Although the best stereoselectivities were observed for those substrates with very bulky β-carbon substituents, it is significant that the vinyl insertion process is still several times faster than M–H addition–β-hydride elimination even for those substrates with relatively small β-carbon substituents. Additionally, vinyl insertion is the primary mode of reaction regardless of the presence of allylic protons.

Normally, a small fraction of the substrate was consumed during the autoinitiation sequence for generation of the vinyl insertion catalyst. However, in the case of the bulkiest of the substrates studied it was shown that addition of a small amount of a smaller olefin was necessary to generate the vinyl insertion catalyst.

We anticipate that this process, analogous to the well-known aryl C–H bond insertion reaction, will continue to be an important consideration in future discussions of transition-metal-catalyzed activation of C–H bonds in olefins.

Acknowledgment. We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

Registry No. $Ir(i\text{-}Pr_3P)_2H_5$, 53470-70-5; $Ir(Et_3P)_2H_5$, 32490-60-1; C_6H_6, 71-43-2; $H_2C{=}C(Me)CMe_3$, 594-56-9; $H_2C{=}CHCMe_3$, 558-37-2; $H_2C{=}C(Me)CHMe_2$, 563-78-0; $H_2C{=}CHCHMe_2$, 563-45-1; $H_2C{=}CMe(CH_2)_2Me$, 763-29-1; $H_2C{=}CH(CH_2)_2Me$, 109-67-1; $H_2C{=}CMe_2$, 115-11-7.

A Mononuclear Oxosulfidomolybdenum(VI) Complex and Other Oxo, Sulfido, and η^2-S_2O Derivatives of (Pentamethylcyclopentadienyl)molybdenum and -tungsten

J. W. Faller* and Yinong Ma

Department of Chemistry, Yale University, New Haven, Connecticut 06520

Received September 7, 1988

The reactions between hydrogen sulfide and $Cp^*W({=}O)_2R$ ($Cp^* = \eta^5$-C_5Me_5, R = methyl (Me) or Me_3SiCH_2) gave $Cp^*W({=}O)({=}S)R$ (**1a**, R = Me; **1b**, R = Me_3SiCH_2). Similarly, $Cp^*Mo({=}O)_2(CH_2SiMe_3)$ gave $Cp^*Mo({=}O)({=}S)(CH_2SiMe_3)$ (**2**). However, on reaction with H_2S, $Cp^*Mo({=}O)_2Me$ gave an air-sensitive red compound, characterized as the disulfide $Cp^*Mo({=}O)(\eta^2\text{-}S_2)Me$, which is readily oxidized to form a stable compound, $Cp^*Mo({=}O)(\eta^2\text{-}S_2O)Me$ (**3**). The crystal structure of $Cp^*Mo({=}O)(\eta^2\text{-}S_2O)Me$ is reported in detail. The compound crystallizes in the orthorhombic space group *Pbca* (No. 61) with $Z = 8$, $a = 25.134$ (9), $b = 10.000$ (6), and $c = 11.009$ (7) Å, and $V = 2767$ Å^3. Anisotropic refinement of all non-hydrogen atoms and inclusion of hydrogen atoms at calculated positions converged to the residuals $R_1 = 0.038$ and $R_2 = 0.045$.

Introduction

Mononuclear Mo and W complexes containing both oxo and sulfido ligands are extremely rare,[1] owing in part to the propensity of the M=S linkage to dimerize via μ-sulfido bridges and form polynuclear complexes of molybdenum and tungsten.[2] The widespread interest in simple oxosulfidomolybdenum complexes and their tungsten counterparts arises in large measure from their potential use as models for biological systems (for example, the molybdenum sites of xanthine reductase, xanthine oxidase, aldehyde oxidase).[3] The structure and reactivity of this type of model system may provide more insight into both the biological environment and activity of pertinent molybdoenzymatic systems such as xanthine oxidase. This prompted us to investigate the syntheses and reactivities of mononuclear oxosulfidomolybdenum and -tungsten complexes. Both theoretical[4] and experimental studies have shown that the transformation of dioxometal species to monoxometal species is a thermodynamically favorable process.[5,6] Taking advantage of the remarkable stability of the M–C bond in dioxometal system $(\eta^5\text{-}C_5Me_5)M({=}O)_2R$ (M = Mo and W), our approach to the syntheses of oxosulfido complexes has centered about the replacement of one of the oxo ligands with a sulfido ligand by exchange with H_2S.

