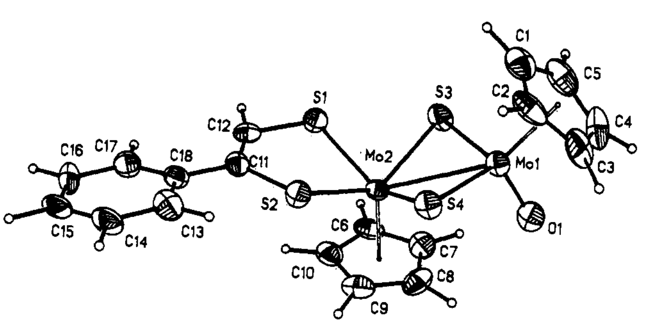

Figure 1. Perspective drawing and numbering scheme for $CpMoO(\mu\text{-}S)_2Mo(SCH{=}C(Ph)S)Cp$ (**1**). Thermal ellipsoids are shown at the 50% probability level.

(CHCPh) (**1**). The complex is a member of a new structural class of dinuclear cyclopentadienylmolybdenum complexes. The reactivity of **1** has been investigated and compared with that of the systems with $Cp_2Mo_2(\mu\text{-}S)_4$ cores.

Results and Discussion

Synthesis and Characterization of Complex 1. The reaction of $[CpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$ with 1 equiv of phenylacetylene in air proceeded in $CHCl_3$ or CH_2Cl_2 for 1 day at room temperature to form several products. Compounds that were identified in the NMR spectrum of the product mixture included isomers of $[CpMoO(\mu\text{-}S)]_2$.[4] Two major molybdenum products that were isolated by chromatography, each in 20% yield, were the bis(alkyne) adduct $[CpMo(SCH{=}C(Ph)S)]_2$[1] (**2**) and a new blue-green complex that was formulated as $CpMoO(\mu\text{-}S)_2Mo(SCH{=}C(Ph)S)Cp$ (**1**). The composition of **1** was confirmed by elemental analysis and by mass spectral data, which showed a strong parent peak. The fragmentation pattern of the spectrum suggested sequential loss of an oxygen atom and of phenylacetylene to form a base peak corresponding to $Cp_2Mo_2S_4$ (*m/e* 450). A strong absorption was observed in the infrared spectrum at 895 cm^{-1}, characteristic of a Mo=O bond. The analogous product with methylcyclopentadienyl ligands was synthesized by a similar procedure.

The ^1H NMR spectrum for **1** showed two Cp resonances that were separated by ca. 1 ppm, suggesting significant electronic and structural differences for the two CpMo moieties. On the basis of reactions of related derivatives, the alkyne was proposed to interact with sulfido ligands in the complex to form an alkenedithiolate ligand. However, the resonance for the vinyl hydrogen on the proposed styrenedithiolate ligand was shifted downfield to 8.66 ppm, compared to 6.68 ppm for the vinyl protons in the bis(styrenedithiolate) complex, $[CpMo(SCH{=}C(Ph)S)]_2$. Such a downfield shift for protons in dithiolate ligands has been observed previously in cyclopentadienyltungsten complexes in which the dithiolates served as terminal bidentate ligands.[5] The downfield chemical shift has been attributed to a dithioglyoxal resonance form for the chelating ligand.[6,7]

X-ray Diffraction Study of $CpMoO(\mu\text{-}S)_2Mo(SCH{=}C(Ph)S)Cp$ (1). The spectral data did not completely establish the structure of **1**, and therefore a crystallographic study was undertaken. Dark blue rectangular crystals were grown from a saturated 2:1 dichloromethane/hexane solution. The complex crystallized in the orthorhombic space group $Pna2_1$ with four molecules per unit cell. A perspective drawing of the molecule is shown in Figure 1, and selected bond distances and angles are presented in Table I. Positional and thermal parameters are given in Table II. The complex is a chiral dinuclear molecule with two bridging sulfido ligands, a terminal oxo ligand on one molybdenum ion, and a bidentate styrenedithiolate ligand coordinated to the second metal ion. The cyclopentadienyl ligands are oriented in anti positions with respect to the metal-metal vector. The Mo(1) ion is in a pseudotetrahedral environment (if the cyclopentadienyl ligand is assigned a single coordination site), while Mo(2) has a distorted square-pyramidal coordination geometry. Each of the molybdenum ions can be assigned a formal oxidation state of +5.

