that occur when two hypothetical Cu(I) monomers are brought together to allow the Cu–Cu interaction is especially informative (Figure 5). A single orbital, $19b_u$, rises high above the other nine filled Cu d orbitals to become the highest occupied molecular orbital (HOMO). The solution spectrum of II exhibits a low-energy absorption (460 nm, $\epsilon = 5500\ M^{-1}\ cm^{-1}$) that can be assigned to a Cu–Cu (σ^*) → ligand π^* transition, which results from destabilization of the Cu d orbital to higher energy in the dimer. There is no evidence in the calculations that the Cu–Cu interaction leads to an enhanced stability. In fact, there appears to be a net destabilization of the entire Cu d band because of the repulsive interaction between the two d^{10} metal centers. Unlike extended Hückel calculations for other Cu(I)[13] dimers, the $X\alpha$ results show <3% mixing of 4s and 4p character into the Cu–Cu $19b_u$ σ^* orbital. The $19a_g$ σ orbital exhibits greater (15%) 4s + 4p hybridization; however, it is also destabilized when compared to the d band in the monomeric fragment (Figure 5). Extensive 3d–4s4p mixing has been postulated[13] to result in attractive Cu–Cu interactions. In these cases, as noted above, the molecular geometry differs from II. Our calculations resemble an SCCC MO study[18] of a $Cu_8S_{12}^{4-}$ cluster where 3d–4s4p hybridization and Cu–Cu bonding did not occur.

At present, the examples of d^{10}–d^{10} dimers without supporting bridging ligands are restricted to compounds of third-row metals such as Pt(0). Because the d–sp energy separation decreases for the third-row late transition metals, they exhibit a greater tendency to undergo oxidative addition reactions [e.g. Pt(0) to Pt(II)] and the dsp hybridization necessary for metal–metal bond formation. To illustrate this point, we contrast the spectroscopic energies[19] of the $3d^94s^1$ (^3D) and $3d^94p^1$ ($^3P_2{}^0$) atomic states in Cu^+ at 2.72 and 8.24 eV above the $3d^{10}$ (^1S) ground state with the case of Pt^0, where the $4d^96s^1$ configuration is the ground state and the $5d^{10}$ (^1S) and $5d^96p^1$ ($^2D_{5/2}$) states occur at 0.76 and 4.04 eV, respectively. Although these values are for monoatomic species in the gas phase, reduced dsp hybridization (or configuration interaction) and reduced metal–metal bond strength can be expected for Cu(I) dimers as compared to Pt(0) d^{10} dimers, because of the large energetic differences in the parent atomic states. Because neither extended Hückel theory nor $X\alpha$ theory can be expected to reliably model the precise amount of 3d–4s4p hybridization, we believe the extent of metal–metal bonding in Cu(I) systems with bridging ligands will be difficult to quantify. The results obtained for II, whose structure forces overlap of two filled antibonding orbitals, suggest that quite short Cu(I)–Cu(I) distances can be enforced without appreciable metal–metal bonding.

Acknowledgment. This work is based on research sponsored by the Air Force Office of Scientific Research, Air Force Systems Command, USAF, under Grant AFOSR-86-0027. We thank the DoD University Research Instrumentation Program (Grant DAAL03-87-G-0071) for funds to purchase an X-ray diffractometer.

Supplementary Material Available: Tables of bond distances, bond angles, anisotropic displacement parameters, and hydrogen atom coordinates (6 pages); tables of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

---

(18) Avdeef, A.; Fackler, J. P., Jr. *Inorg. Chem.* **1978**, *17*, 2182.

(19) Moore, C. E. *Atomic Energy Levels*; NBS Circular 467; U.S. Government Printing Office: Washington, DC, 1952; Vol. II, III.

Contribution from the Department of Chemistry,
Yale University, New Haven, Connecticut 06511-8118

Preparation and Reactions of Sulfido and Persulfido Complexes of (Pentamethylcyclopentadienyl)tungsten

J. W. Faller,* Robin R. Kucharczyk, and Yinong Ma

Received October 25, 1989

Boron sulfide and hydrogen sulfide react with tungsten–oxo compounds to yield $(\eta^5\text{-}C_5Me_5)W(=S)_2R$ (**1a**, R = Me; **1b**, R = CH_2SiMe_3), $(\eta^5\text{-}C_5Me_5)W(=S)(\eta^2\text{-}S_2)Me$ (**2a**), and $(\eta^5\text{-}C_5Me_5)W(=O)(\eta^2\text{-}S_2)Me$ (**3**). Thiophiles such as PPh_3 and CN^- readily abstract sulfur from the persulfido complexes **2a** and **3**; however, the sulfido ligands of **1a** and **1b** are inert to abstraction under similar conditions. In the presence of oxidizing agents, **1a** undergoes intermolecular transfer of sulfur, giving **2a** and $(\eta^5\text{-}C_5Me_5)W(=O)(=S)Me$. Compound **1b** crystallizes in the monoclinic space group $P2_1/c$ with a = 10.967 (2) Å, b = 9.323 (1) Å, c = 18.092 (3) Å, V = 1843.8 Å^3, and Z = 4. Anisotropic refinement of all non-hydrogen atoms and inclusion of hydrogen atoms at calculated positions converged to the residuals R_1 = 0.027 and R_2 = 0.035.

Introduction

The chemistry of molybdenum–sulfido (Mo=S) and molybdenum–persulfido [$Mo(\eta^2\text{-}S_2)$] systems is pertinent to the understanding of a number of biological and catalytic processes. The presence of a Mo=S unit in the active sites of numerous molybdenum enzymes has been demonstrated via EPR and EXAFS techniques.[1] The involvement of persulfido ligands in biological systems as reaction intermediates has been postulated.[2] In addition, compounds containing $Mo(\eta^2\text{-}S_2)$ units have been employed in model studies[3] of the catalytic surface responsible for hydrodesulfurization,[4] a heterogeneous process in which sulfur derived from petroleum products is converted to hydrogen sulfide in the presence of hydrogen. The literature of the last decade reflects a growing interest in sulfur complexes of molybdenum in its higher oxidation states as models for the structures and reactivity of these biochemical and catalytic systems.[3,5–10] The analogous chemistry

---

(1) Gutteridge, S.; Tanner, S. J.; Bray, R. C. *Biochem. J.* **1978**, *175*, 887. Bordas, J.; Bray, R. C.; Garner, C. D.; Gutteridge, S.; Hasnain, S. S. *Biochem. J.* **1980**, *191*, 499. Cramer, S. P.; Wahl, R.; Rajagopalan, K. V. *J. Am. Chem. Soc.* **1981**, *103*, 7721.

(2) Müller, A.; Jaegermann, W.; Enemark, J. H. *Coord. Chem. Rev.* **1982**, *46*, 245 and references therein.

(3) Müller, A. *Polyhedron* **1986**, *5*, 323 and references therein.

(4) Schuman, S. C.; Shalit, H. *Catal. Rev.* **1970**, *4*, 245.

(5) Newton, W. E.; McDonald, J. W.; Yamanouchi, K.; Enemark, J. H. *Inorg. Chem.* **1979**, *18*, 1621.

(6) Young, C. G.; Enemark, J. H.; Collison, D.; Mabbs, F. E. *Inorg. Chem.* **1987**, *26*, 2925. Young, C. G.; Roberts, S. A.; Ortega, R. B.; Enemark, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 2938.

