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C−S Bond Cleavage Routes to the Titanium−Sulfide Complexes $(CpTi)_6(\mu_3\text{-}S)_4(\mu_3\text{-}O)_4$ and $(CpTi)_4(\mu_3\text{-}S)_3(\mu_2\text{-}S)(\mu_2\text{-}SEt)_2$ ($Cp = \eta\text{-}C_5H_5$)

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Introduction

Much of the interest in organometallic early metal−sulfide complexes arises from the variety of structural motifs accessible by simply varying the synthetic method and conditions. In the case of Ti−sulfide complexes, the principal synthetic routes employed to obtain such compounds involve reactions of low-valent Ti species with H_2S,[1] reduction of Ti−sulfhydryl complexes,[2] or reactions of titanium halides with $S(SiMe_3)_2$.[3−6] While studies of metal-mediated C−S bond cleavage reactions have been prompted by interests in desulfurization chemistry,[7] this approach has not been employed to access Ti−sulfide aggregates. In this report, we describe the isolation and structural characterization of two new CpTi−sulfide aggregates obtained via thermolysis of C−S bonds in $CpTiMeCl_2$, thiol, and base mixtures.

Experimental Section

General Information. All preparations were done under an atmosphere of dry, O_2-free N_2 employing either Schlenk-line techniques or a Vacuum Atmospheres inert-atmosphere glovebox. Solvents were of reagent grade and were distilled from the appropriate drying agents under N_2 and degassed by the freeze−thaw method at least three times prior to use. All organic reagents were purified by conventional methods. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AC-300 operating at 300 and 75 MHz, respectively. Trace amounts of protonated solvents were used as references, and chemical shifts are reported relative to $SiMe_4$. Combustion analyses were performed by Galbraith Laboratories Inc., Knoxville, TN, or Schwarzkopf Laboratories, Woodside, NY.

Synthesis of $(CpTi)_6(\mu_3\text{-}S)_4(\mu_3\text{-}O)_4$ (1). To a suspension of $CpTiMeCl_2$ (91 mg, 0.46 mmol) in pentane (2 mL) were added benzyl mercaptan (53.8 μL, 0.46 mmol) and LiOH (11 mg, 0.46 mmol). The reaction mixture was stirred for 1 h, and filtered, and the solution was concentrated. After the concentrate was allowed to stand for several days, dark red-black crystals of **1** were obtained in 5% yield.

Synthesis of $(CpTi)_4(\mu_3\text{-}S)_3(\mu_2\text{-}S)(\mu_2\text{-}SEt)_2$ (2). To a suspension of $CpTiMeCl_2$ (91 mg, 0.46 mmol) in pentane (2 mL) were added ethanethiol (34.2 μL, 0.46 mmol) and NEt_3 (64.1 μL, 0.46 mmol). The reaction mixture was stirred overnight and filtered, and the solvent was removed in vacuo. The residue was extracted with benzene, and the extract was allowed to stand at 25 °C. After 3 days, crystals of **2** were obtained in 5% yield. EPR (C_6H_6, 25 °C): $g = 1.998$.