---

[1] Most of the $[MO_xS_{4-x}]^{2-}$ ions have been reported (see: Müller, A.; Diemann, E.; Jostes, R.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 934 and references therein. Spectroscopic evidence exists for $[MoO_xS_{3-x}(OSiMe_3)]^-$ ions (see: Do, Y.; Simhoun, E. D.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 1831–1838. The only other monomeric complexes to our knowledge are the $Mo(O)(S)(R_2NO)_2$ compounds (Hofer, E.; Holzbach, W.; Wieghardt, K. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 282. Wieghart, K.; Hahn, M.; Weiss, J.; Swiridoff, W. *Z. Anorg. Allg. Chem.* **1982**, *492*, 164). The structure of one of the Wieghardt compounds has been determined (Bristow, S.; Collison, D.; Garner, C. D.; Clegg, W. *J. Chem. Soc., Dalton Trans.* **1983**, 2495).

[2] (a) Stevenson, D. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1967**, *89*, 3721. (b) Winograd, R.; Spivack, B.; Dori, Z. *Cryst. Struct. Commun.* **1976**, *5*, 373. (c) Dirand-Colin, J.; Richard, L.; Weiss, R. *Inorg. Chim. Acta* **1976**, *18*, L12. (d) Rakowski DuBois, M.; DuBois, D. L.; Van Derveer, M. C.; Haltiwanger, R. C. *Inorg. Chem.* **1981**, *20*, 3064. (e) Brunner, H.; Meier, W.; Wachter, J.; Guggolz, E.; Zahn, T.; Ziegler, M. L. *Organometallics* **1982**, *1*, 1107. (f) Baricelli, P. J.; Drew, M. G. B.; Mitchell, P. C. H. *Acta Crystallogr., Sect. C* **1983**, *39*, 843. (g) Halbert, T. R.; Pan, W. H.; Stiefel, E. I. *J. Am. Chem. Soc.* **1983**, *105*, 5476. (h) Howlader, N. C.; Haight, G. P., Jr.; Hambley, T. W.; Snow, M. R.; Lawrence, G. A. *Inorg. Chem.* **1984**, *23*, 1811. (i) Rajan, O. A.; McKenna, M.; Noordik, J.; Haltiwanger, R. C.; Rakowski DuBois, M. *Organometallics* **1984**, *3*, 831. (j) Kubas, G. J.; Wasserman, H. J.; Ryan, R. R. *Organometallics* **1985**, *4*, 419. (k) Brunner, H.; Kauermann, H.; Pfauntsch, J.; Wachter, J.; Enemark, J. H.; Young, C. *J. Organomet. Chem.* **1987**, *331*, 45–52. (l) Tanner, L. D.; Haltiwanger, R. C.; Rakowski DuBois, M. *Inorg. Chem.* **1988**, *27*, 1741. (m) Steifel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 1–223.

[3] (a) Cramer, S. P.; Wahl, R.; Rajagopalan, K. V. *J. Am. Chem. Soc.* **1981**, *103*, 7721. (b) Cramer, S. P.; Hille, R. *J. Am. Chem. Soc.* **1985**, *107*, 8164 and references therein. (c) Spiro, T. G., Ed. *Molybdenum Enzymes*; Wiley: New York, 1985. (d) Holm, R. H.; Berg, J. M. *Acc. Chem. Res.* **1986**, *19*, 363 and references therein.

[4] (a) Rappé, A. K.; Goddard, W. A., III *J. Am. Chem. Soc.* **1982**, *104*, 3287. (b) Goddard, W. A., III *Science (Washington, DC)* **1985**, *227*, 917.

[5] Faller, J. W.; Ma, Y. *Organometallics* **1988**, *7*, 559; *J. Organomet. Chem.* **1988**, *340*, 59; *J. Organomet. Chem.*, in press (preparation of Cp^*MoO_2R).