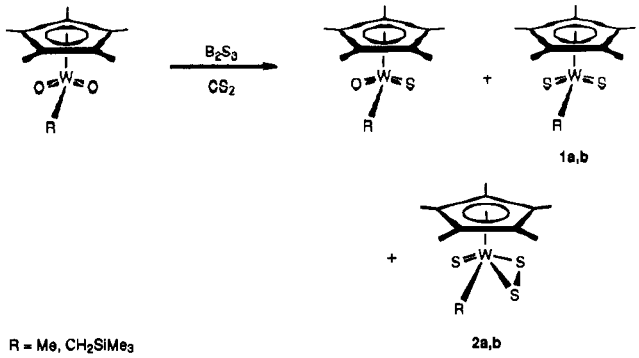
(7) Hofer, E.; Holzbach, W.; Wieghardt, K. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 282. Bristow, S.; Collison, D.; Garner, C. D.; Clegg, W. *J. Chem. Soc., Dalton Trans.* **1983**, 2495.

(8) Wieghardt, K.; Hahn, M.; Weiss, J.; Swiridoff, W. *Z. Anorg. Allg. Chem.* **1982**, *492*, 164.

(9) Müller, A.; Reinsch, U. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 72. Halbert, T. R.; McGauley, K.; Pan, W.-H.; Czernuszewicz, R. S.; Stiefel, E. I. *J. Am. Chem. Soc.* **1984**, *106*, 1849.

0020-1669/90/1329-1662$02.50/0

Scheme I



of tungsten, however, has not been studied extensively,[11-14] although the increased stability associated with tungsten derivatives can facilitate the synthesis and characterization of models for reactive molybdenum–sulfur systems and the study of reaction intermediates.

In our initial report on the introduction of sulfur into molybdenum- and tungsten-dioxo species,[15] we described the synthesis of oxo–sulfido complexes using H_2S. Numerous difficulties were encountered when we attempted to extend the scope of the molybdenum chemistry, but stable disulfido and persulfido complexes of tungsten were obtained in good yield from the corresponding oxo species and H_2S or B_2S_3. The occurrence of mononuclear tungsten(VI) compounds with S^{2-} or S_2^{2-} ligands has been limited to a few examples, namely $(\eta^5\text{-}C_5Me_5)W(=O)(=S)R$,[15] $W(=S)(\eta^2\text{-}S_2)(S_2CNR_2)_2$,[11] and $W(=O)(=S)(R_2NO)_2$ and $W(=S)_2(R_2NO)_2$.[12] The lack of structural and reactivity data for these types of complexes led us to undertake the studies presented here. We now describe the preparation and properties of $(\eta^5\text{-}C_5Me_5)W(=S)_2R$ (**1a**, R = Me; **1b**, R = CH_2SiMe_3), $(\eta^5\text{-}C_5Me_5)W(=S)(\eta^2\text{-}S_2)Me$ (**2a**), and $(\eta^5\text{-}C_5Me_5)W(=O)(\eta^2\text{-}S_2)Me$ (**3**).

Results

Treatment of $(\eta^5\text{-}C_5Me_5)W(=O)_2R$ with B_2S_3 in CS_2 yields the new complexes $(\eta^5\text{-}C_5Me_5)W(=S)_2R$ and $(\eta^5\text{-}C_5Me_5)W(=S)(\eta^2\text{-}S_2)Me$ as summarized in Scheme I. A structure study was undertaken for **1b**, the results of which are shown in Tables I–IV. An ORTEP drawing (Figure 1) and these tables will be introduced at appropriate places in the sections that follow.

Treatment of $(\eta^5\text{-}C_5Me_5)W(=O)(\eta^2\text{-}O_2)Me$ with H_2S in CS_2 solution gave $(\eta^5\text{-}C_5Me_5)W(=O)(\eta^2\text{-}S_2)Me$ (**3**) in addition to other products.

Discussion

Reactions of $(\eta^5\text{-}C_5Me_5)W(=O)_2R$ with B_2S_3. A variety of sulfur-containing reagents have been used to introduce sulfido and persulfido ligands into transition-metal complexes. H_2S, B_2S_3, and $(Me_3Si)_2S$ are most often employed in the synthesis of metal–sulfido compounds.[5-8,12,16-18] Elemental sulfur is preferred when persulfido compounds of low-valent metals are desired; reduction of S(0) to S_2^{2-} is particularly facile at coordinatively unsaturated d^8 metal centers.[2,19] A second synthetic pathway applies to high-oxidation-state metal complexes, which react with sources of reduced sulfur to generate metal–persulfido moieties.[17,20-22]

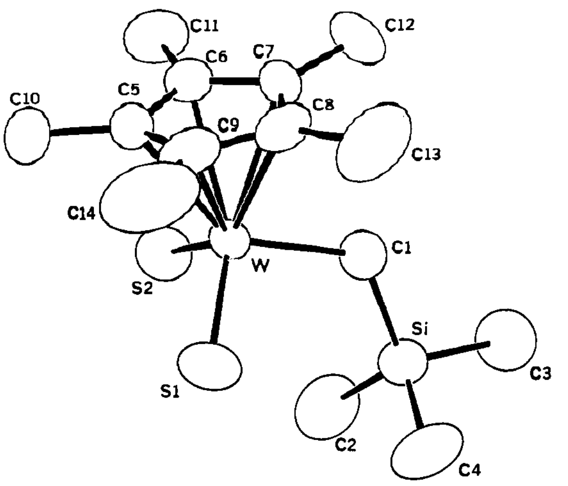


Figure 1. ORTEP diagram of $(\eta^5\text{-}C_5Me_5)W(=S)_2CH_2SiMe_3$ (**1b**), showing 50% probability ellipsoids.

As we reported previously[15] the reaction of H_2S with $(\eta^5\text{-}C_5Me_5)W(=O)_2R$ (R = Me, CH_2SiMe_3) gives a single product (eq 1). We have attributed this result to the high thermodynamic

$$(\eta^5\text{-}C_5Me_5)W(=O)_2R + H_2S \rightarrow (\eta^5\text{-}C_5Me_5)W(=O)(=S)R + H_2O \quad (1)$$

stability of the monoxometal species formed.[23] In contrast, use of B_2S_3 in CS_2 yields three compounds, the products of replacement of one or both oxo ligands by one to three sulfur atoms (Scheme I); formation of strong boron–oxygen bonds provides the driving force for further sulfur substitution. While mixtures of products are unavoidable here, one can bias the reaction in favor of a particular complex by varying both the reagent–substrate ratio and the reaction time. In addition, the progress of the reaction can be easily monitored by thin-layer chromatography. A similar lack of selectivity was observed in the reactions of $M(=O)_2(R_2NO)_2$ (M = Mo, W) with H_2S and B_2S_3.[7,8,12]

The disulfido complexes $(\eta^5\text{-}C_5Me_5)W(=S)_2Me$ (**1a**) and $(\eta^5\text{-}C_5Me_5)W(=S)_2CH_2SiMe_3$ (**1b**) crystallize from hexane as dark red solids. These solids and their solutions are unaffected by exposure to air and moisture during routine manipulations, but they are best kept at −20 °C under nitrogen to prevent oxidative decomposition (vide infra). The IR spectra of both display a pair of weak bands corresponding to $\nu_{W=S}$ in the region 505–490 cm^{-1}. Examination of the tungsten–proton coupling constants for **1a** and **1b** (7.7 and 7.8 Hz, respectively) shows that these values are decreased relative to those for $(\eta^5\text{-}C_5Me_5)W(=O)_2R$ (10.8 and 10.3 Hz)[24] and $(\eta^5\text{-}C_5Me_5)W(=O)(=S)R$ (9.2 Hz; 7.5 and 10.7 Hz).[15] This result is not unexpected given the trend that has been established for $(\eta^5\text{-}C_5Me_5)W$ oxo–alkyl compounds and their derivatives:[15,24] an increase in the electron density at tungsten

---

(10) Rakowski DuBois, M.; VanDerveer, M. C.; DuBois, D. L.; Haltiwanger, R. C.; Miller, W. K. *J. Am. Chem. Soc.* **1980**, *102*, 7456. Berg, J. M.; Holm, R. H. *J. Am. Chem. Soc.* **1985**, *107*, 917.

