Facile Route to the Trithiotungsten(VI) Complex $(PPh_4)[(C_5Me_5)W(S)_3]$ via Carbon−Sulfur Bond Cleavage of Ethanedithiolate and Its Reactions with Alkyl Halides and Alkynes

Hiroyuki Kawaguchi and Kazuyuki Tatsumi*

Department of Chemistry, Faculty of Science
Nagoya University, Furo-cho, Chikusa-ku
Nagoya 464-01 Japan

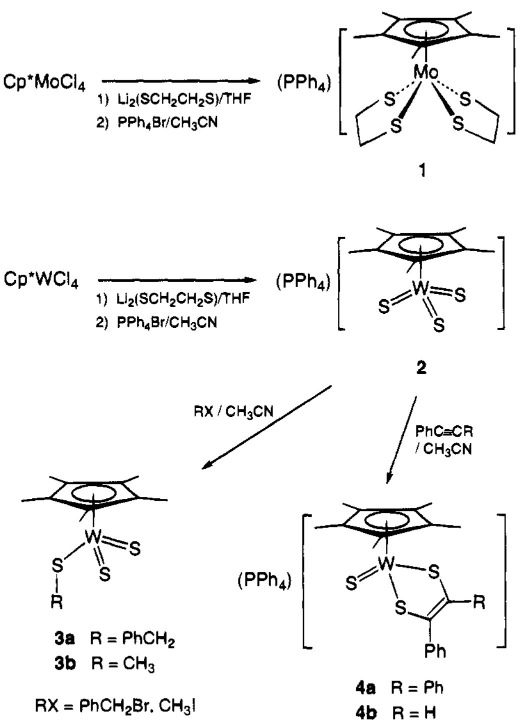
Received October 31, 1994

The chemistry of oxo complexes of group 6 metals has been studied extensively because of their relevance to bioinorganic systems and their potential utility as oxidation catalysts.[1,2] In contrast, metal−sulfur double bonds are less common, in spite of the fact that oxothio and dithio complexes of molybdenum and tungsten are also regarded as important species in understanding the functions of the metalloenzymes.[2] This is partly due to lack of a convenient synthesis for such thio complexes.

We have previously described an unusual isomerization of $(PPh_4)[Nb(SCH_2CH_2S)_3]$ involving a C−S bond cleavage that gave rise to the sulfide complex $(PPh_4)[Nb(S)(SCH_2CH_2S)(SCH_2CH_2SCH_2CH_2S)]$ in good yield.[3] We have also succeeded in isolating the anionic organometallic trithio complexes $[Cp^*M(S)_3]^{2-}$ ($Cp^* = C_5Me_5$, M = Nb, Ta) from the reaction between Cp^*MCl_4 and excess Li_2S_2.[4] As an extension of these studies, we are interested in the behavior of thiolato and thio ligands with group 6 metals and we have reacted Cp^*MoCl_4 and Cp^*WCl_4 with $Li_2(SCH_2CH_2S)$. The reaction of Cp^*MoCl_4, followed by cation exchange with PPh_4Br, yielded a Mo(IV) thiolato complex $[PPh_4][Cp^*Mo(SCH_2CH_2S)_2]$ (**1**). However, a trithio complex of W(VI), $[PPh_4]$ $[Cp^*W(S)_3]$ (**2**), was isolated unexpectedly from the analogous reaction with Cp^*WCl_4. Here we report the facile formation of **2** and its reactions with alkyl halides and alkynes.

Addition of an orange suspension of Cp^*WCl_4 in THF to $Li_2(SCH_2CH_2S)$ in THF at 0 °C gave at first a red suspension, which dissolved to produce an orange-red homogeneous solution in seconds (see Scheme 1). The UV−visible spectrum of this solution indicated formation of $[Cp^*W(S)_3]^-$.[5] In fact, subsequent cation exchange with PPh_4Br in CH_3CN followed by a standard workup generated $(PPh_4)[Cp^*W(S)_3]$ (**2**) as moderately moisture-sensitive orange crystals in 82% isolated yield.[6] The X-ray-derived structure of the anion of **2**[7] is practically the same as that of $(Et_3NH)[Cp^*W(S)_3]$ reported by G. L. Geoffroy et al.[5] The latter complex was isolated in low yield from a $Cp^*WCl_4/H_2S/Et_3N$ reaction system, which also produced a mixture of $Cp^*_2W_2(S)_2(\mu\text{-}S)_2$, $Cp^*_2W_2(S)_2(\mu\text{-}S_2)$, and $(Et_3NH)[Cp^*W(S)_2O]$.