The metal-metal distance of 2.927 (1) Å is somewhat longer than those reported for other bis(sulfido)-bridged cyclopentadienylmolybdenum(V) dimers (2.87–2.90 Å)[4,8,9] and for molybdenum dimers having the $Mo_2O_2(\mu\text{-}S)_2$ core (2.82–2.89 Å).[10-13] However, the distance is still within the range for which

Table I. Bond Distances and Selected Bond Angles for $CpMo(O)(\mu\text{-}S)_2Mo(SCHC(Ph)S)Cp$ (**1**)

Distances, Å			
Mo(1)–Mo(2)	2.927 (1)	Mo(1)–S(3)	2.272 (2)
Mo(1)–S(4)	2.266 (2)	Mo(1)–O(1)	1.690 (6)
Mo(1)–C(1)	2.433 (6)	Mo(1)–C(2)	2.441 (7)
Mo(1)–C(3)	2.408 (7)	Mo(1)–C(4)	2.379 (7)
Mo(1)–C(5)	2.395 (7)	Mo(2)–S(1)	2.389 (2)
Mo(2)–S(2)	2.374 (2)	Mo(2)–S(3)	2.397 (2)
Mo(2)–S(4)	2.395 (2)	Mo(2)–C(6)	2.338 (6)
Mo(2)–C(7)	2.409 (6)	Mo(2)–C(8)	2.422 (6)
Mo(2)–C(9)	2.359 (6)	Mo(2)–C(10)	2.306 (6)
S(1)–C(12)	1.740 (9)	S(2)–C(11)	1.743 (9)
C(11)–C(12)	1.321 (13)	C(11)–C(18)	1.506 (11)

Angles, deg			
S(4)–Mo(1)–S(3)	101.3 (1)	O(1)–Mo(1)–Mo(2)	100.2 (2)
O(1)–Mo(1)–S(3)	107.9 (2)	O(1)–Mo(1)–S(4)	107.9 (2)
S(1)–Mo(2)–Mo(1)	122.6 (1)	S(2)–Mo(2)–Mo(1)	121.0 (1)
S(2)–Mo(2)–S(1)	79.6 (1)	S(3)–Mo(2)–Mo(1)	49.3 (1)
S(3)–Mo(2)–S(1)	77.2 (1)	S(3)–Mo(2)–S(2)	134.3 (1)
S(4)–Mo(2)–Mo(1)	49.2 (1)	S(4)–Mo(2)–S(1)	135.2 (1)
S(4)–Mo(2)–S(2)	75.9 (1)	S(4)–Mo(2)–S(3)	94.2 (1)
C(12)–S(1)–Mo(2)	106.9 (3)	C(11)–S(2)–Mo(2)	107.7 (3)
Mo(2)–S(3)–Mo(1)	77.6 (1)	Mo(2)–S(4)–Mo(1)	77.7 (1)
C(12)–C(11)–S(2)	119.1 (7)	C(18)–C(11)–S(2)	116.4 (6)
C(18)–C(11)–C(12)	124.5 (7)	C(11)–C(12)–S(1)	120.4 (6)
C(13)–C(18)–C(11)	119.5 (4)		

Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for **1**

	x/a	*y/b*	*z/c*	U^a
Mo(1)	2446 (7)	549 (5)	0000 (–)	302 (2)
Mo(2)	103 (7)	–295 (5)	–867 (7)	264 (2)
S(1)	–1929 (2)	–481 (2)	–118 (2)	343 (7)
S(2)	–1223 (2)	892 (2)	–1737 (2)	347 (7)
S(3)	736 (2)	–318 (2)	653 (2)	370 (8)
S(4)	1504 (2)	1226 (2)	–1239 (2)	347 (7)
O(1)	3528 (6)	–438 (5)	–304 (4)	430 (2)
C(1)	2203 (6)	2064 (5)	1050 (4)	460 (3)
C(2)	2793 (6)	2525 (5)	287 (4)	480 (4)
C(3)	4025 (6)	2011 (5)	175 (4)	520 (4)
C(4)	4197 (6)	1233 (5)	870 (4)	570 (4)
C(5)	3070 (6)	1265 (5)	1410 (4)	530 (4)
C(6)	–22 (6)	–2231 (5)	–986 (4)	390 (3)
C(7)	1331 (6)	–1997 (5)	–968 (4)	470 (3)
C(8)	1639 (6)	–1364 (5)	–1730 (4)	450 (3)
C(9)	476 (6)	–1208 (5)	–2219 (4)	490 (4)
C(10)	–550 (6)	–1744 (5)	–1759 (4)	430 (3)
C(11)	–2837 (8)	513 (6)	–1562 (6)	310 (3)
C(12)	–3135 (7)	–81 (6)	–57 (6)	300 (3)
C(13)	–3426 (4)	1704 (5)	–2858 (4)	420 (3)
C(14)	–4310 (4)	2070 (5)	–3492 (4)	450 (3)
C(15)	–5580 (4)	1662 (5)	–3493 (4)	440 (4)
C(16)	–5965 (4)	887 (5)	–2860 (4)	570 (4)
C(17)	–5081 (4)	521 (5)	–2226 (4)	480 (4)
C(18)	–3811 (4)	929 (5)	–2225 (4)	350 (3)