[6] Legzdins, P.; Philips, E. C.; Rettig, S. J.; Sânchez, L.; Trotter, J.; Yee, V. C. *Organometallics* **1988**, *7*, 1877–1878.

$$(\eta^5\text{-}C_5Me_5)M({=}O)_2R + H_2S \rightleftharpoons (\eta^5\text{-}C_5Me_5)M({=}O)({=}S)R + H_2O$$

We report here the use of this route in the isolation and characterization of the compounds $Cp^*W({=}O)({=}S)R$ (**1a**, R = Me; **1b**, R = CH_2SiMe_3), $Cp^*Mo({=}O)({=}S)(CH_2SiMe_3)$ (**2**), and $Cp^*Mo({=}O)(\eta^2\text{-}S_2O)Me$ (**3**).

Results and Discussion

Reactions of $Cp^*W({=}O)_2R$ with Hydrogen Sulfide. Yellow solutions are formed when H_2S-saturated CS_2 solutions of colorless $Cp^*W({=}O)_2R$ are allowed to stand for 30 min (R = methyl) or several days (R = CH_2SiMe_3). Thin-layer chromatographic separation of the residues after solvent removal resulted in formation of yellow compounds of $Cp^*W({=}O)({=}S)Me$ (**1a**) and $Cp^*W({=}O)({=}S)(CH_2SiMe_3)$ (**1b**) in 77 and 40% yields, respectively. Under the same conditions, the introduction of anhydrous Na_2SO_4 to remove the H_2O released in the reaction did not appear to improve the yields significantly.

The spectral features are in good agreement with the formulae. The medium infrared absorptions at 497 and 495 cm^{-1} were assigned to the terminal sulfido stretches[7] for **1a** and **1b**, respectively, in addition to the bands at 930 cm^{-1} for **1a** and 927 cm^{-1} for **1b**, characteristic of metal–oxo stretches. The NMR spectrum of **1b** exhibits the pattern of two inequivalent methylene protons consistent with the chiral metal center environment of the molecule. As demonstrated previously in the case of $Cp^*W({=}O)(\eta^2\text{-}O_2)(CH_2SiMe_3)$,[5] the diastereotopic methylene protons have very different coupling constants to tungsten (7.5, 10.7 Hz). This seems to be an intrinsic feature of this type of system. The coupling constant (9.2 Hz) between the methyl protons and W in compound **1a** is significantly smaller than that of its parent compound $Cp^*W({=}O)_2Me$ (10.8 Hz). This follows the similar trend observed in the tungsten–hydrogen coupling constants of $Cp^*W({=}O)Me_3$ and $Cp^*W({=}O)(\eta^2\text{-}O_2)Me$: the coupling constant decreases as the π-donation from the oxo group to the metal center increases. In **1a**, the sulfur atom cannot compete effectively with the oxo group in π-donation to the only remaining unfilled d orbital on the metal. This breaking of the balance that existed in the dioxo compound produces increased triple-bond character between oxygen and tungsten by greater π-donation to the unoccupied d orbital on the tungsten. Since the system requires less methyl C–H bond interaction with the metal center to stabilize the system from within, the coupling constants J_{W-H} become smaller as a result of the reduced interaction.

The reactions of $Cp^*W({=}O)(\eta^2\text{-}O_2)R$ with H_2S also formed products **1a** and **1b**. In these reactions it appears that the H_2S reduces the peroxo complex to $Cp^*W({=}O)_2R$ more rapidly than the H_2O–H_2S exchange reaction occurs. The potentially interesting chemistry involving the sequential oxidation of sulfur ligands is currently under investigation.

Reaction of $Cp^*Mo({=}O)_2R$ with Hydrogen Sulfide. Treatment of $Cp^*Mo({=}O)_2(CH_2SiMe_3)$ with H_2S promoted the same transformation as its tungsten analogues, yielding the red, stable complex $Cp^*Mo({=}O)({=}S)(CH_2SiMe_3)$ (**2**) (yield 70%). Compound **2** was fully characterized by conventional analytical and spectroscopic techniques (vide infra). Its mononuclear nature has been established by a single-crystal X-ray crystallographic analysis; however, disorder between the sulfido and oxo groups prevented us from obtaining accurate metrical data. The compound has a piano-stool-type structure similar to that found for $Cp^*W({=}O)_2CH_2SiMe_3$.[5,6] A similar disorder has also been encountered in the X-ray analysis of its congener analogue **1b**. We are continuing our efforts to find conditions to obtain crystals which are not disordered.