(11) Pan, W.-H.; Halbert, T. R.; Hutchings, L. L.; Stiefel, E. I. *J. Chem. Soc. Chem. Commun.* **1985**, 927.

(12) McDonell, A. C.; Vasudevan, S. G.; O'Connor, M. J.; Snow, M. R.; Wedd, A. G. *Aust. J. Chem.* **1985**, *38*, 1017.

(13) A series of poorly characterized compounds formulated as Cp'_2WOS, Cp'_2WS_2, and Cp'_4WS has been reported: Rastogi, M. K.; Multani, R. K. *Indian J. Chem.* **1977**, *15A*, 150.

(14) Danzer, W.; Fehlhammer, W. P.; Lin, A. T.; Thiel, G.; Beck, W. *Chem. Ber.* **1982**, *115*, 1682. Brunner, H.; Meier, W.; Wachter, J.; Guggolz, E.; Zahn, T.; Ziegler, M. L. *Organometallics* **1982**, *1*, 1107.

(15) Faller, J. W.; Ma, Y. *Organometallics* **1989**, *8*, 609.

(16) Callahan, K. P.; Durand, P. J. *Inorg. Chem.* **1980**, *19*, 3211.

(17) Do, Y.; Simhon, E. D.; Holm, R. H. *Inorg. Chem.* **1983**, *22*, 3809. Do, Y.; Simhon, E. D.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 2827.

(18) Tanner, L. D.; Haltiwanger, R. C.; Rakowski DuBois, M. *Inorg. Chem.* **1988**, *27*, 1741.

(19) Herberhold, M.; Schmidkonz, B. *J. Organomet. Chem.* **1988**, *301*, 358. Herberhold, M.; Hill, A. F. *J. Chem. Soc., Dalton Trans.* **1988**, 2027.

(20) Treichel, P. M.; Werber, G. P. *J. Am. Chem. Soc.* **1968**, *90*, 1753. Dirand, J.; Ricard, L.; Weiss, R. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 661. Köpf, H.; Hazari, S. K. S.; Leitner, M. *Z. Naturforsch.* **1978**, *33B*, 1398.

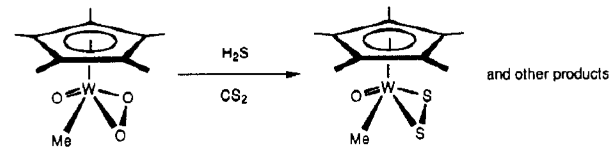
(21) Leonard, K.; Plute, K.; Haltiwanger, R. C.; Rakowski DuBois, M. *Inorg. Chem.* **1979**, *18*, 3246.

(22) Rittner, W.; Müller, A.; Neumann, A.; Bäther, W.; Sharma, R. C. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 530. Müller, A.; Rittner, W.; Neumann, A.; Sharma, R. C. *Z. Anorg. Allg. Chem.* **1981**, *472*, 69.

(23) Rappé, A. K.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1982**, *104*, 3287. Goddard, W. A., III. *Science* **1985**, *227*, 917.

(24) Faller, J. W.; Ma, Y. *Organometallics* **1988**, *7*, 559. Faller, J. W.; Ma, Y. *J. Organomet. Chem.* **1989**, *368*, 45.

Scheme II



3

gives rise to a smaller value of $J(^{183}W\text{-}H)$. Here, substitution of the less electronegative sulfur for oxygen increases the extent of ligand electron donation to tungsten, and less alkyl α-C–H bond interaction is necessary to stabilize the 16-electron metal center. Values of $J(^{183}W\text{-}C)$ obtained from $^{13}C\{^1H\}$ NMR spectra correlate in a similar fashion.[25]

The molecular structure of **1b** was established by a single-crystal X-ray crystallographic analysis (see Figure 1). Bond lengths and angles are within normal limits for a molecule possessing two tungsten–sulfur double bonds and an overall piano-stool structure. The W=S distances, 2.134 and 2.136 Å, are slightly shorter than those reported for $Mo(=S)_2(C_5H_{10}NO)_2$ (2.145 Å)[8] and for $Mo(=S)_2(Et_2NO)_2\cdot 0.5C_6H_6$ (2.153 and 2.155 Å)[26] but virtually identical with the value of 2.136 Å obtained for $W(=S)(\eta^2\text{-}S_2)[S_2CN(i\text{-}C_4H_9)_2]_2$.[11] A comparable value of 2.13 Å for the W=S bond distance in $(\eta^5\text{-}C_5Me_5)_2W_2(CO)_2(\mu\text{-}S)_2(=S)$ is also known.[14] The S—W—S angle is 107.8°, which is the same value as that found for the O—W—O angle in $CpW(=O)_2CH_2SiMe_3$.[27] The W—C—Si angle is opened up to 121.8° owing to strong π-interactions. This compares with the lesser distortion in $CpW(=O)_2CH_2SiMe_3$ of 115.8°.[27]

Reaction of $(\eta^5\text{-}C_5Me_5)W(=O)_2Me$ with excess B_2S_3 for extended periods yields significant amounts of purple $(\eta^5\text{-}C_5Me_5)W(=S)(\eta^2\text{-}S_2)Me$ (**2a**), which can be isolated via preparative TLC. Under similar conditions, very little of the analogous $(\eta^5\text{-}C_5Me_5)W(=S)(\eta^2\text{-}S_2)CH_2SiMe_3$ (**2b**) forms; this difference is presumably steric in origin. The IR spectral features of **2a** are in accordance with its formulation as a mononuclear species possessing one multiply bonded sulfur and an S_2^{2-} unit bound in a side-on fashion. The sulfur–sulfur stretch at 549 cm^{-1} is accompanied by a single terminal sulfido band at 511 cm^{-1}. The values of J(W–H) and J(W–C) are even lower than those found for $(\eta^5\text{-}C_5Me_5)W(=S)_2Me$ and reflect the increase in electron density at tungsten concomitant with formation of a partial tungsten–sulfur triple bond.[23] A molecular ion at $m/z = 430$ was observed in the electron-ionization mass spectrum of **2a**; fragment ions corresponding to loss of sulfur and methyl were also found.

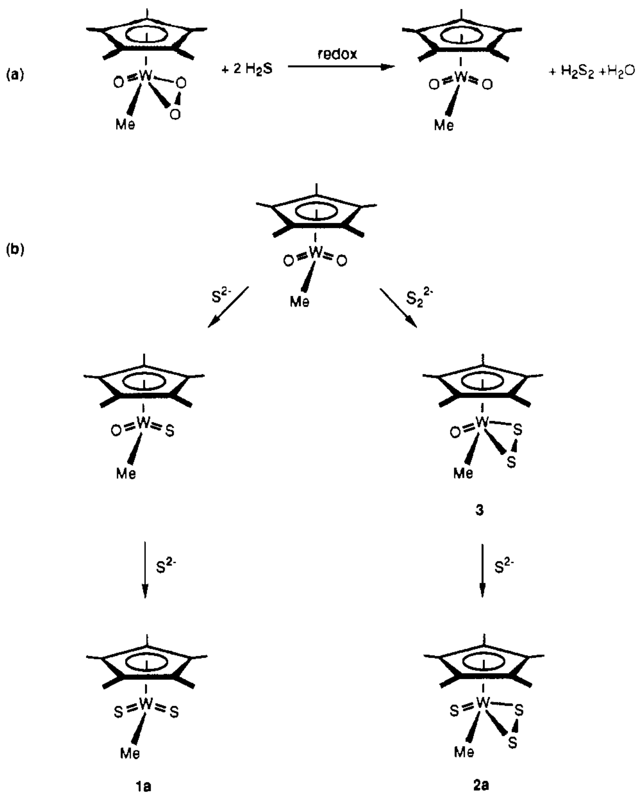
Reactions of $(\eta^5\text{-}C_5Me_5)W(=O)(\eta^2\text{-}O_2)R$ with H_2S. The reactions of $(\eta^5\text{-}C_5Me_5)W(=O)(\eta^2\text{-}O_2)R$ (R = Me, CH_2SiMe_3) with hydrogen sulfide to give $(\eta^5\text{-}C_5Me_5)W(=O)(=S)R$ were briefly described in an earlier report.[15] A closer look at these processes was prompted by the finding that treatment of the molybdenum alkyl $(\eta^5\text{-}C_5Me_5)Mo(=O)(\eta^2\text{-}O_2)CH_2SiMe_3$ with H_2S in CS_2 overwhelmingly favored production of an oxo-persulfido complex (eq 2); the oxo-sulfido compound was formed