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

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a direct metal–metal interaction is possible. The $Mo(\mu\text{-}S)_2Mo$ unit is not planar. The dihedral angle between the Mo–S(1)–S(2) planes is 144.6°. The four sulfur atoms, which form the base of the square pyramid around Mo(2), lie in a plane with the metal ion displaced 0.91 Å out of the plane toward its Cp ligand. All of the Mo(2)–S distances are significantly longer than the Mo(1)–S bonds. This is consistent with the larger coordination number of Mo(2). The longer bond lengths may also be, in part, a result of the contribution of the dithioglyoxal resonance form to the dithiolate ligand, which was discussed above in the interpretation of the NMR spectrum for **1**. The use of such a resonance form in electron-counting schemes would result in a formal oxidation state for Mo(2) of +3 rather than +5, and longer metal–ligand bonds are expected for this electronic distribution. The structural parameters of the dithiolate ligand also suggest some dithioglyoxal contribution. The C(12)–S(1) and C(11)–S(2) distances of ca. 1.740 Å are shorter than the analogous bonds observed for bridging alkenedithiolate ligands in molybdenum complexes (1.790 (3) Å).[14]

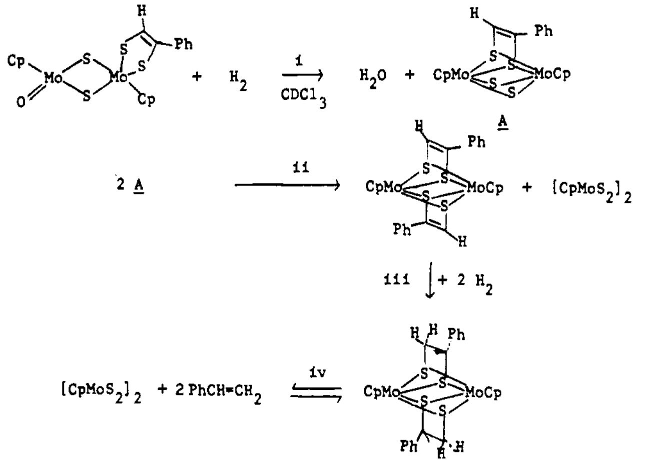
Although cyclopentadienylmolybdenum complexes with the structural features of **1** have not been reported previously, related tungsten derivatives have been characterized.[5] For example, the spectroscopic data for $CpW(S)(\mu\text{-}S)_2W(SCH{=}CHS)Cp$ suggest it has an analogous structure, and a related dinuclear complex with two terminal dithiolene ligands, $[CpW(\mu\text{-}S)(SC_2H_2S)]_2$, has been characterized by a crystallographic study.

Other Routes to the Formation of 1. In the synthesis of **1** described above, the initial oxidation of $[CpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$ in air to form $(CpMo)_2(\mu\text{-}S)_2(\mu\text{-}S_2)$[15] and water could occur prior to interaction with the alkyne; further reaction in the presence of the alkyne might lead to **1**. In order to determine whether water or oxygen was the source of the oxo ligand in **1**, the reaction of an isolated sample of $(MeCpMo)_2(\mu\text{-}S)_2(\mu\text{-}S_2)$ with phenylacetylene (1 equiv) was carried out under anhydrous conditions under ca. 0.5 atm of dry oxygen. The major products observed under these conditions were **1** and syn and anti isomers of $[MeCpMoO(\mu\text{-}S)]_2$.[4] In contrast, when the reaction was carried out in the presence of ca. 100 equiv of water under a vacuum, **1** was not detected in the NMR spectrum of the products. The bis(alkyne) adduct $[MeCpMo(SCH{=}C(Ph)S)]_2$ and the starting reagent were the major products observed. These results indicate that oxygen, but not water, is necessary for the formation of **1**.

These studies led us to investigate in more detail the oxidation behavior of $[CpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$ or $(MeCpMo)_2(\mu\text{-}S)_2(\mu\text{-}S_2)$ in the absence of alkynes. Several oxidation products were isolated and characterized, and the reactivity of each of these with alkynes was studied. A synthesis of **1** was also developed by this route. The results of this investigation are presented in the following paper.[4]

An alternate synthesis of **1** was developed from the bis(alkyne) adduct **2**. Previous preliminary results had suggested that addition of a protic acid to **2** resulted in cleavage of a C–S bond of at least one of the dithiolate ligands.[16] When **2** was reacted with 2 equiv of trifluoroacetic acid in the presence of air, a complex mixture of products was formed, which has not been completely characterized. However, **1** was isolated from this reaction in 19% yield. A second purple product, **3**, which was isolated by chromatography in 11% yield, was proposed to have the same composition as **1** on the basis of mass spectral and elemental analysis data. The ^1H NMR spectrum of **3** was similar to that of **1** with two Cp resonances at 5.13 and 6.15 ppm, phenyl multiplets at 7.30 and 7.62 ppm, and a resonance for the vinyl proton of the dithiolate ligand at 8.65 ppm. This isomer of **1** is proposed to have similar coordination environments around each metal ion with the cyclopentadienyl ligands in a syn orientation.