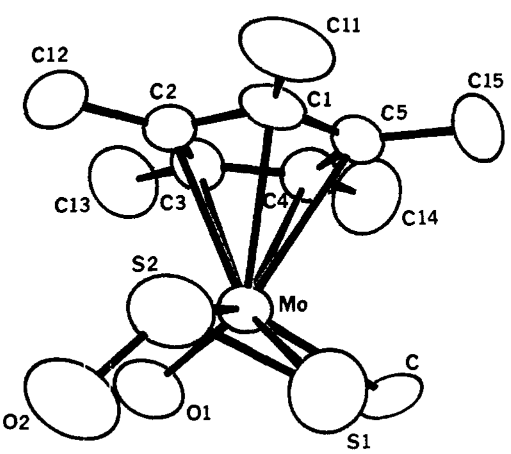


Figure 1. Molecular structure of $Cp^*Mo({=}O)(\eta^2\text{-}S_2O)Me$ showing 50% probability ellipsoids.

Presumably owing to the smaller steric effect of the methyl, the reaction of $Cp^*Mo({=}O)_2Me$ with H_2S proceeded differently. Unlike its tungsten analogue, no simple metathesis reaction product of composition $Cp^*Mo({=}O)({=}S)Me$ was obtained in the reaction of $Cp^*Mo({=}O)_2Me$ with H_2S. The compound $Cp^*Mo({=}O)_2Me$ reacted with H_2S for 3 days first to give a red air-sensitive compound believed to be $Cp^*Mo({=}O)(\eta^2\text{-}S_2)Me$, as characterized by its IR (ν = 925 cm^{-1} (CS_2)) and its mass spectrum (*m/z* 328). Upon oxidation by O_2 or peroxide, a relatively stable yellow compound was isolated by preparative TLC. This oxidation product was characterized as having a formula of $Cp^*Mo({=}O)(\eta^2\text{-}S_2O)(Me)$ (**3**) by its spectroscopic properties, chemical analysis, and also the observation of a molecular ion (*m/z* 344) in its electron ionization mass spectrum. The molecular structure of the compound was established by single-crystal X-ray diffraction measurements as well (see Figure 1). This is the first structurally characterized d^0 metal S_2O complex of which we are aware. Since the synthesis of the complex $[(dppe)_2Ir(S_2O)]^+$ by Schmid et al. in 1975,[8] only a very limited number of S_2O complexes have been reported.[9]

The reaction of **3** with a deficiency of PPh_3 only resulted in the formation of compound $Cp^*Mo({=}O)_2Me$ and unreacted **3**. Apparently, the reaction proceeded by the path of consecutive abstractions of sulfur by triphenylphosphine, which agrees with the result observed by Rauchfuss et al. on the compound $Cp_2Nb(S_2O)Cl$.[9] With respect to the mechanism of sulfur abstraction, it is unclear whether the first step involves nucleophilic attack by PPh_3 on the oxo-substituted sulfur S(2) or on the unsubstituted sulfur S(1) as has been proposed.[9]

Structural Aspects of 3. The structure of $Cp^*Mo({=}O)(\eta^2\text{-}S_2O)Me$ is shown in Figure 1. The bond distances have expected values based on previous structures; however, the unsymmetrical electronic character of the oxo and methyl group cause the S–S bond to be aligned with the Mo–Me bond. The extent of the alignment is indicated

---

(7) Brunner, H.; Meier, W.; Wachter, J.; Guggolz, E.; Zahn, T.; Ziegler, M. L. *Organometallics* **1982**, *1*, 1107.

(8) Schmid, G.; Ritter, G. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 645.

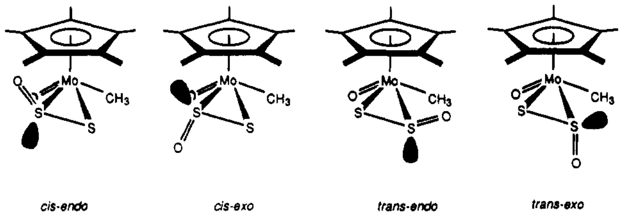
(9) (a) Dirand-Colin, J.; Schappacher, M.; Ricard, L.; Weiss, R. *J. Less Common Met.* **1977**, *54*, 91. (b) Hoots, J. E.; Lesch, D. A.; Rauchfuss, T. B. *Inorg. Chem.* **1984**, *23*, 3130. (c) Herberhold, M.; Schmidkonz, B.; Ziegler, M. L.; Zahn, T. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 515. (d) Herberhold, M.; Schmidkonz, B. *J. Organomet. Chem.* **1986**, *308*, 35–45. For a recent review of sulfur oxide coordination compounds, see: Schenk, W. A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 98–109.