$$(\eta^5\text{-}C_5Me_5)Mo(=O)(\eta^2\text{-}O_2)CH_2SiMe_3 + 2H_2S \rightarrow (\eta^5\text{-}C_5Me_5)Mo(=O)(\eta^2\text{-}S_2)CH_2SiMe_3 + 2H_2O \quad (2)$$

to the extent of only 5%.[28] A second example of the $W(\eta^2\text{-}S_2)$ unit was sought with the hope that it would prove more amenable to crystallographic analysis than **2a**, for which good quality crystals could not be obtained.

Four products were identified and isolated from the reaction of $(\eta^5\text{-}C_5Me_5)W(=O)(\eta^2\text{-}O_2)Me$ with H_2S after 4 days (Scheme II). This result contrasts with that obtained from the reaction of $(\eta^5\text{-}C_5Me_5)W(=O)_2Me$ with H_2S, in which only $(\eta^5\text{-}C_5Me_5)W(=O)(=S)Me$ was produced in significant quantity.[15] The new complex $(\eta^5\text{-}C_5Me_5)W(=O)(\eta^2\text{-}S_2)Me$ (**3**) was separated from the three known sulfur-containing compounds via preparative TLC and was fully characterized by IR spectroscopy, ^1H NMR spectroscopy, mass spectrometry, and elemental analysis. An X-ray crystallographic analysis was performed and was sufficient to establish the atomic connectivity; however, the quality of the structure was low and the accuracy of the material data was marginal. When the same transformation was attempted with $(\eta^5\text{-}C_5Me_5)W(=O)(\eta^2\text{-}O_2)CH_2SiMe_3$, a small amount of $(\eta^5\text{-}C_5Me_5)W(=O)(=S)CH_2SiMe_3$ formed, but the dioxo complex $(\eta^5\text{-}C_5Me_5)W(=O)_2CH_2SiMe_3$ was the predominant product.

Scheme III



Formation of the oxo-persulfido complex **3** requires the presence of S_2^{2-}, presumably generated via the redox process shown in Scheme IIIa. Spectroscopic evidence for the oxidation–reduction exists: infrared monitoring of the reaction indicates that reduction of the peroxo ligand occurs initially. The dioxo compound then reacts readily with the small amount of S_2^{2-} formed and with the excess S^{2-} as shown in Scheme IIIb, and both **3** and $(\eta^5\text{-}C_5Me_5)W(=O)(=S)Me$ are isolated as major products. Subsequent transformations of these yield the other two compounds, **1a** and **2a**. When $(\eta^5\text{-}C_5Me_5)W(=O)(\eta^2\text{-}O_2)CH_2SiMe_3$ is employed, the redox products, S_2^{2-} and the dioxo compound, fail to react further. Introduction of the bulkier (trimethylsilyl)methyl ligand changes the relative rates of reaction of S^{2-} and S_2^{2-} with the dioxo complex. In the methyl derivative, the reaction rates with S^{2-} and S_2^{2-} are comparable, whereas for the (trimethylsilyl)methyl complex the rate of reaction with S^{2-} is much faster and essentially no $(\eta^5\text{-}C_5Me_5)W(=O)(\eta^2\text{-}S_2)CH_2SiMe_3$ is produced. This contrasts with the relative ease of preparation of $(\eta^5\text{-}C_5Me_5)Mo(=O)(\eta^2\text{-}S_2)CH_2SiMe_3$ from its dioxo precursor (vide supra), in which the much more reactive molybdenum center shows less discrimination in the two paths.

Reactions of Disulfido and Persulfido Compounds. Abstraction of atomic sulfur by thiophilic nucleophiles is a reaction common to both sulfido[5,29,30] and persulfido[21,31] complexes and is of bio-

---

(25) Faller, J. W.; Ma, Y. Unpublished results.

(26) Gheller, S. F.; Hambley, T. W.; Traill, P. R.; Brownlee, R. T. C.; O'Connor, M. J.; Snow, M. R.; Wedd, A. G. *Aust. J. Chem.* **1982**, *35*, 2183.

(27) Legzdins, P.; Rettig, S. J.; Sánchez, L. *Organometallics* **1985**, *4*, 1470.

(28) Faller, J. W.; Kucharczyk, R. R. Unpublished results.

(29) Müller, A.; Krickemeyer, E.; Reinsch, U. *Z. Anorg. Allg. Chem.* **1980**, *470*, 35.

(30) Traill, P. R.; Tiekink, E. R. T.; O'Connor, M. J.; Snow, M. R.; Wedd, A. G. *Aust. J. Chem.* **1986**, *39*, 1287.

chemical significance: the active sites of the molybdoproteins xanthine oxidase, xanthine dehydrogenase, and aldehyde oxidase possess a sulfur atom that can be abstracted by cyanide ion to yield thiocyanate ion and an inactive form of the enzyme.[32] When the disulfido compounds **1a** and **1b** were treated with PPh_3 in $CDCl_3$ no $S{=}PPh_3$ was observed by ^1H NMR after several hours. The persulfido ligand proved much more reactive; under the same conditions compounds **2a** and **3** lost sulfur within 30 min (eq 3).

$$(\eta^5\text{-}C_5Me_5)W({=}X)(\eta^2\text{-}S_2)Me + PPh_3 \rightarrow (\eta^5\text{-}C_5Me_5)W({=}X)({=}S)Me + S{=}PPh_3 \quad (3)$$
$$X = S\ (\mathbf{2a}) \qquad X = O\ (\mathbf{3})$$

Triphenylphosphine sulfide was identified by its IR spectrum (KBr pellet; $\nu_{P{=}S} = 639\ cm^{-1}$). Compounds **2a** and **3** also reacted with an alcoholic solution of NaCN in CH_2Cl_2. Sulfido products were characterized by IR spectroscopy, and the presence of SCN^- was determined qualitatively via reaction with Fe(III) to yield blood-red $Fe(SCN)^{2+}$. Unreacted starting materials were recovered from similar reactions with **1a** and **1b**.