Scheme I



Reactivity of CpMoO(μ-S)₂Mo(SCH=C(Ph)S)Cp (1). Several different sulfur-transfer reagents have been used to exchange terminal oxo ligands for sulfido ligands in metal complexes.[17-20] Hexamethyldisilthiane has been a relatively successful reagent for this transformation.[17,18] Complex **1** was found to react with this sulfide to form $(CpMo)(S)(\mu\text{-}S)_2Mo(SCH{=}C(Ph)S)Cp$ (**4**), which was isolated in 90% yield and characterized by mass spectral and ^1H NMR data. An absorption in the infrared spectrum at 495 cm^{-1} was assigned to the Mo–S stretch associated with the terminal sulfido ligand. Complex **4** was extremely air and/or moisture sensitive and quickly reverted to **1** when its solutions were exposed to air. Although the hexamethyldisilthiane reagent provided the most efficient syntheses of **4**, a more unusual pathway was found, based on the cleavage of carbon–sulfur bonds of thiol reagents. For example, **4** was isolated in 75% yield from the reaction of **1** with excess ethanethiol. Other products were not characterized, but further studies of the thiol reactions are planned. Diphosphorus pentasulfide, P_2S_5, which has been used as a sulfide donor for molybdenum dimers with terminal and bridging oxo ligands,[20] did not form **4** when it was reacted with **1** under conditions used previously for sulfide transfer.

Reactivity of 1 with Hydrogen. Cyclopentadienylmolybdenum(III) complexes with bridging alkenedithiolate ligands have been reported to react with hydrogen under mild conditions to form complexes with alkanedithiolate bridges.[1,3] Although both the electronic and structural characteristics of **1** are different from those of the previously studied quadruply bridged Mo(III) complexes, we have found that **1** also undergoes a reaction with an atmosphere of hydrogen at room temperature. The reaction is complex, and several products have been identified. An initial process appears to involve hydrogenolysis of the terminal oxo ligand. In the NMR spectrum a resonance assigned to water grew in intensity as the reaction with hydrogen proceeded, and molybdenum products that were formed after a few days at room temperature contained the $Cp_2Mo_2S_4$ core. Major products were tentatively identified as $[CpMoSCH_2CH(Ph)S)]_2$, $(CpMo)_2(\mu\text{-}S_2)(\mu\text{-}S)_2$, and $[CpMoS(\mu\text{-}S)]_2$ (relative ratios 16:6:5) by comparison of ^1H NMR resonances with authentic samples that were prepared independently. (See Experimental Section.) The sul-

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fido-bridged complexes were isolated by chromatography, but the dithiolate-bridged derivative was found to lose styrene on the chromatographic column. The NMR spectrum also showed evidence for additional minor cyclopentadienylmolybdenum products, which were not identified.

Under different conditions, when a reaction mixture of **1** with hydrogen was heated in a sealed NMR tube at 50 °C, the sulfido-bridged complexes described above were major products, but the alkanedithiolate complex had apparently undergone a further reaction. In addition to water, other volatile products were observed when the product solution was distilled; these were identified by GC/mass spectroscopy as styrene (relative yield 48%), ethylbenzene (29%), acetophenone (8%), and a product of formulation $C_8H_{10}S$, possibly $PhCH_2CH_2SH$ or $PhCH(SH)CH_3$ (15%).

The way in which the hydrogen molecule is activated and the mechanism for the hydrogenolysis of the terminal oxo ligand in **1** are not known. However, this initial reduction of **1** appears to permit a rearrangement to the quadruply bridged structures with $[CpMoS_2]_2$ cores and provides an entry into the extensive reaction chemistry associated with these systems (Scheme I). For example, a possible pathway for the formation of styrene is shown in steps ii–iv of Scheme I. Our inability to isolate A in various reaction systems suggests that its disproportionation (Scheme I, step ii) is facile. The hydrogenation of the bis(styrenedithiolate) complex (Scheme I, step iii) has been characterized in separate experiments, and the hydrogenated product has been found to lose styrene readily (Scheme I, step iv).

Some of the other organic products observed in the reaction of **1** with hydrogen may also result from reactions of the quadruply bridged intermediates. In related systems, the phenylacetylene adduct of $(CpMoS)_2S_2CH_2$ has been observed to react with water to generate acetophenone,[21] and the styrene adduct has been found to react with hydrogen to produce ethylbenzene.[22] Both of these conversions required the presence of protonic acids. In the present system catalytic amounts of acid present in the solvent may promote the formation of acetophenone and ethylbenzene.