Scheme 1



Evidently the oxidation of W(V) to W(VI) is induced by ethanethiolate C−S bond cleavage, and this unexpected reaction turned out to be a novel, convenient route to the trithiotungsten complex. Interestingly, the analogous reaction of Cp^*MoCl_4 reduces the molybdenum center from Mo(V) to Mo(IV), producing **1** in 75% yield, where the C−S bonds remain intact.[8] The contrast may arise from the tendency of tungsten to favor higher oxidation states than molybdenum. It should be mentioned here that the Mo(II) complexes $Mo(CO)(PMe_3)_2\{SC_6H_4S(CH_2)_nSC_6H_4S\}$ (*n* = 1, 2) have been shown to dealkylate, forming $Mo^{IV}(PMe_3)_2(S_2C_6H_4)_2$, and that the reaction between $MoCl_2(CO)_2(PMe_3)_3$ and $Na_2(SC_6H_4SCMe_2SC_6H_4S)$ gave rise to $Mo^{II}(CO)_3(PMe_3)_2(S_2C_6H_4)$.[9]

The facile high-yield synthesis of **2** allowed us to examine the reactivity of the terminal sulfides on W(VI). The reactions of **2** with 1 equiv of $PhCH_2Br$ or CH_3I in CH_3CN are straightforward, generating the neutral dithio/thiolato W(VI) complexes $Cp^*W(S)_2(SR)$ ($R = CH_2Ph$ (**3a**), CH_3 (**3b**)) as red crystals in 91% and 83% yields, respectively.[10] The remaining two W═S bonds do not react with excess alkyl halide. The X-ray crystal structure of **3a** is shown in Figure 1.[11] The complex assumes a normal three-legged piano stool geometry

---

(1) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401−1449.

(2) Enemark, J. H.; Young, C. G. *Adv. Inorg. Chem.* **1993**, *40*, 1−88 and references therein.

(3) Tatsumi, K.; Sekiguchi, Y.; Nakamura, A; Cramer, R. E.; Rupp, J. J. *J. Am. Chem. Soc.* **1986**, *108,* 1358−1359.

(4) (a) Tatsumi, K.; Inoue, Y; Nakamura, A.; Cramer, R. E.; VanDorne, W.; Gilje, J. W. *J. Am. Chem. Soc.* **1989**, *111*, 782−783. (b) Tatsumi, K..; Inoue, Y.; Kawaguchi, H.; Kohsaka, M.; Nakamura, A.; Cramer, R. E.; VanDoorne, W.; Taogoshi, G. J.; Richmann, P. N. *Organometallics* **1993**, *12*, 352−364.

(5) Rau, M. S.; Kretz, C. M.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1993**, *12*, 3447−3460.

(6) $(PPh_4)[Cp^*W(S)_3]$ (**2**): ^1H NMR ($CDCl_3$) δ 7.6−7.8 (PPh_4, m, 20H), 2.16 (Cp*, s, 15H); IR (Nujol) ν(W═S) 437 (m), 466 (s) cm^{-1}; UV−vis (λ_{max}, nm (ϵ_{max}, M^{-1} cm^{-1}), CH_3CN) 377 (8200), 428 (sh, 1300). Anal. Calcd for $C_{34}H_{35}S_3PW$: C, 54.11; H, 4.67; S, 12.75; P, 4.10. Found: C, 53.97; H, 4.77; S, 12.55; P, 3.88.

(7) Crystal data for $(PPh_4)[Cp^*W(S)_3]$ (**2**): orthorhombic, *Pbca* (No. 61), $a = 18.070$ (4) Å, $b = 20.181$ (5) Å, $c = 17.482$ (5) Å, $V = 6374$ (2) Å^3, $Z = 8$, $D_c = 1.572$ g cm^{-3}, μ(Mo Kα) = 38.97cm^{-1}, λ(Mo Kα) = 0.710 69 Å (graphite monochromated); $2\theta_{max} = 50.0°$, 6201 measured reflections of which 3954 with $I > 3.00\sigma(I)$ were used for the refinement; $R = 0.038$, $R_w = 0.039$, GOF = 2.23.

