Synthesis of (Pentamethylcyclopentadienyl)tantalum Sulfido Complexes via C−S Bond Cleavage of Triphenylmethanethiolate and Formation of a Novel Trithioborato Ligand

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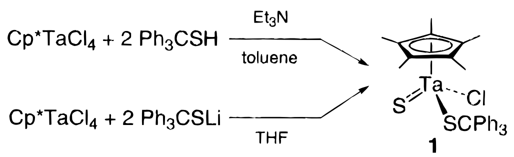
*Summary: Treatment of Cp^*TaCl_4 with triphenylmethanethiol via C−S bond cleavage gave rise to $Cp^*TaCl(S)(SCPh_3)$ (**1**), which was treated with LiSR, Li_2S, and $NaBH_4$ to afford $Cp^*TaS(SR)(SCPh_3)$ (R = CPh_3 (**2**), CMe_3 (**3**)), $[Cp^*Ta(S)_3Li_2(THF)_2]_2$ (**4**), and $Cp^*_3Ta_3(S)_3(S_3BH)$ (**5**), respectively. The crystal structures of **1** and **5** were determined by X-ray diffraction.*

Synthetic routes to transition-metal sulfido complexes containing terminal M═S multiple bonds remain limited because of the propensity of sulfides to bridge metal atoms.[1,2] Thiolato complexes of early transition metals often undergo C−S bond cleavage, resulting in formation of sulfido and sulfido/thiolato complexes.[3] We have searched for such a synthesis of a M═S bond, e.g., by C−S bond cleavage of a thiolato complex.[4] We recently reported that Cp^*WCl_4 ($Cp^* = C_5Me_5$) reacts with $Li_2(SCH_2CH_2S)$ to give $[Cp^*W(S)_3]^-$ with concomitant C−S bond cleavage.[4a] We report here the use of C−S bond rupture of a triphenylmethanethiolato derivative to prepare the Ta═S complex $Cp^*TaCl(S)(SCPh_3)$ (**1**). In addition to reactions of **1** with $LiSCPh_3$, $LiSCMe_3$, and Li_2S, we also describe the intriguing reaction of **1** with $NaBH_4$. This last reaction produces a Ta_3 cluster in which the trithioborato ligand is incorporated into the tantalum sulfido cluster.

Scheme 1



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No isolable product was obtained from the reaction between Cp^*TaCl_4 and 1 equiv of $HSCPh_3$ in the presence of NEt_3. When the amount of $HSCPh_3$ was increased to 2 equiv, yellow crystals of $Cp^*TaCl(S)(SCPh_3)$ (**1**) were isolated in 50% yield,[5] along with a trace amount of uncharacterizable dark red crystals. The identity of **1** was proved by its ^1H NMR spectrum and combustion analysis. The IR and Raman spectra of **1** exhibit strong bands at 502 and 503 cm^{-1}, respectively, arising from a Ta═S stretching vibration. Evidently, coordination of the triphenylmethanethiolato group at the Ta(V) center promoted partial C−S bond cleavage. We isolated Ph_3CCl and Ph_3CH along with **1** from the $Cp^*TaCl_4/HSCPh_3/NEt_3$ (1:2:2) reaction.[6] The presence of Ph_3CH among the byproducts indicates formation of a trityl radical upon cleavage of the C−S bond, with hydrogen atom abstraction from the solvent.

The X-ray-derived structure of **1** is shown in Figure 1.[7] In the three-legged piano-stool structure, the CPh_3 group is oriented away from the Cp* ligand in order to avoid steric congestion. The Ta═S distance is 2.161(2) Å, which is slightly shorter than the known Ta═S

[⊗] Abstract published in *Advance ACS Abstracts*, January 1, 1997.

[1] (a) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 56−76. (b) Müller, A.; Diemann, E. *Adv. Inorg. Chem.* **1987**, *31*, 89−122. (c) Wachter, J. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1613−1626.

[2] Recent examples of early-transition-metal complexes containing the M═S bond are shown in the following references: (a) Carney, M. J.; Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *Organometallics* **1992**, *11*, 761−777. (b) Howard, W. A.; Parkin, G. *Organometallics* **1993**, *12*, 2363−2366. (c) Howard, W. A.; Parkin, G. *J. Organomet. Chem.* **1994**, *472*, C1−C4. (d) Mandimutsira, B. S.; Chen, S.-J.; Demadis, K. D.; Coucouvanis, D. *Inorg. Chem.* **1995**, *34*, 2267−2268.