Summary and Conclusions. The reaction of 1 equiv of phenylacetylene with $[CpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$ in air or of $[CpMo(SCH{=}C(Ph)S)]_2$ with trifluoroacetic acid under air leads to the formation of a new type of oxidized product, $CpMoO(\mu\text{-}S)_2Mo(SCH{=}C(Ph)S)Cp$. The complex contains pseudotetrahedral and square-pyramidal metal centers. The tetrahedral metal center is the site of observed reactivity in this complex. It undergoes terminal oxo ligand exchange with thiols as well as with a more conventional sulfur-transfer agent. The tetrahedral metal center also appears to be involved in the initial activation of hydrogen by the complex. Hydrogenolysis of the oxo ligand at this site produces water and appears to permit rearrangement of the complex to a quadruply bridged $Cp_2Mo_2S_4$ derivative. In further studies we wish to determine whether the vacant coordination site, generated at the tetrahedral molybdenum ion by elimination of water, might be long-lived enough to be exploited in the activation of other substrates.

Experimental Section

Materials and Instrumentation. $[CpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$,[2] $[MeCpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$,[2] $(MeCpMo)_2(\mu\text{-}S)_2(\mu\text{-}S_2)$,[15] and $[CpMo(SC(Ph){=}CHS)]_2$[1] were prepared by published procedures. Oxygen (extra dry grade, <10 ppm of H_2O) was purchased from Matheson. Phenylacetylene and hexamethyldisilthiane were purchased from Aldrich and used without purification. Dichloromethane was distilled from P_4O_{10}. ^1H NMR spectra were recorded in $CDCl_3$ at 90 MHz on a JEOL FX-90Q or Varian EM-390 spectrometer. Chemical shifts were reported relative to 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 cells. Mass spectra were recorded on a VG Analytical 7070 EQ-HF mass spectrometer. GC/MS analyses were carried out on the VG Analytical instrument with a Hewlett-Packard 5790A gas chromatograph using a Hewlett-Packard cross-linked SE-54 fused-silica capillary column (0.2-mm i.d. × 25 m). Elemental analyses were performed by Spang Microanalytical Laboratories.

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 a standard in determining potentials.

Synthesis of *anti*-$CpMoO(\mu\text{-}S)_2Mo(SCH{=}C(Ph)S)Cp$ (1). Method A. $[CpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$ (0.50–0.60 g, 0.88–1.06 mmol) was dissolved in ca. 50 mL of dichloromethane in a 250-mL Schlenk flask fitted with a septum to prevent evaporation of solvent. A 1 equiv amount of phenylacetylene was syringed into the solution. The solution was stirred at ambient temperature under air for 24 h, during which time it changed from purple to dark green. The solvent was removed, and the products were separated by chromatography on alumina. The first yellow fraction was eluted with 2:1 hexane/dichloromethane. The product was identified as the bis(phenylacetylene) adduct[1] by ^1H NMR spectral analysis and EI-MS data. Yield: 18–22%.

The second green-blue fraction, eluted with 1:4 hexane/dichloromethane, was the desired product, **1**. Yield: 16–24%. Solvent was removed to give the product as a green-blue powder or dark blue crystals. The complex was further purified by recrystallization from diethyl ether. ^1H NMR ($CDCl_3$), δ: 8.66 (s, 1, $HC{=}C$); 7.78, 7.36 (2 m, 5, Ph); 6.22, 5.27 (2 s, 10, Cp). MS(EI), m/z: 568 (P^+), 552 ($P^+ - O$), 450 ($Cp_2Mo_2S_4^+$), 434 ($Cp_2Mo_2S_3O^+$), 418 ($Cp_2Mo_2S_3^+$). IR (cm^{-1}): 895 m ($\nu_{Mo{=}O}$); 475 w, 465 w, 425 w ($\nu_{Mo\text{-}S\text{-}Mo}$). $E_{1/2}$, V vs SCE: −0.96 (ΔE_p = 50 mV, $i_{pc}/i_{pa} = 1$), −1.54 (ΔE_p = 70), +0.94 (irrev). Anal. Calcd for $C_{18}H_{16}Mo_2S_4O$: C, 38.03; H, 2.84; S, 22.56. Found: C, 38.13; H, 2.94; S, 22.38.

The MeCp analogue of **1** was prepared in a similar procedure. ^1H NMR ($CDCl_3$), δ: 8.66 (s, 1, $HC{=}C$); 7.78, 7.36 (2 m, 5, Ph); 6.26, 5.51, 5.20, 4.83 (4 m, 8, Cp); 2.16, 2.04 (2 s, 6, MeCp).