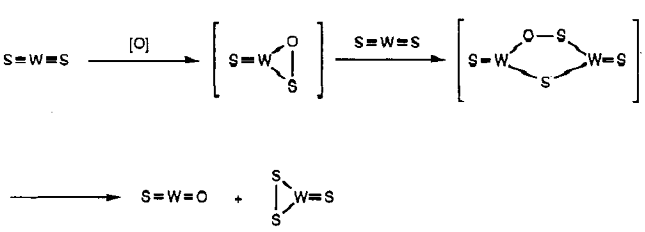
Complexes bearing persulfido groups are also known to undergo oxidation to $\eta^2\text{-}S_2O$ complexes.[15,19,33] Evidence for disulfur monoxide products was obtained when the persulfido species **2a** and **3** were each treated with one equivalent of *m*-chloroperoxybenzoic acid (*m*-CPBA) in $CDCl_3$: transient resonances attributable to $(\eta^5\text{-}C_5Me_5)W({=}S)(\eta^2\text{-}S_2O)Me$ and $(\eta^5\text{-}C_5Me_5)W({=}O)(\eta^2\text{-}S_2O)Me$ were observed in the 250-MHz ^1H NMR spectra of the reaction mixtures. Upon completion of the reaction, the $W({=}S)(\eta^2\text{-}S_2)$ complex (**2a**) yielded a mixture of $(\eta^5\text{-}C_5Me_5)W({=}O)_2Me$, $(\eta^5\text{-}C_5Me_5)W({=}O)({=}S)Me$, and $(\eta^5\text{-}C_5Me_5)W({=}O)(\eta^2\text{-}S_2)Me$ (**3**). Likewise, **3** gave $(\eta^5\text{-}C_5Me_5)W({=}O)_2Me$ and a precipitate of elemental sulfur. This reactivity contrasts with that of $(\eta^5\text{-}C_5Me_5)Mo({=}O)(\eta^2\text{-}S_2)Me$, which is readily oxidized by diethyl ether–hydroperoxide to form a stable $\eta^2\text{-}S_2O$ complex.[15]

A novel intermolecular sulfur transfer reaction was observed when compound **1a** was treated with *m*-CPBA in diethyl ether. The purple reaction mixture was separated via preparative TLC after 30 min to yield compound **2a** and $(\eta^5\text{-}C_5Me_5)W({=}O)({=}S)Me$ (eq 4). ^1H NMR monitoring of the process revealed

$$(\eta^5\text{-}C_5Me_5)W({=}S)_2Me + m\text{-CPBA} \rightarrow (\eta^5\text{-}C_5Me_5)W({=}S_2)Me + (\eta^5\text{-}C_5Me_5)W({=}O)({=}S)Me + m\text{-CBA} \quad (4)$$

that the two products were in fact formed in a 1:1 ratio. The (trimethylsilyl)methyl analogue **1b** failed to show similar reactivity with the peroxyacid. Clearly the steric constraints imposed by a bulky alkyl ligand can effectively preclude reaction paths that are available for methyl complexes (vide supra). In this instance one or both sulfido ligands were replaced by oxo groups, and mixtures of $(\eta^5\text{-}C_5Me_5)W({=}O)({=}S)CH_2SiMe_2$ and $(\eta^5\text{-}C_5Me_5)W({=}O)_2CH_2SiMe_3$ resulted. The oxidation-promoted transfer of sulfur from one molecule of **1a** to another was also found to take place more slowly in the solid and in solution as long as oxygen was present. Significant amounts of compound **2a** could be isolated from solid samples of **1a** that had been stored for months in the presence of atmospheric oxygen. The ^1H NMR spectrum of a $CDCl_3$ solution of **1a** purged with nitrogen and sealed showed little change after 8 days, whereas an oxygen-purged sample reacted rapidly in the same period of time to give 43% **2a**, 25% $(\eta^5\text{-}C_5Me_5)W({=}O)_2Me$, 4% **3**, and a trace of $(\eta^5\text{-}C_5Me_5)W({=}O)({=}S)Me$.[34] A third sample sealed in the presence of air developed a similar product distribution at a slower rate. That oxidative conditions are prerequisite to sulfur atom transfer was further demonstrated via anaerobic reaction of the disulfido complex with elemental sulfur; $(\eta^5\text{-}C_5Me_5)W({=}O)({=}S)Me$ and **2a** did not form.

Scheme IV



A possible mechanism for this transformation, invoking the intermediacy of η^2-SO and $(\mu\text{-}S)(\mu\text{-}\eta^2\text{-}SO)$ species, can be outlined as shown in Scheme IV. In this instance, ligand-based reactivity is guaranteed by the d^0 electronic configuration of tungsten. Interestingly, $(\eta^5\text{-}C_5Me_5)Mo({=}O)({=}S)CH_2SiMe_3$ also undergoes oxidation-promoted sulfur transfer. $(\eta^5\text{-}C_5Me_5)Mo({=}O)(\eta^2\text{-}S_2)CH_2SiMe_3$ and $(\eta^5\text{-}C_5Me_5)Mo({=}O)_2CH_2SiMe_3$ are produced, and the former compound is further oxidized to $(\eta^5\text{-}C_5Me_5)Mo({=}O)(\eta^2\text{-}S_2O)CH_2SiMe_3$.[28] The intramolecular redox chemistry of molybdenum- and tungsten–sulfur systems in which both metal and ligand undergo changes in oxidation state is well-documented;[3,22,35] on the other hand, ligand-based processes are less frequently observed.[9,11,29,31] We have found only two examples of related chemical behavior in the literature, both occurring in dinuclear molybdenum–sulfur species. Intermolecular metal–metal sulfur transfer was observed during the thermal rearrangement of *syn*-$(\eta^5\text{-}MeC_5H_4Mo)_2({=}O)({=}S)(\mu\text{-}S)_2$ to give $(\eta^5\text{-}MeC_5H_4Mo)_2({=}O)_2(\mu\text{-}S)_2$ and $(\eta^5\text{-}MeC_5H_4Mo)_2({=}S)_2(\mu\text{-}S)_2$.[18] Reaction of $(\eta^5\text{-}C_5Me_5)_2Mo_2S_4$ with oxygen yielded $[(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu,\eta^2\text{-}S_2)(\mu\text{-}S)(\mu,\eta^1\text{-}S_2O_3)]$, the product of an intermolecular metal-to-sulfur transfer.[36]

Conclusions

Mononuclear sulfido and persulfido complexes of (pentamethylcyclopentadienyl)tungsten are quite robust, as they are stabilized by the substantial donor capability of the sulfur ligands and the steric requirements of the $\eta^5\text{-}C_5Me_5$ ligand. The complexes are not prone to dimerization. The chemistry of these high-oxidation-state sulfur species resembles that of their oxo and peroxo analogues: ligand transformations are effected without reduction of the d^0 metal center or cleavage of the metal–alkyl bond. The role of steric interactions in determining the course of reactions, however, is much more pronounced in these compounds. Replacement of methyl by the bulkier (trimethylsilyl)methyl ligand effectively blocks otherwise thermodynamically accessible reaction pathways. The W=S unit of **1a** and **1b** is an inadequate model for the reactivity of the biological Mo=S sytem, for nucleophilic abstraction of sulfur to give a W(IV) species does not take place. Sulfur is, however, transferred between molecules of **1a** under oxidative conditions, and thiophiles rapidly transform persulfido complexes **2a** and **3** into their sulfido equivalents. As the persulfido complexes are chiral, we are currently exploring the use of these and other atom-transfer processes for the preparation of optically active organic and organometallic molecules.

---

(31) Miller, K. F.; Bruce, A. E.; Corbin, J. L.; Wherland, S.; Stiefel, E. I. *J. Am. Chem. Soc.* **1980**, *102*, 5102.

(32) Massey, V.; Edmondson, D. *J. Biol. Chem.* **1970**, *245*, 6595. Hille, R.; Massey, V. In *Molybdenum Enzymes*; Spiro, T. G., Ed.; Wiley: New York, 1985, Chapter 9.

(33) Schmid, G.; Ritter, G. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 645. Dirand-Colin, J.; Schappacher, M.; Ricard, L.; Weiss, R. *J. Less Common Met.* **1977**, *54*, 91. Hoots, J. E.; Lesch, D. A.; Rauchfuss, T. B. *Inorg. Chem.* **1984**, *23*, 3130. Herberhold, M.; Schmidkonz, B.; Ziegler, M. L.; Zahn, T. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 515. Herberhold, M.; Schmidkonz, B. *J. Organomet. Chem.* **1986**, *308*, 35.