(8) $(PPh_4)[Cp^*Mo(SCH_2CH_2S)_2]$ CH_3CN (**1**): ^1H NMR ($CDCl_3$) δ 7.6−7.9 (PPh_4, m, 20H), 2.70 (SCH_2CH_2S, br, 8H), 1.99 (CH_3CN, s, 3H), 1.84 (Cp*, s, br, 15H). Anal. Calcd for $C_{40}H_{46}NS_4PMo$: C, 60.36; H, 5.83; N, 1.76; S, 16.11; P, 3.89. Found: C, 60.19; H, 5.99; N, 1.57; S, 16.00; P, 4.01.

(9) Sellmann, D.; Reisser, W. *J. Organomet. Chem.* **1985**, *294*, 333−346.

(10) $Cp^*W(S)_2(SCH_2Ph)$ (**3a**): ^1H NMR ($CDCl_3$) δ 7.3−7.2 (Ph, s, 5H), 4.66 (SCH_2Ph, s, 2H), 2.31 (Cp*, s, 15H); IR (Nujol) ν(W═S) 480 (s), 493 (s) cm^{-1}. Anal. Calcd for $C_{17}H_{22}S_3W$: C, 40.32; H, 4.38. Found: C, 40.66; H, 4.48. $Cp^*W(S)_2(SCH_3)$ (**3b**): ^1H NMR ($CDCl_3$) δ 3.28 (SCH_3, s, 3H), 2.31 (Cp*, s, 15H); IR (Nujol) ν(W═S) 481 (s), 494 (s) cm^{-1}. Anal. Calcd for $C_{11}H_{18}S_3W$: C, 30.70; H, 4.22. Found: C, 31.53; H, 4.40.

(11) Crystal data for $Cp^*W(S)_2(SCH_2Ph)$ (**3a**): orthorhombic, $P2_12_12_1$ (No. 19), $a = 13.736$ (5) Å, $b = 15.640$ (8) Å, $c = 8.837$ (4) Å, $V = 1898$ (1) Å^3, $Z = 4$, $D_c = 1.772$ g cm^{-3}, μ(Mo Kα) = 64.14 cm^{-1}, λ(Mo Kα) = 0.710 69 Å (graphite monochromated); $2\theta_{max} = 55.0°$, 2512 measured reflections of which 1903 with $I > 3.00\sigma(I)$ were used for the refinement; $R = 0.034$, $R_w = 0.034$, GOF = 1.26.

0002-7863/95/1517-3885$09.00/0

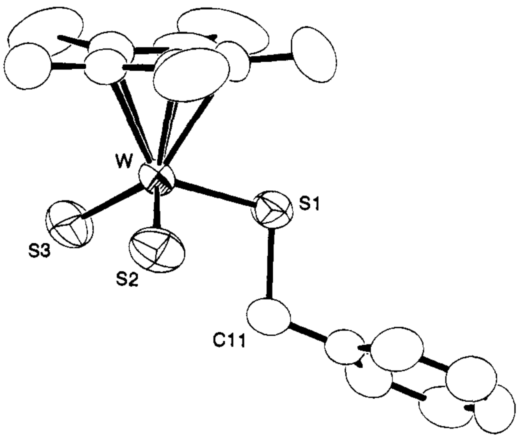


Figure 1. The structure of $Cp^*W(S)_2(SCH_2Ph)$ (**3a**) showing 50% thermal ellipsoids. Selected bond distances (Å) and angles (deg): W−S1 2.328 (4), W−S2 2.149 (3), W−S3 2.149 (3), S1−C11, 1.86 (1); S1−W−S2 103.1 (1), S1−W−S3 103.8 (2), S2−W−S3 105.9 (2), W−S1−C11 104.9 (5).

in which the thiolate S1−C11 bond orients parallel to the Cp*-(centroid)−W vector, thus allowing the occupied sulfur p orbital (p_y) to interact with the vacant W $d_{xy}-p_y$ hybrid. The W=S bond distances (2.149 (3) Å) are shorter by 0.043 Å than the mean W=S distance of **2** (2.192 Å), which is theoretically understandable. The IR bands of **3a** arising from the W=S stretching vibrations appear at 480 and 493 cm^{-1} (481 and 494 cm^{-1} for **3b**), and they are clearly shifted to higher energies relative to the corresponding IR bands of **2** (437 and 466 cm^{-1}).[12]