[3] (a) Leverd, P. C.; Lance, M.; Vigner, J.; Nierlich, M.; Ephritikhine, M. *J. Chem. Soc., Dalton Trans.* **1995**, 237−244. (b) Coucouvanis, D.; Hadjikyriacou, A.; Lester, R.; Kanatzidis, M. G. *Inorg. Chem.* **1994**, *33*, 3645−3655.

[4] (a) Kawaguchi, H.; Tatsumi, K. *J. Am. Chem. Soc.*, **1995**, *117*, 3885−3886. (b) Tatsumi, K.; Sekiguchi, Y.; Nakamura, A.; Cramer, R. E.; Rupp, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 1358−1359. (c) Tatsumi, K.; Kawaguchi, H.; Matsubara, I.; Nakamura, A.; Miki, K.; Kasai, N. *Inorg. Chem.* **1993**, *32*, 2604−2606.

[5] **Preparation of 1. Method A.** Upon addition of a benzene (20 mL) solution of Ph_3CSH (2.0 g, 7.2 mmol) to a suspension of Cp^*TaCl_4 (1.6 g, 3.6 mmol) in benzene (40 mL) in the presence of Et_3N (1.0 mL, 7.2 mmol) at room temperature, the solution immediately turned brown. After it had been stirred for 2 h, the mixture was centrifuged to remove insoluble material. The supernatant solution was evaporated to dryness, leaving a brown powder. Recrystallization from DME (1,2-dimethoxyethane) afforded yellow crystals first, and then a trace amount of dark red crystals was obtained. The yellow product was characterized as **1** (1.2 g, 50% yield). The dark red solid has not fully been characterized, but it contains Ta, Cp*, and sulfur. **Method B.** A THF (20 mL) solution of Cp^*TaCl_4 (1.26 g, 2.75 mmol) was added at 0 °C to $LiSCPh_3$ (5.57 mmol) in THF (20 mL). The mixture immediately became yellow and homogeneous. It was stirred for 1 h at room temperature. After removal of the solvent, the residue was extracted with benzene (60 mL), after which the benzene was evaporated at reduced pressure. The resulting yellow solid was dissolved in DME. Cooling the solution produced **1** as yellow crystals (1.04 g, 58%).

[6] The byproducts Ph_3CH, Ph_3CCl, and Ph_3CSCPh_3 were isolated, and they were characterized by elemental analyses for C, H, S, and Cl and also by IR spectra.

[7] Crystallographic data for **1**: $C_{29}H_{30}S_2ClTa$, fw 659.08, monoclinic, space group $P2_1/a$, with $a = 15.72(2)$ Å, $b = 8.2733(9)$ Å, $c = 21.071(4)$ Å, $\beta = 102.80(3)°$, $V = 2673(3)$ Å^3, $D_{calcd} = 1.638$ g cm^{-3} for $Z = 4$, μ(Mo Kα) = 43.30 cm^{-1}, $F(000) = 1304$. Intensity data were collected at room temperature on a Rigaku AFC5R diffractometer using the $\omega-2\theta$ scan method ($2\theta < 60.1°$). An absorption correction (Lorentz/polarization) was applied. The data were processed using the TEXSAN package of programs. The structure was solved by Patterson methods, from which the location of the Ta atom was obtained. The rest of the non-H atom positions were obtained from subsequent difference Fourier maps. All non-H atoms were refined anisotropically, while all of the H atoms were placed at calculated positions. The final cycle of full-matrix least-squares refinement was based on 4984 observed reflections ($I > 3.00\sigma(I)$) and 298 variable parameters and converted with unweighted and weighted agreement factors of $R = 0.032$ and $R_w = 0.041$ (GOF = 1.93).

[8] (a) Coucouvanis, D.; Chen, S.-J.; Mandimutsira, B. S.; Kim, C. G. *Inorg. Chem.* **1994**, *33*, 4429−4430. (b) Lee, S. C.; Li, J.; Mitchell, J. C.; Holm, R. H. *Inorg. Chem.* **1992**, *31*, 4333−4338. (c) Schreiner, S.; Aleandri, L. E.; Kang, D.; Ibers, J. A. *Inorg. Chem.* **1989**, *28*, 392−393. (d) Drew, M. G. B.; Rice, D. A.; Williams, D. M. *J. Chem. Soc., Dalton Trans.* **1984**, 845−848 and references therein.