(34) The oxo–sulfido product itself reacts under similar conditions to give $(\eta^5\text{-}C_5Me_5)W({=}O)_2Me$ and **3a**. This additional reactivity accounts for the absence of significant $(\eta^5\text{-}C_5Me_5)W({=}O)({=}S)Me$ in the product mixture. In addition, the sulfido and persulfido species decompose to oxo species in $CDCl_3$ over time.

(35) Pan, W.-H.; Harmer, M. A.; Halbert, T. R.; Stiefel, E. I. *J. Am. Chem. Soc.* **1984**, *106*, 459. Harmer, M. A.; Halbert, T. R.; Pan, W.-H.; Coyle, C. L.; Cohen, S. A.; Stiefel, E. I. *Polyhedron* **1986**, *5*, 341.

(36) Brunner, H.; Kauermann, H.; Pfauntsch, J.; Wachter, J.; Enemark, J. H.; Young, C. G. *J. Organomet. Chem.* **1987**, *331*, 45.

Experimental Section

Syntheses. Reagents and solvents were used as supplied without additional purification. The compounds $(\eta^5\text{-}C_5Me_5)W(=O)_2R$ and $(\eta^5\text{-}C_5Me_5)W(=O)(\eta^2\text{-}O_2)R$ were prepared as described elsewhere.[24] During the course of this work, an efficient photolytic preparation of $(\eta^5\text{-}C_5Me_5)W(=O)_2R$ was also developed. Preparative thin-layer chromatography was performed on 0.25-mm silica gel plates using 1:1 diethyl ether/hexanes as eluant.

^1H and ^{13}C NMR spectra were recorded at 250 and 125 MHz, respectively, with Bruker spectrometers and are reported as parts per million downfield from tetramethylsilane by using the solvent resonance for calibration. Infrared spectra were obtained with a Nicolet 5SX FTIR spectrometer. Mass spectra were obtained with a Hewlett-Packard 5985 mass spectrometer (using the direct injection option). Elemental analyses were performed by Atlantic Microlabs, Inc., Norcross, GA.

Improved Preparation of the Starting Materials $(\eta^5\text{-}C_5Me_5)W(=O)_2R$. A benzene solution of 500 mg (1.2 mmol) $(\eta^5\text{-}C_5Me_5)W(CO)_3Me$ contained in a quartz apparatus was irradiated with a medium-pressure mercury lamp; NO gas was bubbled through the solution during the photolysis. The disappearance of the carbonyl bands of the starting material was monitored by IR spectroscopy. Upon completion of the reaction (~10 min), the solvent was removed in vacuo and the residue was extracted with several portions of diethyl ether in vessels open to the air. These extracts were combined, concentrated, and chromatographed on a 30 × 2 cm column of silica gel by using diethyl ether as eluant to give 236 mg (0.64 mmol, 54%) of $(\eta^5\text{-}C_5Me_5)W(=O)_2Me$. The (trimethylsilyl)methyl analogue may be prepared via this route as well.

Preparation of $(\eta^5\text{-}C_5Me_5)W(=S)_2R$ (1a, R = Me; 1b, R = CH_2SiMe_3). To a solution of 35 mg (0.096 mmol) of $(\eta^5\text{-}C_5Me_5)W(=O)_2Me$ in 35 mL of CS_2 was added 24 mg (0.20 mmol) of solid B_2S_3. The reaction mixture was stirred under nitrogen overnight; at this point TLC indicated that no starting material or $(\eta^5\text{-}C_5Me_5)W(=O)(=S)Me$ was present. Concentration of the reaction mixture in vacuo left a red-violet residue, and this was separated via preparative TLC. The principal red band yielded 20 mg of **1a** (0.050 mmol, 52%).

Compound **1b** was prepared in a similar fashion from 29 mg (0.066 mmol) of $(\eta^5\text{-}C_5Me_5)W(=O)_2CH_2SiMe_3$ and 23 mg (0.20 mmol) of B_2S_3. Reaction for 2 h followed by preparative TLC purification gave 20 mg of **1b** (0.043 mmol, 64%). X-ray crystallographic quality dark red crystals were obtained from a saturated solution of hexane at −20 °C.

Data for compound **1a**: ^1H NMR ($CDCl_3$, 25 °C) δ 2.17 (s, 15 H, C_5Me_5), 1.03 (s, 3 H, Me; $J(W\text{-}H) = 7.7$ Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C) δ 116.8 (s, $\eta^5\text{-}C_5Me_5$), 20.5 (s, W-Me; $J(W\text{-}C) = 89.4$ Hz), 12.5 (s, $\eta^5\text{-}C_5Me_5$); IR (CS_2) $\nu_{W=S}$ 499 (w, sh) and 495 (w) cm^{-1}; MS-EI (20 eV) *m/z* for $C_{11}H_{18}S_2{}^{184}W$ = 398 (P^+), 383 (P − Me). Anal. Calcd for $C_{11}H_{18}S_2W$: C, 33.18; H, 4.56; S, 16.10. Found: C, 33.12; H, 4.57; S, 16.00.

Data for compound **1b**: ^1H NMR ($CDCl_3$, 25 °C) δ 2.13 (s, 15 H, C_5Me_5), 0.38 (s, 2 H, CH_2; $J(W\text{-}H) = 7.8$ Hz), 0.11 (s, 9 H, $SiMe_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C) δ 116.4 (s, $\eta^5\text{-}C_5Me_5$), 37.0 (s, W-CH_2; $J(W\text{-}C) = 85.0$ Hz), 12.6 (s, $\eta^5\text{-}C_5Me_5$), 0.4 (s, $SiMe_3$); IR (CS_2) $\nu_{W=S}$ 502 (w) and 491 (w) cm^{-1}; MS-EI (20 eV) *m/z* for $C_{14}H_{26}SiS_2{}^{184}W$ = 470 (P^+), 455 (P − Me). Anal. Calcd for $C_{14}H_{26}SiS_2W$: C, 35.75; H, 5.57; Si, 13.63. Found: C, 35.82; H, 5.59; S, 13.56.

Preparation of $(\eta^5\text{-}C_5Me_5)W(=S)(\eta^2\text{-}S_2)Me$ (2a). A solution of 32 mg of $(\eta^5\text{-}C_5Me_5)W(=O)_2Me$ (0.087 mmol) in 20 mL of CS_2 was treated with 30 mg (0.26 mmol) of B_2S_3, and the reaction mixture was stirred under nitrogen. After 7 h, TLC showed the presence of only **1a** and **2a**; following solvent removal and preparative TLC purification, 14 mg of **2a** (0.033 mmol, 37%) was obtained from the purple band; a significant amount of **1a** was recovered from the red band preceding the product band.

Data for compound **2a**: ^1H NMR ($CDCl_3$, 25°C) δ 2.08 (s, 15 H, C_5Me_5), 1.80 (s, 3 H, Me; $J(W\text{-}H) = 6.2$ Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25°C) δ 114.0 (s, $\eta^5\text{-}C_5Me_5$), 13.5 (s, W-Me; $J(W\text{-}C) = 63.2$ Hz), 11.8 (s, $\eta^5\text{-}C_5Me_5$); IR (CS_2) $\nu_{S\text{-}S}$ 549 (m), $\nu_{W=S}$ 511 (w) cm^{-1}; MS-EI (20 eV) *m/z* for $C_{11}H_{18}S_3{}^{184}W$ = 430 (P^+), 415 (P − Me), 398 (P − S). Anal. Calcd for $C_{11}H_{18}S_3W$: C, 30.70; H, 4.22; S, 22.35. Found: C, 30.96; H, 4.27; S, 22.22.