Table I. Crystallographic Data for X-ray Diffraction Studies of $(\eta^5\text{-}C_5(CH_3)_5)Mo(O)(\eta^2\text{-}S_2O)(CH_3)$

(A) Crystal Parameters at 23 ± 2 °C	
formula	$Mo_1S_2O_2C_{11}H_{18}$
space group	*Pbca* (No. 61, orthorhombic)
a, Å	25.134 (9)
b, Å	10.000 (6)
c, Å	11.009 (7)
V, Å^3	2767.0
fw	342.33, *F*(000) = 1392
ρ_{calcd}, g/cm^3	1.64 (*Z* = 8)
(B) Intensity Measurements	
diffractometer	Enraf-Nonius CAD4
monochromater	graphite
radiatn	Mo Kα (0.71073 Å)
reflctns measd	$+h,+k,-l$
max 2θ, deg	50
no. of reflctns measd	2861
(C) Structure Solution and Refinement	
data used, $F^2 > 3\sigma(F^2)$	1501
parameters refined	145
abs coeff, cm^{-1}	12.0
abs correctn	empirical 0.904–0.997
p factor	0.02
final residuals R_1, R_2	0.038, 0.045
esd of unit weight	2.50
convergence, largest shift/error	0.00

by the displacement of the methyl carbon from the Mo–S(1)–S(2) plane of 0.21 Å. Another simply calculated indication is the dihedral angle between the Mo–S(1)–S(2) plane and the [midpoint-S(1)–S(2)]–Mo–C plane of 5.4°. The O–O bond in $Cp^*M(=O)(\eta^2\text{-}O_2)R$ shows a similar tendency for alignment with the weaker π-interacting ligand.[5] We have seen this effect (in the reverse acceptor sense) numerous times previously from the differential backbonding to nitrosyl and carbonyl ligands.[10] The asymmetry at the metal also enhances the difference between the Mo–S(1) and Mo–S(2) bond lengths, which are 2.307 and 2.500 Å, respectively. In $Cp^*Mn(CO)_2(S_2O)$, the analogous Mo–S distances are 2.328 and 2.400 Å.[9]

There are isomers which could arise from an effective rotation about the Mo–(S–S) axis. A convenient designation is endo for an O near the Cp ring and exo for an O distal to it; thus, the structure found here is an exo isomer. Furthermore, the O-substituted sulfur S(2) is cis to the oxygen; hence, this structure could be delineated from the other three isomers as the cis-exo isomer.



One might note also that there are two asymmetric centers in the molecule; one at the Mo and the other at S(2). Although we have not yet resolved this system or seen evidence for the other isomers or interconversions between them, in some instances delineations on the basis of asymmetric centers may be useful. In this case, in Figure 1 the configuration at Mo is *R* and that at S(2) is *S*.

Experimental Section

X-ray Crystallographic Analyses. Data collection parameters for **3** are given in Table I. The methods used follow those we have published elsewhere,[11] and only features specific to these structures are given here. From the systematic absences of 0*kl*, $k = 2n + 1$, *h*0*l*, $l = 2n + 1$, and *hk*0, $h = 2n + 1$, the space group was determined to be *Pbca*. The structure was solved by using the Patterson heavy-atom method, which revealed the position of the molybdenum atom. The coordinates of the remaining non-hydrogen atoms were located in subsequent difference Fourier synthesis. At least one hydrogen atom was located on each methyl group and was used to determine the orientation of the calculated hydrogen atom positions. These hydrogen atoms, with isotropic thermal parameters fixed at 5 Å^3, were included in full-matrix least-squares refinement. Neutral atom scattering factors were calculated by standard procedures.[12a] Anomalous dispersion corrections were applied to all atoms.[12b,13]