S0276-7333(96)00864-3 CCC: $14.00

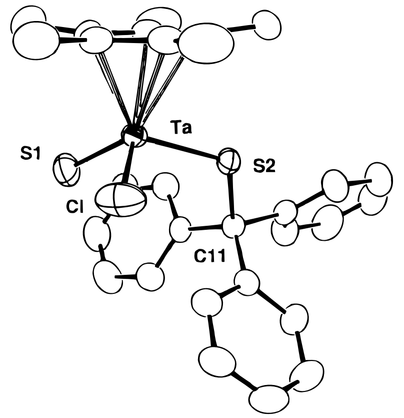
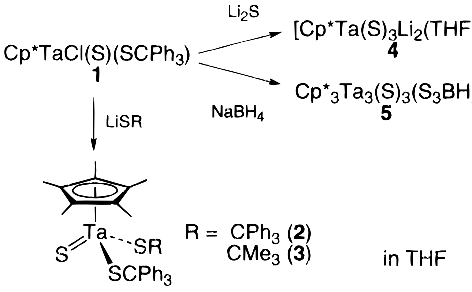


Figure 1. Structure of Cp*TaCl(S)(SCPh$_3$) (**1**). Selected bond distances (Å) and angles (deg): Ta−Cl, 2.332(2); Ta−S1, 2.161(2); Ta−S2, 2.342(1); C2−C11, 1.893(5); Cl−Ta−S1, 104.22(8); Cl−Ta−S2, 107.56(6); S1−Ta−S2, 105.84(5); Ta−S2−C11, 121.8(1).

Scheme 2



distances (2.18−2.30 Å).[8] The Ta−S2 distance (2.342(1) Å) is also at the short end of the reported Ta(V)−thiolate distances (2.35−2.47 Å).[9]

The chloride ligand of **1** does not react further with triphenylmethanethiol, and treatment of Cp*TaCl$_4$ with an excess of HSCPh$_3$/NEt$_3$ generated only **1**. On the other hand, **1** was found to react readily with LiSCPh$_3$ to give Cp*TaS(SCPh$_3$)$_2$ (**2**), which was isolated as yellow crystals,[10] and the direct reaction of Cp*TaCl$_4$ with 3 equiv of LiSCPh$_3$ in THF resulted in formation of **2** in 25% yield. The analogous reaction with 2 equiv of LiSCPh$_3$ afforded **1** in 58% yield. In these reactions, the by-products were Ph$_3$CSCPh$_3$, Ph$_3$CCl, and Ph$_3$CH. Ph$_3$CSCPh$_3$ appears to be derived from the reaction between Ph$_3$CCl and LiSCPh$_3$.[6] Consumption of LiSCPh$_3$ by this side reaction is a reason for the relatively low yield of **2** in the Cp*TaCl$_4$/LiSCPh$_3$ (1:3) reaction.

We have examined the reactions of **1** with LiSCMe$_3$, Li$_2$S, and NaBH$_4$. Addition of LiSCMe$_3$ to **1** in THF afforded Cp*TaS(SCMe$_3$)(SCPh$_3$) (**3**),[11] while treatment of **1** with an excess of Li$_2$S resulted in formation of [Cp*Ta(S)$_3$Li$_2$(THF)$_2$]$_2$ (**4**) in 56% yield.[12,13] Previously we reported that the sulfido complex **4** can be synthesized by the reaction of Cp*TaCl$_4$ with 3−5 equiv of Li$_2$S$_2$ and that use of Li$_2$S, instead of Li$_2$S$_2$, gave rise to **4** and Cp*$_3$Ta$_3$(S)$_6$Li$_2$(THF)$_2$.[14] Interestingly, partial reduction of tantalum was not observed in the reaction of **1** with Li$_2$S.