Preparation of $(\eta^5\text{-}C_5Me_5)W(=O)(\eta^2\text{-}S_2)Me$ (3). A 35-mg (0.092-mmol) sample of $(\eta^5\text{-}C_5Me_5)W(=O)(\eta^2\text{-}O_2)Me$ was dissolved in 35 mL of CS_2. The colorless solution was saturated with gaseous H_2S and the flask sealed with a septum. A red solution formed over a period of 4 days; TLC of the reaction mixture showed the absence of dioxo and peroxo species. The solution was concentrated in vacuo and the red-orange residue then purified via preparative TLC. Two separations were required to obtain the desired product (yellow-orange band with larger R_f value) free from the oxo–sulfido compound (yellow band with smaller R_f value). Compound **3** was isolated in 37% yield (14 mg, 0.034 mmol). Orange crystals suitable for X-ray diffraction analysis were obtained from a solution of diethyl ether at −20 °C.

Table I. Crystallographic Data for $[\eta^5\text{-}C_5(CH_3)_5]W(S)_2[CH_2SiMe_3]$

$WS_2Si_1C_{14}H_{26}$	fw = 470.43
a = 10.967(2) Å	$P2_1/c$ (No. 14)
b = 9.323(1) Å	T = 23 °C
c = 18.092(3) Å	λ = 0.71073 Å
β = 94.59(2)°	ρ_{calcd} = 1.69 g/cm^3
V = 1843.8 Å^3	μ = 66.7 cm^{-1}
Z = 4	transm coeff = 89.25–99.85%
R_1 = 0.027	R_2 = 0.035

Table II. Positional and Thermal Parameters for $[\eta^5\text{-}C_5(CH_3)_5]W(S)_2[CH_2SiMe_3]$

atom	x/a	y/a	z/a	B_{eqv}, Å^2
W	0.69080 (2)	0.75953 (2)	0.85633 (1)	2.931 (4)
S(1)	0.6316 (2)	0.5423 (2)	0.8654 (1)	5.03 (4)
S(2)	0.6879 (2)	0.8107 (2)	0.7413 (1)	5.44 (5)
Si	0.9719 (2)	0.5890 (2)	0.8445 (1)	4.56 (4)
C(1)	0.8820 (6)	0.7399 (7)	0.8838 (4)	4.2 (1)
C(2)	0.9399 (9)	0.565 (1)	0.7431 (5)	8.5 (3)
C(3)	1.1361 (7)	0.630 (1)	0.8650 (6)	8.5 (3)
C(4)	0.9418 (8)	0.4167 (9)	0.8899 (6)	8.1 (3)
C(5)	0.5287 (5)	0.9073 (6)	0.8846 (4)	3.7 (1)
C(6)	0.6280 (6)	1.0030 (6)	0.8799 (3)	3.7 (1)
C(7)	0.7171 (6)	0.9673 (7)	0.9389 (4)	4.1 (1)
C(8)	0.6707 (6)	0.8544 (7)	0.9802 (3)	4.7 (1)
C(9)	0.5546 (6)	0.8210 (7)	0.9484 (4)	4.5 (1)
C(10)	0.4092 (6)	0.9112 (8)	0.8361 (5)	6.1 (2)
C(11)	0.6335 (8)	1.1229 (8)	0.8244 (5)	6.1 (2)
C(12)	0.8346 (7)	1.0468 (9)	0.9564 (5)	8.2 (2)
C(13)	0.735 (1)	0.789 (1)	1.0487 (5)	9.5 (3)
C(14)	0.4633 (8)	0.7166 (9)	0.9781 (5)	8.4 (2)

Table III. Selected Bond Distances (Å) for $[\eta^5\text{-}C_5(CH_3)_5]W(S)_2[CH_2SiMe_3]$

W–S(1)	2.136 (2)	Si–C(4)	1.849 (9)
W–S(2)	2.134 (2)	C(5)–C(6)	1.417 (9)
W–C(1)	2.118 (6)	C(5)–C(9)	1.414 (9)
W–C(5)	2.340 (6)	C(5)–C(10)	1.513 (9)
W–C(6)	2.418 (6)	C(6)–C(7)	1.428 (9)
W–C(7)	2.447 (6)	C(6)–C(11)	1.508 (9)
W–C(8)	2.433 (6)	C(7)–C(8)	1.407 (9)
W–C(9)	2.393 (7)	C(7)–C(12)	1.50 (1)
Si–C(1)	1.873 (7)	C(8)–C(9)	1.391 (9)
Si–C(2)	1.852 (9)	C(8)–C(13)	1.51 (1)
Si–C(3)	1.850 (8)	C(9)–C(14)	1.53 (1)

Data for compound **3**: ^1H NMR ($CDCl_3$, 25 °C) δ 2.06 (s, 15 H, C_5Me_5), 1.66 (s, 3 H, Me; $J(W\text{-}H) = 7.4$ Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C) δ 115.8 (s, $\eta^5\text{-}C_5Me_5$), 13.8 (s, W-Me; $J(W\text{-}C) = 85.0$ Hz), 10.8 (s, $\eta^5\text{-}C_5Me_5$); IR (CS_2) $\nu_{W=O}$ 944 (s), $\nu_{S\text{-}S}$ 549 (m) cm^{-1}; MS-EI (20 eV) *m/z* for $C_{11}H_{18}OS_2{}^{184}W$ = 414 (P^+), 399 (P − Me). Anal. Calcd for $C_{11}H_{18}OS_2W$: C, 31.89; H, 4.38; S, 15.48. Found: C, 31.95; H, 4.32; S, 15.55.

X-ray Crystallographic Analyses. $(\eta^5\text{-}C_5Me_5)W(=S)_2CH_2SiMe_3$. A red crystal of dimensions 0.17 × 0.19 × 0.26 mm was mounted in a glass capillary, and diffraction data were collected with an Enraf-Nonius CAD4 diffractometer using graphite-monochromatized Mo Kα radiation. Data collection parameters for **1b** are summarized in Table I. The methods used follow those we have pulblished elsewhere,[37] and only features specific to these structures are given here. From the systematic absences of $0k0$, $k = 2n + 1$, and $h0l$, $l = 2n + 1$, the space group was determined to be $P2_1/c$. The structure was solved by using the Patterson heavy-atom method, which revealed the position of the tungsten 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 held at 1.3 times the B_{eqv} of the atom to which they were attached, were included in full-matrix least-squares refinement. Neutral-atom scattering factors were calculated by standard procedures.[38] Anomalous dispersion corrections were applied to all atoms.[38,39]

---

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

(38) 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.

Table IV. Selected Bond Angles (deg) for $[\eta^5\text{-}C_5(CH_3)_5]W(S)_2[CH_2SiMe_3]$

S(1)–W–S(2)	107.84 (8)	C(5)–C(6)–C(7)	107.1 (5)
S(1)–W–C(1)	101.1 (2)	C(5)–C(6)–C(11)	125.6 (6)
S(2)–W–C(1)	100.5 (2)	C(7)–C(6)–C(11)	127.3 (6)
C(1)–Si–C(2)	113.4 (4)	W–C(7)–C(12)	125.3 (5)
C(1)–Si–C(3)	108.1 (4)	C(6)–C(7)–C(8)	108.4 (6)
C(1)–Si–C(4)	111.1 (4)	C(6)–C(7)–C(12)	124.8 (6)
C(2)–Si–C(3)	108.7 (5)	C(8)–C(7)–C(12)	126.7 (6)
C(2)–Si–C(4)	108.1 (5)	W–C(8)–C(13)	122.5 (5)
C(3)–Si–C(4)	107.2 (4)	C(7)–C(8)–C(9)	107.7 (6)
W–C(1)–Si	121.8 (3)	C(7)–C(8)–C(13)	124.9 (7)
W–C(5)–C(10)	121.5 (5)	C(9)–C(8)–C(13)	127.4 (7)
C(6)–C(5)–C(9)	107.4 (5)	W–C(9)–C(14)	123.7 (5)
C(6)–C(5)–C(10)	125.9 (6)	C(5)–C(9)–C(8)	109.3 (6)
C(9)–C(5)–C(10)	126.3 (6)	C(5)–C(9)–C(14)	123.7 (6)
W–C(6)–C(11)	123.3 (5)	C(8)–C(9)–C(14)	126.9 (6)

A ψ-scan was used to estimate the maximum and minimum transmission coefficients. An empirical absorption correction (DIFABS[40]) 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–IV. Tables of calculated hydrogen positions, thermal parameters, and structure factor tables are provided in the supplementary material.