Table II. Positional and Thermal Parameters for $Cp^*Mo(O)(\eta^2\text{-}S_2O)Me$

atom	*x*/*a*	*y*/*a*	*z*/*a*	*B*(eq), Å^2
Mo	0.13704 (2)	0.03832 (5)	0.11550 (5)	2.913 (9)
S(1)	0.05753 (8)	0.1453 (3)	0.0537 (2)	6.95 (6)
S(2)	0.09097 (9)	0.2390 (2)	0.2006 (2)	5.72 (5)
O(1)	0.1921 (2)	0.1153 (5)	0.0651 (4)	4.7 (1)
O(2)	0.1179 (3)	0.3663 (5)	0.1691 (6)	7.9 (2)
C	0.1145 (4)	–0.0693 (8)	–0.0527 (6)	5.9 (2)
C(1)	0.1019 (2)	–0.0555 (6)	0.3076 (6)	3.4 (1)
C(2)	0.1567 (3)	–0.0129 (6)	0.3197 (6)	3.3 (1)
C(3)	0.1882 (2)	–0.0979 (6)	0.2462 (6)	3.4 (1)
C(4)	0.1536 (2)	–0.1850 (6)	0.1832 (6)	3.3 (1)
C(5)	0.1004 (2)	–0.1589 (6)	0.2217 (5)	3.0 (1)
C(11)	0.0559 (3)	–0.0053 (8)	0.3795 (7)	5.9 (2)
C(12)	0.1773 (3)	0.0883 (8)	0.4068 (6)	5.4 (2)
C(13)	0.2476 (3)	–0.0983 (9)	0.2427 (8)	6.1 (2)
C(14)	0.1696 (3)	–0.3004 (8)	0.1068 (8)	6.0 (2)
C(15)	0.0522 (3)	–0.2353 (8)	0.1851 (7)	5.6 (2)

Table III. Selected Bond Distances (Å) for $Cp^*Mo(O)(\eta^2\text{-}S_2O)Me$

Mo–S(2)	2.500 (2)	C(1)–C(2)	1.447 (9)
Mo–O(1)	1.677 (5)	C(1)–C(5)	1.402 (9)
Mo–C	2.216 (7)	C(1)–C(11)	1.49 (1)
Mo–C(1)	2.477 (6)	C(2)–C(3)	1.417 (9)
Mo–C(2)	2.357 (6)	C(2)–C(12)	1.487 (9)
Mo–C(3)	2.363 (6)	C(3)–C(4)	1.413 (9)
Mo–C(4)	2.391 (6)	C(3)–C(13)	1.493 (9)
Mo–C(5)	2.470 (6)	C(4)–C(5)	1.426 (8)
S(1)–S(2)	2.050 (3)	C(4)–C(14)	1.48 (1)
S(2)–O(2)	1.482 (6)	C(5)–C(15)	1.488 (9)

Table IV. Selected Bond Angles (deg) for $Cp^*Mo(O)(\eta^2\text{-}S_2O)Me$

S(1)–Mo–S(2)	49.74 (8)	Mo–S(2)–O(2)	112.9 (3)
S(1)–Mo–O(1)	113.2 (2)	S(1)–S(2)–O(2)	113.3 (3)
S(1)–Mo–C	76.3 (2)	Mo–C(1)–C(11)	127.1 (5)
S(2)–Mo–O(1)	97.9 (2)	C(2)–C(1)–C(5)	107.7 (5)
S(2)–Mo–C	125.8 (2)	Mo–C(2)–C(12)	122.7 (4)
O(1)–Mo–C	99.1 (3)	C(1)–C(2)–C(3)	107.7 (5)
C(1)–Mo–C(2)	34.7 (2)	Mo–C(3)–C(13)	122.0 (5)
C(1)–Mo–C(5)	32.9 (2)	C(2)–C(3)–C(4)	107.7 (5)
C(2)–Mo–C(3)	34.9 (2)	Mo–C(4)–C(14)	126.6 (5)
C(3)–Mo–C(4)	34.6 (2)	C(3)–C(4)–C(5)	108.6 (5)
C(4)–Mo–C(5)	34.1 (2)	Mo–C(5)–C(15)	125.8 (4)
Mo–S(1)–S(2)	68.51 (9)	C(1)–C(5)–C(4)	108.1 (5)
Mo–S(2)–S(1)	61.75 (9)		

An empirical psi-scan absorption correction was applied. Calculations were performed on a VAX-station 2000 computer using SDP-Plus Software developed by Enraf-Nonius and B.A. Frenz & Associates. Positional parameters, bond distances, and bond angles are given in Tables II, III, and IV, respectively. Tables of calculated hydrogen positions and structure factor tables are provided in the supplementary material.