The most intriguing reaction which we have found for **2** is formation of thio/1, 2-enedithiolate complexes upon treating **2** with 5 equiv of PhC≡CPh or PhC≡CH in CH_3CN. The reaction with PhC≡CPh is complete at room temperature in 1 day, and $(PPh_4)[Cp^*W(S)(S_2C_2Ph_2)]$ (**4a**) was isolated as yellow green crystals in 76% yield.[13a] The reaction with PhC≡CH is faster and is complete in several hours, giving $(PPh_4)[Cp^*W(S)(S_2C_2PhH)]$ (**4b**) in 80% yield.[13b] Figure 2 shows the structure of the anion of **4a**, where coordination of the 1,2-enedithiolate ligand occurs with a nearly planar WS_2C_2 framework.[14] The W−S2 and W−S3 distances of 2.318 (2) and 2.334 (2) Å fall in the normal range for W(IV)−S bond lengths[15] and are comparable to the W−S1 length of **3a**. The W=S1 distance (2.186 (2) Å) of **4a**, on the other hand, is longer by 0.037 Å than those of **3a**, and this lengthening is consistent with the lower W=S stretching frequency (465 cm^{-1}) observed for **4a** relative to **3a**. The difference in oxidation state between these thio complexes, W(IV) *vs* W(VI), is probably one reason behind the trend.

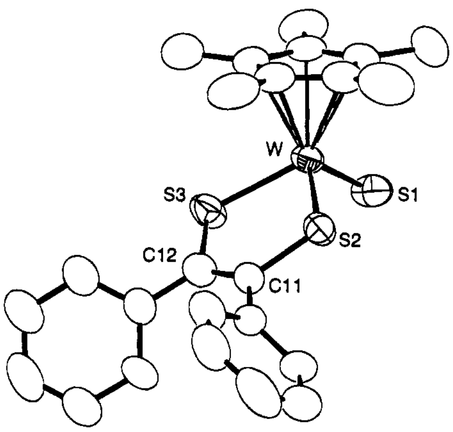


Figure 2. The structure of the anion part of $(PPh_4)[Cp^*W(S)(S_2C_2Ph_2)]$thf (**4a**) showing 50% thermal ellipsoids. Selected bond distances (Å) and angles (deg): W−S1 2.186 (2), W−S2 2.318 (2), W−S3 2.334 (2), S2−C11, 1.782 (6), S3−C12 1.799 (6), C11−C12 1.35 (1), S1−W−S2 108.3 (1), S1−W−S3 109.6 (1), S2−W−S3 82.5 (1), W−S2−C11 110.5 (2), W−S3−C12 109.7 (2), S2−C11−C12 118.9 (4), S3−C12−C11 118.5 (4).

Reaction of alkynes with polysulfides has occasionally been observed, though activated alkynes such as MeOCOC≡CC(O)-OMe (DMAC) and $CF_3C≡CF_3$ are used in most cases.[16] The direct addition of an alkyne to bridging monothio ligands is more unusual. The μ-S ligands in $(C_5H_5)_2Mo_2(\mu\text{-}S)_2(\mu\text{-}SH)_2$[17ab] and $(C_5H_4Me)_2V_2(\mu\text{-}S)_2(\mu\text{-}S_2)$[17c] were reported to react with HC≡CH and $CF_3C≡CF_3$, respectively, and recently various alkynes were found to add to the μ-bridging thio ligands in $[Mo^{3}\text{-}(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2(H_2O)_9]^{4+}$.[17d] Even more scarce is the reaction of terminal monothio ligands, and the single example reported so far is the formation of a 1,2-enedithiolate by addition of DMAC to $\{HB(Me_2pz)_3\}WS_2X$ (X = OPh, SPh, SePh).[18] Our finding shows that terminal thio ligands on W(VI) are capable of reacting even with nonactivated alkynes.

The differing reaction patterns between $[Cp^*W(S)_3]^-$ and its oxo analogue $[Cp^*W(O)_3]^-$ deserve comment. DMAC (2 equiv) and $[(Ph_3P)_2N][Cp^*W(O)_3]$ have been found to undergo a [2 + 2 + 3] cycloaddition leading to $[(Ph_3P)_2N][Cp^*(O)_2WOC(R)=C(R)C(R)=CR]$ (R = C(O)OMe), where the W(VI) oxidation state is retained.[5] In the case of the trithio complex, a facile [2 + 3] cycloaddition takes place with concomitant reduction of W(VI) to W(IV). Thus terminal thio ligands at W(VI) seem to facilitate reduction of the metal center and thereby allow nonactivated alkynes to form 1,2-enedithiolates.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond lengths, and bond angles for **2**, **3a**, and **4a** and ORTEP drawing of the anion of **2** (22 pages); observed and calculated structure factors for **2**, **3a**, and **4a** (45 pages). This material is contained in many libraries on microfiche, immediately follows this article in microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA943521T

---

(12) In ref 5, the W=S stretching frequencies in the IR spectrum of $(Et_3NH)[Cp^*W(S)_3]$ were observed at 471 (m), 447 (s), and 432 (m) cm^{-1}.