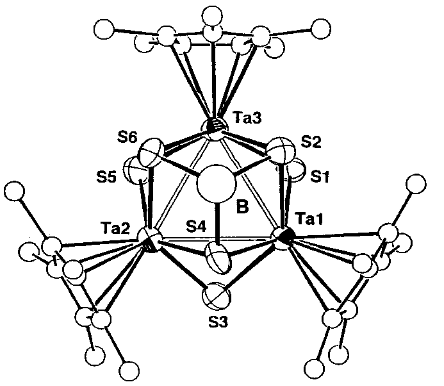


Figure 2. Structure of Cp*$_3$Ta$_3$(S)$_3$(S$_3$BH) (**5**). Selected bond distances (Å) and angles (deg): Ta1−Ta2, 3.104(3); Ta1−Ta3, 3.095(3); Ta2−Ta3, 3.096(3); Ta1-S1 2.36(1); Ta1−S2 2.56(1); Ta1−S3, 2.38(1); Ta1−S4 2.52(1); Ta2−S3, 2.35(1); Ta2−S4, 2.52(1); Ta2−S5, 2.37(1); Ta2−S6, 2.54(1); Ta3−S1, 2.36(1); Ta3−S2, 2.54(1); Ta3−S5, 2.35(1); Ta3−S6, 2.54(1); S2−B, 2.07(7); S4−B, 1.92(6); S6−B, 2.07(6); Ta1−Ta2−Ta3, 59.90(6); Ta1−Ta3−Ta2, 60.17(6); Ta2−Ta1−Ta3, 59.93(6).

A more intriguing reaction is that of **1** with NaBH$_4$, which proceeded slowly in THF at room temperature to give Cp*$_3$Ta$_3$(S)$_3$(S$_3$BH) (**5**). This trinuclear cluster was obtained in 62% yield in the form of air-stable green crystals.[15] The ^{1}H NMR signal of the Cp* ligand appears as a singlet; detection of the signal of the proton bound to B has not been successful. However, the IR spectrum shows the ν_{BH} stretch at 2405 cm^{-1}, which moves to a lower frequency (1904 cm^{-1}) upon deuteration.[16] The ^{11}B NMR spectrum exhibits a relatively sharp resonance at δ −21.3 ($\Delta H_{1/2}$ = 54 Hz), which is characteristic of tetrahedral coordination.[17] The FD mass spectrum, showing the molecular ion peak (M$^+$)

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(9) (a) Curnow, O. J.; Curtis, M. D.; Rheingold, A.; Haggerty, B. S. *Inorg. Chem.* **1991**, *30*, 4043−4047. (b) Koo, S.-M.; Bergero, R.; Salifoglou, A.; Coucouvanis, D. *Inorg. Chem.* **1990**, *29*, 4844−4846. (c) Tatsumi, K.; Matsubara, I.; Inoue, Y.; Nakamura, A.; Miki, K.; Kasai, N. *J. Am. Chem. Soc.* **1989**, *111*, 7766−7777. (d) Martin, J. L.; Takats, J. *Inorg. Chem.* **1975**, *14*, 1358−1364 and references therein.

(10) **Preparation of 2**: **Method A.** Addition of a THF (20 mL) solution of Cp*TaCl$_4$ (1.83 g, 4.00 mmol) to LiSCPh$_3$ (12.0 mmol) in THF (30 mL) at 0 °C immediately gave a red, homogeneous solution. After the mixture was stirred for 2 h at room temperature, the solvent was removed *in vacuo* and the residue was extracted with benzene (80 mL). The benzene was pumped off, leaving a yellow, sticky material which was washed with Et$_2$O. Recrystallization from DME afforded **2** as yellow crystals (0.90 g, 25%). **Method B.** A THF (20 mL) solution of **1** (0.32 g, 0.49 mmol) was added at 0 °C to LiSCPh$_3$ (0.50 mmol). Workup similar to that in method A above yielded **2** (0.17 g, 39%).

(11) **Reaction of 1 with LiSCMe$_3$.** At room temperature, a THF (15 mL) solution of LiSCMe$_3$ (1.69 mmol) was added to **2** (1.10 g, 1.67 mmol). After the mixture was stirred at room temperature for 24 h, the solvent was pumped off, and the yellow residue was extracted with 30 mL of hexane. Concentrating and cooling the extract to −50 °C yielded **3** as yellow crystals (0.33 g, 28%).

(12) **Reaction of 1 with Li$_2$S.** A THF (20 mL) solution of **1** (0.52 g, 7.9 mmol) was added to a suspension of Li$_2$S (0.22 g, 74.8 mmol) in THF, and the mixture was stirred at room temperature for 17 h. After removal of the solvent, the residue was extracted with 40 mL of benzene. The solution was evaporated to dryness, and recrystallization of the resulting solid from THF/hexane afforded **4** as light yellow crystals (0.25 g, 56%).

(13) Tatsumi, K.; Inoue, Y.; Nakamura, A.; Cramer, R. E.; VanDorne, W.; Gilje, J. W. *J. Am. Chem. Soc.* **1989**, *111*, 782−783.

(14) 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.