---

(10) Adams, R. D.; Chodosh, D. F.; Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1979**, *101*, 2570–2578.

(11) Faller, J. W.; Shvo, Y.; Chao, K.; Murray, H. H. *J. Organomet. Chem.* **1982**, *226*, 251–275.

(12) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol. IV: (a) Table 2.2B, pp 99–101; (b) Table 2.3.1, pp 149–150.

(13) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

For **1b** and **2** X-ray analyses provided adequate structures to establish the stereochemistry, but not reliable metrical data owing to ~1:1 disorder between the oxo and sulfido ligands.

Crystal parameters for 1b: monoclinic space group $P2_1/c$ (No. 14) with $Z = 4$, $a = 11.091$ (4), $b = 9.341$ (3), and $c = 17.451$ (5) Å, and $V = 1803.9$ Å^3; Mo Kα (0.71073 Å). Anisotropic refinement of all atoms with hydrogen atoms omitted converged to the residuals $R_1 = 0.037$ and $R_2 = 0.046$.

Crystal parameters for 2: orthorhombic space group $Pna2_1$ (No. 33) with $Z = 4$, $a = 9.3544$ (6), $b = 14.951$ (1), and $c = 12.765$ (2) Å, and $V = 2785.3$ (5) Å^3. Anisotropic refinement of all non-hydrogen atoms and omission of hydrogen atoms converged to the residuals $R_1 = 0.053$ and $R_2 = 0.065$. The structure could also be solved in orthorhombic space group $Pnma$ (No. 62) with $Z = 4$ (disordered about molecular mirror plane), $a = 9.3544$ (6), $b = 12.765$ (2), and $c = 14.951$ (1) Å, and $V = 1785.2$ (5) Å^3; Cu Kα (1.54178 Å). Isotropic refinement of all atoms with hydrogen atoms omitted converged to the residuals $R_1 = 0.070$ and $R_2 = 0.083$. Both space groups showed abnormally short Mo=S and long Mo=O bond lengths and difference Fourier peaks in the vicinity of the oxygen and sulfur. Attempts to find a suitable disorder model which provided nearly equal Mo=O and Mo=O′ distances were unsuccessful.

Syntheses. Reagent grade solvents and hydrogen sulfide gas were used as supplied by the manufacturers. The preparation of compounds Cp*W(=O)$_2$R were published elsewhere[5] and compounds Cp*Mo(=O)$_2$R were prepared in the similar fashion to those of their tungsten analogues.[5]

Proton NMR spectra were recorded at 250 MHz with a Bruker spectrometer and are reported as parts per million downfield from tetramethylsilane using the solvent resonance for calibration. Infrared spectra were obtained with a Nicolet 5SX FTIR spectrometer. Mass spectra were obtained with a HP 5985 GC/MS mass spectrometer (using direct injection).

Preparation of Cp*W(=O)(=S)R (1a, R = Me; 1b, R = Me$_3$SiCH$_2$). Solutions of compounds Cp*W(=O)$_2$R (15–30 mg) in 50 mL of CS$_2$ saturated with H$_2$S were incubated at room temperature for 30 min (R = Me) to 3 days (R = CH$_2$SiMe$_3$) during which time the color of the solutions changed from colorless to yellow. The solvents were removed with a stream of N$_2$. The yellow residues were separated and purified by means of thin-layer chromatography on a 0.25-mm silica gel plate with diethyl ether as eluant. The yellow crystalline solids collected from the yellow bands near the solvent front were dried in vacuo to give compound **1a** in 77% and **1b** in 40% yields, respectively. The second colorless bands trailing the yellow bands were identified as starting materials. In the case of **1b**, the yield was almost quantitative on the basis of Cp*W(=O)$_2$R actually consumed in the reaction.

Compound **1a**: ^{1}H NMR (CDCl$_3$, 25 °C, 250 MHz) δ 2.12 (s, 15 H, C$_5$Me$_5$), 0.98 (s, 3 H, $J_{\text{W-H}} = 9.2$ Hz); IR (CS$_2$) $\nu_{\text{W=O}}$ 930 (s), $\nu_{\text{W=S}}$ 497 (w) cm^{-1}. Anal. Calcd for WOSC$_{11}$H$_{18}$: C, 34.57; H, 4.75. Found: C, 34.46; H, 4.77.