X-ray Data Collection and Reduction. X-ray-quality crystals of **1** and **2** were obtained directly from the preparation as described above. The crystals were manipulated and mounted in capillaries in a glovebox, thus maintaining a dry, O_2-free environment for each crystal. Diffraction experiments were performed on a Rigaku AFC6 diffractometer using graphite-monochromatized Mo Kα radiation. The initial orientation matrix was obtained from 20 machine-centered reflections selected by an automated peak-search routine. These data were used to determine the crystal systems. Automated Laue system check routines around each axis were consistent with the crystal system. Ultimately, 25 reflections ($20° < 2\theta < 25°$) were used to obtain the final lattice parameters and the orientation matrices. Crystal data are summarized in Table 1. The observed extinctions were consistent with the space groups in each case. The data sets were collected in three shells ($4.5° < 2\theta < 45−50.0°$), and three standard reflections were recorded every 197 reflections. Fixed scan rates were employed. Up to four repetitive scans of each reflection at the respective scan rates were averaged to ensure meaningful statistics. The number of scans of each reflection was determined by the intensity. The intensities of the standards showed no statistically significant change over the duration of the data collections. The data were processed using the TEXSAN crystal solution package operating on a SGI Challenger mainframe with remote X-terminals. The reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinements.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[8] The Ti atom positions were determined using direct methods employing either the SHELX-86 or Mithril direct-methods routines. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F, minimizing the function $w(|F_o| - |F_c|)^2$ where the weight w is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes. In the final cycles of each refinement, the number of non-hydrogen atoms assigned anisotropic temperature factors was determined so as to maintain a reasonable data:variable ratio. The remaining atoms were assigned isotropic temperature factors. In the case of **1**, a 75:25 disorder of the S and O atoms was modeled; thus O1, S2, S3, O4 were refined with site occupancy factors of 0.75 while the corresponding atoms S1, O2, O3, S4 were refined with occupancies of 0.25. Empirical absorption corrections were applied to the data sets based either on ψ-scan data or on a DIFABS calculation and employing the software resident in the TEXSAN package. Hydrogen atom positions were calculated and allowed to ride on the carbons to which they are bonded, assuming a C−H bond length of 0.95 Å. Hydrogen atom temperature factors were fixed at 1.10 times the isotropic temperature factors of the carbon atoms to which they are bonded. The hydrogen atom contributions were calculated but not refined. The final values of R, R_w, and the goodness of fit in the final cycles of the refinements are given in Table 1. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitudes of the residual electron densities in each case were of no chemical significance.

Results and Discussion

The potential of C−S bond cleavage reactions as a viable route to Ti−S aggregates was suggested by the observation of the cluster ion $(CpTi)_5(\mu_3\text{-}S)_6$ in the mass spectra of complexes of the form $CpTi(SR)_3$.[9] In a preparative reaction, $CpTiCl_3$ was combined with 3 equiv of benzyl mercaptan and triethylamine in benzene. Thermolysis of this reaction mixture at 80 °C for 12 h resulted in the formation of a mixture of products. One of the species crystallized from solution and was identified as

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[1] Bottomley, F.; Egharevba, G. O.; White, P. S. *J. Am. Chem. Soc.* **1985**, *107*, 4354.

[2] Bottomley, F.; Day, R. W. *Can. J. Chem.* **1992**, *70*, 1250.

[3] Darkwa, J.; Lockmeyer, J. R.; Boyd, P. D. W.; Rauchfuss, T. B.; Rheingold, A. L. *J. Am. Chem. Soc.* **1988**, *110*, 141.

[4] Lundmark, P. J.; Kubas G. J.; Scott, B. L. *Organometallics* **1996**, *15*, 3631.

[5] Maue, P. G.; Fenske, D. *Z. Naturforsch.* **1988**, *43B*, 1213.

[6] Muller, U.; Krug, V. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 293.

[7] (a) Massoth, F. E. *Adv. Catal.* **1978**, *27*, 265. (b) Nikshioka, M. *Energy Fuels* **1988**, *2*, 214. (c) Dance, I. G. *Polyhedron* **1986**, *5*, 1037. (d) Pasquali, M.; Leoni, P.; Floriani, C.; Chiesi-Vzilla, A.; Guastini, C. *Inorg. Chem.* **1983**, *22*, 841. (e) Boorman, P. M.; Gao, X.; Parvez, M. *J. Chem. Soc., Dalton Trans.* **1992**, 25.

[8] (a) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A*: *Cryst. Phys., Theor. Gen. Crystallogr.* **1968**, *A24*, 324. (b) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A*: *Cryst. Phys., Theor. Gen. Crystallogr.* **1968**, *A24*, 390. (c) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974.

[9] Klapotke, T.; Kopf, H.; Gowik, P. *J. Chem. Soc., Dalton Trans.* **1988**, 1529.