Method B. $[CpMo(SCH{=}C(Ph)S)]_2$ (**2**) (0.415 g, 0.64 mmol) was dissolved in ca. 75 mL of dichloromethane in a 250-mL Schlenk flask fitted with a septum. Trifluoroacetic acid (94 μL, 1.2 mmol) was syringed into the solution. The solution was stirred under air at ambient temperature for 7 days. The solvent was removed, and the products were separated by chromatography on alumina. The first very dilute yellow fraction, eluted with 2:1 hexane/dichloromethane, was not characterized. The second yellow-green fraction, eluted with 1:3 dichloromethane/hexane, gave a green-blue powder upon removal of solvent. The product was identified as compound **1** by ^1H NMR spectral analysis. Yield: 0.069 g, 19%.

The third light violet fraction, eluted with 1:4 hexane/dichloromethane, gave a brown-purple powder upon removal of solvent. This purple product, **3**, was identified as the syn isomer of **1**. Yield: 0.039 g, 11%. The product was recrystallized from 2:1 diethyl ether/dichloromethane. MS(EI), m/z: 568 (P^+), 418 ($Cp_2Mo_2S_3$), 402 ($Cp_2Mo_2S_2O$). IR: 892 cm^{-1} ($\nu_{Mo{=}O}$). ^1H NMR (in $CDCl_3$), δ: 8.65 (s, 1, $HC{=}C$); 7.62, 7.30 (2 m, 5, Ph); 6.15, 5.13 (2 s, 10, Cp). Anal. Calcd for $C_{18}H_{16}Mo_2S_4O$: C, 38.03; H, 2.84; S, 22.56. Found: C, 37.92; H, 2.91; S, 22.42.

Synthesis of 1 Using Oxygen as Source of the Oxo Ligand. $(MeCpMo)_2(\mu\text{-}S)_2(\mu\text{-}S_2)$ (0.016 g, 0.03 mmol) was dissolved in ca. 2 mL of freshly distilled dichloromethane, and phenylacetylene (3 μL, 0.027 mmol) was added. The solution was freeze–pump–thaw degassed two times and stirred for ca. 2 h, and then ca. 0.5 atm of oxygen was added. The reaction flask was sealed and the solution stirred at room temperature for 6 days. The solvent was then evaporated, and the remaining solid was dissolved in dry CD_2Cl_2. The NMR spectrum showed the presence of **1** (MeCp analogue) (yield ca. 50%) and of *syn*- and *anti*-$[MeCpMoO(\mu\text{-}S)]_2$[4] (yield ca. 50%).

Attempted Synthesis of 1 Using Water as Source of the Oxo Ligand. $(MeCpMo)_2(\mu\text{-}S)_2(\mu\text{-}S_2)$ (0.016 g, 0.03 mmol) was dissolved in ca. 2 mL of $CDCl_3$, and phenylacetylene (3 μL, 0.027 mmol) and water (56 μL, 3 mmol) were added. The solution was freeze–pump–thaw degassed three times, and the reaction flask was sealed with a high-vacuum Teflon stopcock. After the solution was stirred at room temperature for 6 days, the flask was opened and the NMR spectrum was recorded immediately. Complex **1** (MeCp analogue) was not observed in the NMR spectrum. Major products were $[MeCpMo(SCH{=}C(Ph)S)]_2$ (**2**, MeCp analogue), and the starting complex. NMR for **2** (MeCp analogue) ($CDCl_3$), δ: 7.2 (m, Ph); 6.74 (s, $HC{=}C$); 5.82 (s, Cp); 2.05 (s, Me).

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[21] Laurie, J. C. V.; Duncan, L.; Haltiwanger, R. C.; Weberg, R. T.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1986**, *108*, 6234.

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Table III. Crystal Data and Details of the Structure Determination and Refinement for [$C_5H_5MoO(\mu\text{-}S)_2Mo(SC_6H_5C{=}CHS)C_5H_5$] (**1**)

Crystal Data

formula	$Mo_2S_4OC_{18}H_{16}$	c, Å	15.175 (8)	ρ_{measd}, g/cm$^{3\,c}$	2.180
mol wt	568	α, deg	90	Z	4
space group[a]	$Pna2_1$	β, deg	90	ρ_{calcd}, g/cm^3	2.04
cryst syst	orthorhombic	γ, deg	90	F(000)	1120
a, Å[b]	10.284 (6)	vol, Å^3	1876 (2)	μ, cm^{-1}	17.4
b, Å	12.018 (7)				