(13) $(PPh_4)[Cp^*W(S)(S_2C_2Ph_2)]$thf (**4a**): ^1H NMR (CD_3CN) δ 7.0−7.8 ($S_2C_2Ph_2$ and PPh_4, m, 30H), 3.59 (THF, 4H, m), 1.97 (Cp*, s, 15H), 1.73 (THF, 4H, m); IR (Nujol) ν(W=S) 465 (s) cm^{-1}. Anal. Calcd for $C_{52}H_{53}OS_3PW$: C, 62.15; H, 5.32. Found: C, 62.25; H, 5.35. $(PPh_4)[Cp^*W(S)(S_2C_2PhH)]$ (**4b**): ^1H NMR (CD_3CN) δ 7.0−7.8 (S_2C_2*Ph*H and PPh_4, m, 25H), 6.64 (S_2C_2Ph*H*, s, 1H), 1.92 (Cp*, s, 15H); IR (Nujol) ν(W=S) 466 (s) cm^{-1}. Anal. Calcd for $C_{42}H_{41}S_3PW$: C, 58.88; H, 4.82. Found: C, 58.11; H, 5.19.

(14) Crystal data for $(PPh_4)[Cp^*W(S)(S_2C_2Ph_2)]$thf (**4a**): monoclinic, $P2_1/n$ (No. 14), a = 13.221 (6) Å, b = 27.83 (1) Å, c = 13.456 (4) Å, b = 104.47 (3)°, V = 4793 (3) Å^3, Z = 4, D_c = 1.397 g cm^{-3}, μ(Mo Kα) = 24.76 cm^{-1}, λ(Mo Kα) = 0.710 69 Å (graphite monochromated); $2\theta_{max}$ = 45.0°, 6769 measured reflections of which 4979 with $I > 3.00\sigma(I)$ were used for the refinement; R = 0.034, R_w = 0.040.

(15) (a) Matsubayashi, G.; Douki, K.; Tamura, H.; Nakano, M.; Mori, W. *Inorg. Chem.* **1993**, *32*, 5990−5996. (b) Ueyama, N.; Oku, H.; Nakamura, A. *J. Am. Chem. Soc.* **1992**, *114*, 7310−7311. (c) Brown, G. F.; Stiefel, E. I. *Inorg. Chem.* **1973**, *12*, 2140. (d) Debaerdemaeker, T.; Kutoglu, A. *Acta Crystallogr.* **1973**, *B29*, 2664−2668.

(16) (a) Coucouvanis, D.; Toupadakis, A.; Lane, J. D.; Koo, S. M.; Kim, C. G.; Hadjikyriacou, A. *J. Am. Chem. Soc.* **1991**, *113*, 5271−5282. (b) Pilato, R. S.; Eriksen, K. A.; Greaney, M. A.; Stiefel, E. D.; Goswami, S.; Kilpatrick, L.; Spiro, T. G.; Taylor, E. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1991**, *113*, 9372−9374 and references therein.

(17) (a) Weberg, R.; Haltiwanger, R. C.; Rakowski DuBois, M. *Organometallics* **1985**, *4*, 1315−1318. (b) Rakowski DuBois, M.; VanDerveer, M. C.; Dubois, D. L.; Haltiwanger, R. C.; Miller, W. K. *J. Am. Chem. Soc.* **1980**, *102*, 7456−7461. (c) Bolinger, C. M.; Rauchfuss, T. B.; Rheingold, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 6321−6323. (d) Shibahara, T.; Sakane, G.; Mochida, S. *J. Am. Chem. Soc.* **1993**, *115*, 10408−10409.

(18) Eagle, A. A.; Harben, S. M.; Tiekink, E. R. T.; Young, C. G. *J. Am. Chem. Soc.* **1994**, *116*, 9749−9750.