Compound **1b**: ^{1}H NMR (CDCl$_3$, 25 °C, 250 MHz) δ 2.10 (s, 15 H, C$_5$Me$_5$), 0.59 (d, 1 H, CHH′, $J_{\text{H-H}'} = 13.3$ Hz, $J_{\text{W-H}} = 7.5$ Hz), 0.23 (d, 1 H, CHH′, $J_{\text{H-H}'} = 13.3$ Hz, $J_{\text{W-H}'} = 10.7$ Hz), 0.10 (s, 9 H, SiMe$_3$); IR (CS$_2$) $\nu_{\text{W=O}}$ 927 (s), $\nu_{\text{W=S}}$ 495 (w) cm^{-1}. Anal. Calcd for WSiOSC$_{14}$H$_{26}$: C, 37.01; H, 5.77. Found: C, 37.08; H, 5.74.

Preparation of Cp*Mo(=O)(=S)(CH$_2$SiMe$_3$) (2). A solution of compound Cp*Mo(=O)$_2$(CH$_2$SiMe$_3$) (25 mg, 0.071 mmol) in 10 mL of CS$_2$ saturated with H$_2$S was incubated at room temperature for 3 days during which time the color of the solution changed from tinted yellow to red. The solvent was removed with a stream of N$_2$. The red residue was spotted on a 0.25-mm silica gel TLC plate and then developed with diethyl ether. The red band was collected to give 20.2 mg of compound **2** (77%). The X-ray crystallographic quality dark red crystals were grown from a saturated solution of hexane at −20 °C.

Compound **2**: ^{1}H NMR (CDCl$_3$, 25 °C, 250 MHz) δ 1.95 (s, 15 H, C$_5$Me$_5$), 0.78 (d, 1 H, CHH′, $J_{\text{H-H}'} = 12.7$ Hz), 0.38 (d, 1 H, CHH′, $J_{\text{H-H}'} = 12.7$ Hz), 0.07 (s, 9 H, SiMe$_3$); IR (CS$_2$) $\nu_{\text{Mo=O}}$ 906 (s), $\nu_{\text{Mo=S}}$ 495 (w) cm^{-1}; MS-EI (20 eV) for C$_{14}$H$_{24}$^{98}MoOSSi m/z 368 (P$^+$), 353 (P − Me), 336 (P − S). Anal. Calcd for MoSiOSC$_{14}$H$_{26}$: C, 45.89; H, 7.15. Found: C, 45.82; H, 7.23.

Preparation of Cp*Mo(=O)(η^2-S$_2$O)Me (3). A solution of Cp*Mo(=O)$_2$Me (10 mg, 0.036 mmol) in 10 mL of CS$_2$ saturated with H$_2$S was incubated at room temperature for 3 days during which time the color of the solution changed from tinted yellow to red. The solvent was removed with a stream of N$_2$. The red residue was dissolved in 1 mL of diethyl ether which had been allowed to stand in air and contained hydroperoxide (EtOC(OOH)HMe). The solution was spotted on a 0.25-mm silica gel TLC plate and then developed with diethyl ether. The yellow band near the origin was collected to give 8.1 mg of analytically pure compound **3** (72%). The X-ray crystallographic quality yellow-orange crystals were grown from a diethyl ether solution at −20 °C.

Compound **3**: ^{1}H NMR (C$_6$D$_6$, 25 °C, 250 MHz) δ 1.30 (s, 15 H, C$_5$Me$_5$), 1.80 (s, 3 H); IR (CS$_2$) $\nu_{\text{Mo=O}}$ 935 (m), $\nu_{\text{S=O}}$ 1080 (s) cm^{-1}; MS-EI (20 eV) for C$_{11}$H$_{18}$^{98}MoO$_2$S$_2$ m/z 344 (P$^+$), 329 (P − Me). Anal. Calcd for MoO$_2$S$_2$C$_{11}$H$_{18}$: C, 38.61; H, 5.30; S, 18.74. Found: C, 38.51; H, 5.31; S, 18.68.

Acknowledgment. We wish to thank the National Science Foundation for support of this work.

Supplementary Material Available: A table of calculated hydrogen positions (1 page); a listing of calculated and observed structure factors (11 pages). Ordering information is given on any current masthead page.