Data Collection and Reduction

diffractometer	Nicolet P$\bar{1}$	bkgd	stationary crystal–stationary counter; bkgd time = 0.5 scan time
radiation (λ, Å)	Cu Kα (1.5418) Mo Kα (0.71069)		
takeoff angle for graphite monochromator, deg	4.0	check reflcns	(455), (-4,-3,-3)
		freq	every 2 measmts
temp, K	294–297	variation	statistically random
cryst habit	parallepiped	no. of reflcns measd	4398
cryst color	dark blue	no. of unique reflcns	1972
cryst dimens, mm	0.12 × 0.17 × 0.35	agreement factor during averaging[d]	0.03
scan technique	θ–2θ	no. of obsd reflcns	1852
2θ, deg: min–max	3.0–42.0	σ criterion	$F > 6\sigma(F)$
hkl values scanned	$\pm h,\pm k,\pm l$	abs cor	none
scan speed, deg/min	2.0		
scan range, deg	0.7 below Kα_1 to 0.7 above Kα_2		

Structure Determination and Refinement

method of phase determination	Patterson	ratio of observns to params	9.5:1
programs	SHELX76[e]	esd of observn of unit weight	n.a.
scattering factors	neutral atoms[f]	av shift/error	0.000
R, R_w[g] for obsd data	0.031, 0.039	max shift/error	0.001
weight	$1.0/(\sigma^2(F) + 0.0009F^2)$	obsd for	z/c of S1
no. of params	195	residual electron density, e/Å^3	1.4 (1.1 Å from Mo(2))

[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 for 15 reflections with 2θ in the range 13.5–27.1°. [c] By flotation methods in 1,2-dibromoethane. [d] $R_{merge} = [\sum N(\sum w(F_{mean} - F)^2)/\sum((N-1)\sum wF^2)]^{1/2}$. [e] Sheldrick, G. M. "Shelx76. A Program for Crystal Structure Determination"; University of Cambridge: Cambridge, England, 1976. [f] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4. [g] The quantity minimized in the block-cascade least-squares procedures is $\sum w(|F_o| - |F_c|)^2$. $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = \sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2$.

X-ray Diffraction Study of 1. Dark blue rectangular crystals of **1** were obtained by slow evaporation of a 2:1 dichloromethane/hexane solution. Details of the crystal data and the structure solution and refinement are presented in Table III. In the final refinement phenyl and cyclopentadienyl rings were constrained and hydrogen atoms were included in fixed idealized positions.

The absolute configuration of this structure was determined by using the method of Hamilton.[23] The R_w values for both structures were calculated from data for which Friedel pairs were not averaged. The ratio of the resulting R_w values (0.0411, 0.0395) was 1.0405, significantly greater than the R factor ratio value of 1.0026. Thus, at the 99.5% confidence level, the absolute configuration shown is correct for the crystal examined. We have no evidence to indicate that the other enantiomer is not also present in the reaction product.

Synthesis of [CpMoS(μ-S)$_2$Mo(SCH=C(Ph)S)Cp] (4). Complex **1** (15 mg, 0.026 mmol) was dissolved in ca. 2 mL of $CDCl_3$. [$(CH_3)_3Si]_2S$ (30.0 μL, 0.14 mmol) was syringed into the solution, which was degassed and sealed under vacuum. The tube was placed in an oil bath at 70 °C. After 4 weeks the solvent was removed by vacuum distillation and the green-blue solid was washed with pentane under nitrogen. The product was then stored under nitrogen. Crude yield: 90.0%. ^{1}H NMR ($CDCl_3$), δ: 8.62 (s, 1, HC=C); 7.78, 7.35 (2 m, 5, Ph); 6.00, 5.43 (2 s, 10, Cp). MS(EI), m/z: 584 (P$^+$), 552 (P$^+$ – S), 482 ($Cp_2Mo_2S_5^+$), 450 ($Cp_2Mo_2S_4^+$), 418 ($Cp_2Mo_2S_3^+$). IR (cm^{-1}): 495 m ($\nu_{Mo=S}$); 462 w, 445 w ($\nu_{Mo\text{-}S\text{-}Mo}$).

Reaction of CpMoO(μ-S)$_2$Mo(SCH=C(Ph)S)Cp (1) with Ethanethiol. Complex **1** (0.065 g, 0.11 mmol) was dissolved in ca. 25 mL of dichloromethane. Ethanethiol (0.3 mL, 4.0 mmol) was syringed into the solution, which was degassed and sealed under vacuum. The solution was maintained at ambient temperature. After 2 days the solvent was removed by vacuum distillation, leaving a blue solid, which was washed with diethyl ether to remove excess ethanethiol. ^{1}H NMR spectral analysis identified one product as CpMoS(μ-S)$_2$Mo(SCH=C(Ph)S)Cp in a ratio of 3:1 with an unidentified product having a resonance at 5.25 ppm. MS(EI), m/z: 482 ($Cp_2Mo_2S_5^+$), 450 ($Cp_2Mo_2S_4^+$), 418 ($Cp_2Mo_2S_3^+$). Resonances for the starting reagent **1** reappeared in the ^{1}H NMR spectrum after the solid product was kept for several months in air.