(15) **Reaction of 1 with NaBH$_4$.** Complex **1** (100 mg, 0.15 mmol) was treated with NaBH$_4$ (13 mg, 0.34 mmol) in THF (10 mL). The mixture was stirred at room temperature for 12 h, during which time the solution gradually changed from yellow to brown. The mixture was centrifuged to remove insoluble solid, followed by concentration until green microcrystals appeared. Standing for 2 days at −20 °C gave 36 mg of **5** as green crystals in 62% yield. Recrystallization from THF afforded green platelike crystals of **5** (recovery 70%).

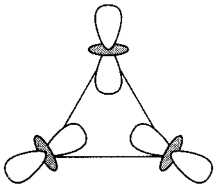
(16) The deuterated complex Cp*$_3$Ta$_3$(S)$_3$(S$_3$BD) was prepared from the reaction of **1** with NaBD$_4$.

(17) Krebs, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 113−134.

at *m*/*z* 1152, is also consistent with the indicated composition.

The molecular structure of **5** was determined by the X-ray analysis (Figure 2).[18] Complex **5** contains a triangular Ta_3 frame, in which six monosulfides bridge the Ta atoms above and below the edges. A BH group caps one S_3 triangular face, forming the novel trithioborato ligand S_3BH^-. We were unable to locate the hydrogen position of the ligand in our final Fourier map. A complex which resembles **5** is $(C_5Me_4Et)_3Nb_3(S)_3(S_3BSH)$, prepared by reaction of $(C_5Me_4Et)_2Nb_2(B_2H_6)_2$ with sulfur, in which the B−H bond in **5** is replaced by the B−SH bond.[19] The average Ta−S distance of 2.54 Å in the S_3BH ligand is significantly longer than that of the other Ta−S bonds (average 2.36 Å).

Chart 1



$1a_1$ orbital

The tantalum atom in **1** is partially reduced during the reaction with $NaBH_4$, resulting in the formal Ta(IV)−Ta(IV)−Ta(V) oxidation state of **5**. The d^2 $Cp^*{}_3Ta_3(S)_6{}^{2-}$ core is also present in the aforementioned cluster complex $Cp^*{}_3Ta_3(S)_6Li_2(THF)_2$, and it is isoelectronic with $(C_5Me_4Et)_3Nb_3(S)_3(S_3BSH)$. On the other hand, the d^4 $Cp^*{}_3Re_3O_6{}^{2+}$ cluster carries two more d electrons, although its core geometry is similar to that of **5**.[20] Two d electrons of the Ta_3 triangle reside in the $1a_1$ bonding cluster orbital and are delocalized over the three Ta atoms (Chart 1). The relatively short Ta-Ta distance of 3.098 Å agrees with this bonding scheme.[21]

Supporting Information Available: Tables giving crystal data, atomic coordinates, thermal parameters, and bond distances and angles for **1** and **5** and spectroscopic data for **1**, **2**, **3**, and **5** (24 pages). Ordering information is given on any current masthead page.

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[18] Crystallographic data for **5**: $C_{30}H_{46}S_6Ta_3B{\cdot}2C_4H_8O$, fw 1296.92, orthorhombic, space group *Pbca*, with $a = 33.51(2)$ Å, $b = 16.54(1)$ Å, $c = 16.108(8)$ Å, $V = 8929$ Å^3, $D_{calcd} = 1.929$ g cm^{-3} for $Z = 8$, μ(Mo Kα) = 75.50 cm^{-1}, $F(000) = 5008$. Intensity data were collected at room temperature on a Rigaku AFC5R diffractometer using the ω scan method ($2\theta < 50.1°$), and the data were processed using the TEXSAN package of programs. The structure was solved by direct methods in conjunction with standard difference Fourier techniques. The Ta and S atoms were refined anisotropically, while the other atoms were refined isotropically. All H atoms (except for the B−H hydrogen, which was not located) were introduced on calculated positions. The final cycle of full-matrix least-squares refinement was based on 2202 observed reflections ($I > 3.00\sigma(I)$) and 246 variable parameters and converted with unweighted and weighted agreement factors of $R = 0.069$ and $R_w = 0.073$ (GOF = 1.88).

[19] Brunner, H.; Gehart, G.; Nuber, B.; Wachter, J.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1021−1022.

[20] (a) Hofmann, P.; Rösch, N.; Schmidt, H. R. *Inorg. Chem.* **1986**, *25*, 4470−4478. (b) Hofmann, P.; Rösch, N. *J. Chem. Soc., Chem. Commun.* **1986**, 843−844.

[21] Kwon, D.; Real, J.; Curtis, M. D.; Rheingold, A. L.; Haggerty, B. S. *Inorg. Chem.* **1992**, *31*, 3489−3490.