$(\eta^5\text{-}C_5Me_5)W({=}O)(\eta^2\text{-}S_2)Me$. A 0.11 × 0.28 × 0.32 mm crystal was selected and a data set collected by using Mo Kα radiation. Despite a numerical absorption correction, the relatively low transmission (10–37%) and poor crystal quality of this and other crystals yielded a structure of marginal quality, which established the atomic connectivity. Compound 3 crystallizes in the orthorhombic system with a = 14.878 (3) Å, b = 7.202 (3) Å, c = 12.755 (3) Å, V = 1366.8 Å^3, and Z = 4. Anisotropic refinement of tungsten and sulfur atoms and isotropic refinement of other non-hydrogen atoms converged to the residuals R_1 = 0.058 and R_2 = 0.067 in the space group $Pca2_1$ (No. 29). The structure is similar to that of $(\eta^5\text{-}C_5Me_5)W({=}O)(\eta^2\text{-}O_2)CH_2SiMe_3$[24] including the alignment of the S–S bond of the $\eta^2\text{-}S_2$ with the W–Me bond.

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

Supplementary Material Available: Tables S1–S3, listing complete data collection parameters, anisotropic thermal parameters, and calculated hydrogen atom positions (3 pages); Table S4, listing observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

---

(39) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.
(40) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 159.

Contribution from the 3M Corporate Research Laboratories, St. Paul, Minnesota 55144, and Department of Chemistry, Stanford University, Stanford, California 94305

Solid-State Chemistry of Molecular Metal Oxide Clusters. Bis(triphenylphosphine)rhodium(I) Carbonyl Derivatives

A. R. Siedle,*,† W. B. Gleason,† R. A. Newmark,† R. P. Skarjune,† P. A. Lyon,† C. G. Markell,†
K. O. Hodgson,‡ and A. L. Roe‡

Received June 7, 1989

Hydronium salts of the Keggin-type $XM_{12}O_{40}$ molecular metal oxide cluster anions $SiW_{12}O_{40}^{4-}$, $SiMo_{12}O_{40}^{4-}$, $PW_{12}O_{40}^{3-}$, $PMo_{12}O_{40}^{3-}$, $PMo_{12}O_{40}^{4-}$, and $PVMo_{11}O_{40}^{4-}$ react with $[(Ph_3P)_3Rh(CO)][HC(SO_2CF_3)_2]$ in $CH_3CN\text{–}C_2H_5OH$ to form $[\text{trans-}(Ph_3P)_2Rh(CO)(CH_3CN)]_nXM_{12}O_{40}$. These salts lose CH_3CN on heating to provide $[(Ph_3P)_2Rh(CO)]_nXM_{12}O_{40}$, which may also be obtained directly from $[(Ph_3P)_3Rh(CO)][HC(SO_2CF_3)_2]$ in pure ethanol. These oxometalates have been characterized by IR, NMR, and X-ray absorption spectroscopy and are considered to contain isolated, lattice-stabilized $(Ph_3P)_2Rh(CO)(CH_3CN)^+$ and $(Ph_3P)_2Rh(CO)^+$ cations, with the latter being a three-coordinate, 14-electron Rh(I) species. The activity and selectivity of these compounds as catalysts for olefin isomerization and hydroformylation are described. Reaction of $[(Ph_3P)_3Rh(CO)][HC(SO_2CF_3)_2]$ with CH_3CN produces $[\textit{trans-}(Ph_3P)_2Rh(CO)(CH_3CN)][HC(SO_2CF_3)_2]$, triclinic, $P\bar{1}$, a = 10.669 (1) Å, b = 22.241 (2) Å, c = 9.257 (5) Å, α = 96.22 (2)°, β = 97.51 (2)°, γ = 79.19 (1)°, Z = 2, V = 2131 Å^3, R = 0.032, and R_w = 0.039.

Introduction

We are seeking to explore and develop the synthetic and solid-state reaction chemistry of organometallic derivatives of molecular metal oxide clusters.[1-3] Clusters of particular interest and utility are the $X^{n+}M_{12}O_{40}^{(8-n)-}$ Keggin ions, where M is molybdenum or tungsten and where the heteroatom X, phosphorus or silicon, has the formal oxidation number n. Examples are $PMo_{12}O_{40}^{3-}$ and $SiW_{12}O_{40}^{4-}$. These anionic clusters have net T_d symmetry and feature a tetrahedral XO_4 unit, at each vertex of which are three edge-shared MO_6 octahedra. The four M_3O_{13} trimeric groups are bonded to one another by corner sharing of oxygen atoms.[4] The $XM_{12}O_{40}^{n-}$ ions are close-packed in the sense that the exterior comprises a cuboctahedral array of oxygen atoms and it is not possible to insert an additional metal atom into the cluster. These features distinguish Keggin ions from lacunary metal oxide clusters: non-close-packed species such as $SiW_{11}O_{39}^{8-}$,[5] A-$PW_9O_{34}^{9-}$,[6] $P_2W_{15}O_{56}^{2-}$,[7] and $P_3O_9^{3-}$[8] into which transition metals may be inserted.

Charge in the $XM_{12}O_{40}^{n-}$ anions is delocalized so that the oxygen atoms lying on the surface of the cluster are weakly nucleophilic. In homogeneous solution, reagents such as R_3O^+ salts are required to effect O-alkylation of $PMo_{12}O_{40}^{3-}$,[9] but heating solid ArN_2^+ salts of $XM_{12}O_{40}^{n-}$ produces $(\text{aryl})_nXM_{12}O_{40}$.[10] Nucleophilicity of anionic molecular metal oxide clusters is substantially increased by using smaller clusters that have a higher charge:mass ratio or by incorporation of group Vb elements.

---

† 3M Corporate Research Laboratories.
‡ Stanford University.

(1) Siedle, A. R.; Markell, C. G.; Lyon, P. A.; Hodgson, K. O.; Roe, A. L. *Inorg. Chem.* **1987**, *26*, 219.
(2) Siedle, A. R.; Newmark, R. A.; Gleason, W. B.; Skarjune, R. P.; Hodgson, K. O.; Roe, A. L.; Day, V. W. *Solid State Ionics* **1988**, *26*, 1988.
(3) Siedle, A. R. U.S. Pat. 4,673,753.
(4) Pope, M. T. *Heteropoly and Isopoly Oxometallates*; Springer Verlag: New York, 1983.
(5) (a) Knoth, W. H. *J. Am. Chem. Soc.* **1979**, *101*, 2211. (b) Ho, R. K. C.; Klemperer, W. G. *J. Am. Chem. Soc.* **1978**, *100*, 1006.
(6) Knoth, W. H.; Domaille, P. J.; Harlow, R. L. *Inorg. Chem.* **1986**, *25*, 1577.
(7) Finke, R. G.; Droge, M. W. *Inorg. Chem.* **1983**, *22*, 1006.
(8) Besecker, C. J.; Day, V. W.; Klemperer, W. G. *Organometallics* **1985**, *4*, 564.
(9) Knoth, W. H.; Harlow, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 4625.
(10) Siedle, A. R.; Lyon, P. A.; Hunt, S. L.; Skarjune, R. P. *J. Am. Chem. Soc.* **1986**, *108*, 6430.

0020-1669/90/1329-1667$02.50/0