Attempted Reaction of CpMoO(μ-S)$_2$Mo(SCH=C(Ph)S)Cp with P_2S_5. Complex **1** (0.062 g, 0.11 mmol) and P_2S_5 (0.054 g, 0.24 mmol) were dissolved in ca. 25 mL of xylene. The solution was refluxed under nitrogen for 4 h. Insoluble brown precipitate was separated from the red-purple solution by filtration and discarded. Upon removal of solvent, the filtrate gave a red-purple solid, which was washed with diethyl ether to remove excess xylene. No resonances were observed in the ^{1}H NMR spectrum of this product, and its composition was not determined. MS(EI), m/z: 760 (P$^+$), 556 (P$^+$ – 2 alkyne), 540 (P$^+$ – O (2 alkyne)), 524 (P$^+$ – S (2 alkyne)), 450 ($Cp_2Mo_2S_4^+$), 418 ($Cp_2Mo_2S_3^+$).

Synthesis of [CpMoSCH$_2$CH(Ph)S]$_2$. [CpMo(μ-S)(μ-SH)]$_2$ (0.022 g, 0.049 mmol) was dissolved in ca. 0.5 mL of $CDCl_3$ in an NMR tube, and styrene (11 μL, 0.96 mmol) was syringed into the solution. The solution was flushed with nitrogen. After 2 days, the solvent was evaporated to give a red-brown powder. ^{1}H NMR ($CDCl_3$), δ: 7.22 (m, 10, Ph); 5.20 (m, 10, Cp); 3.00, 2.66, 1.80 (3 m, 6, CH_2CH). MS(EI), m/z: 480 ($Cp_2Mo_2S_4C_2H_6$), 464 ($Cp_2Mo_2S_4CH_2$), 450 ($Cp_2Mo_2S_4$). The same product was formed in the room temperature hydrogenation of **2**.

Synthesis of (CpMo)$_2$(μ-S)$_2$(μ-S$_2$). The previously reported synthesis of the MeCp analogue of this complex[15] did not appear to be successful for the synthesis of the unsubstituted Cp derivative. However, this complex was tentatively identified as a product formed during chromatography of [CpMo(μ-S)(μ-SH)]$_2$. The latter complex was eluted in air on an alumina column with dichloromethane. A slow-moving blue fraction gave a brown powder upon removal of the solvent. ^{1}H NMR ($CDCl_3$), δ: 6.55 (s, Cp).

Synthesis of [CpMoS(μ-S)]$_2$. Aqueous $(NH_4)_2S$ (41 mL, 23%) and S_8 (2.21 g, 8.6 mmol) were refluxed in 40 mL of THF for 20 min. The solution was cooled, and [CpMo(CO)$_3$]$_2$ (1.98 g, 4.0 mmol) in 110 mL of THF was added. The solution was refluxed for 5 h. After the solution was cooled, 250 mL of H_2O with NaCl (30 g) was added, and the solution was extracted with three 150-mL portions of ether. The ether extract was evaporated, and the solid was washed with 50 mL of H_2O and 100 of mL acetone. The product remained as a brown-purple solid. Yield: 1.26 g, 69%. ^{1}H NMR ($CDCl_3$), δ: 5.91 (s, Cp). MS(EI), m/z: 450 (P$^+$), 418 (P$^+$ – S), 386 (P$^+$ – 2S). IR (Nujol), cm^{-1}: 485 ($\nu_{Mo=S}$); 440 ($\nu_{Mo\text{-}S\text{-}Mo}$).[24]

Reaction of CpMoO(μ-S)$_2$Mo(SC(Ph)=CHS)Cp (1) with Hydrogen. Complex **1** (0.047 g, 0.08 mmol) was dissolved in ca. 6 mL of $CDCl_3$ in

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(23) Hamilton, W. C. *Acta Crystallogr.* **1965**, *18*, 502.

(24) This compound was first synthesized in our laboratory by W. K. Miller: Miller, W. K.; Rakowski DuBois, M., unpublished results.

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.

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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; $PhC{\equiv}CH$, 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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(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]

Contribution from the Department of Chemistry and Biochemistry,
University of Colorado, Boulder, Colorado 80309

Structures and Reactivities of Cyclopentadienylmolybdenum Complexes with Oxo and Sulfido Ligands

L. D. Tanner, R. C. Haltiwanger, and M. Rakowski DuBois*

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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 $\beta = 106.51$ (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, $\alpha = 103.73$ (1)°, $\beta = 90.16$ (1)°, and $\gamma = 107.92$ (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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(11) A similar result has been observed in the oxidation of $[Me_5C_5MoS(\mu\text{-}S)]_2$.[8]