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Table 1. Crystallographic Data[a]

	1	2		1	2
empirical formula	$C_{24}H_{30}O_4S_4Ti_6$	$C_{24}H_{30}S_6Ti_4$	T, °C	24	24
fw	870.20	702.46	μ, cm^{-1}	13.25	14.97
a, Å	10.641(6)	16.07(1)	no. of data collected	3907	2885
b, Å	9.973(3)	16.412(10)	no. of data with $F_o^2 > 3\sigma(F_o^2)$	1103	812
c, Å	19.719(4)	10.884(8)	d(calc), g cm^{-3}	1.39	1.62
β, deg	95.97(3)		R, %	8.3	7.8
V, Å^3	2081(1)	2870(6)	R_w, %	8.3	7.2
space group	$P2_1/n$	$Pna2_1$	goodness of fit	2.65	1.85
Z	2	4			

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum(|F_o| - |F_c|)^2|/\sum|F_o|^2]^{0.5}$, GOF $= \sum((|F_o| - |F_c|)/\sigma)/(n - m)$.

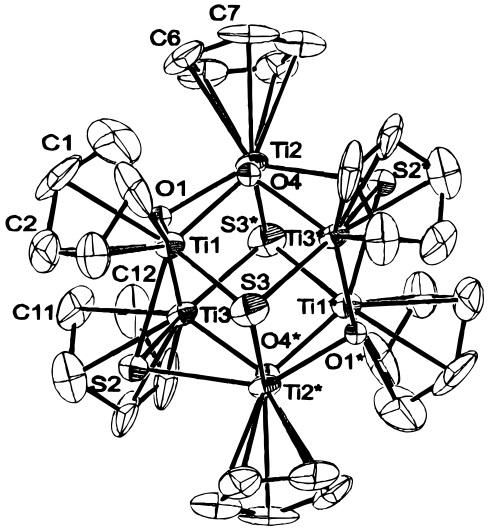

Figure 1. ORTEP drawing of **1**. 20% thermal ellipsoids are shown. Only the S and O atoms that were refined with site occupancy factors of 0.75 are shown for clarity. Distance and angles: Ti1−S2 2.427(9), Ti1−S3 2.34(1), Ti1−O1 2.00(2), Ti1−O4 1.94(3), Ti2−S2 2.443(9), Ti2−S3 2.36(1), Ti2−O1 1.94(2), Ti2−O4 1.96(3), Ti3−S1 2.28(2), Ti3−S3 2.37(1), Ti3−O1 2.01(2), Ti3−O4 1.97(3) Å; S1−Ti1−S4 94(1), S2−Ti1−S3 84.2(3), S2−Ti1−O1 84.2(5), S2−Ti1−O4 140.2(8), S3−Ti1−O1 138.6(6), S3−Ti1−O4 84.7(8), S3−Ti1−C1 134(1), O1−Ti1−O4 79.2(9), S2−Ti2−S3 83.5(3), S2−Ti2−O1 140.4(5), S2−Ti2−O4 84.6(8), S3−Ti2−O1 83.9(5), S3−Ti2−O4 138.1(8), O1−Ti2−O4 80.1(9), S2−Ti3−S3 151.9(4), S2−Ti3−O1 83.8(5), S2−Ti3−O4 84.7(8), S3−Ti3−O1 82.2(5), S3−Ti3−O4 83.4(8), O1−Ti3−O4 124.6(9), Ti1−S2−Ti2 80.3(3), Ti1−S2−Ti3 79.3(3), Ti2−S2−Ti3 78.0(3), Ti1−S3−Ti2 83.9(4), Ti1−S3−Ti3 80.6(3), Ti2−S3−Ti3 81.3(3), Ti1−O1−Ti2 98.4(8), Ti1−O1−Ti3 101.3(7), Ti2−O1−Ti3 102.3(8), Ti1−O4−Ti2 100(1), Ti1−O4−Ti3 102(1), Ti2−O4−Ti3 102(1)°.

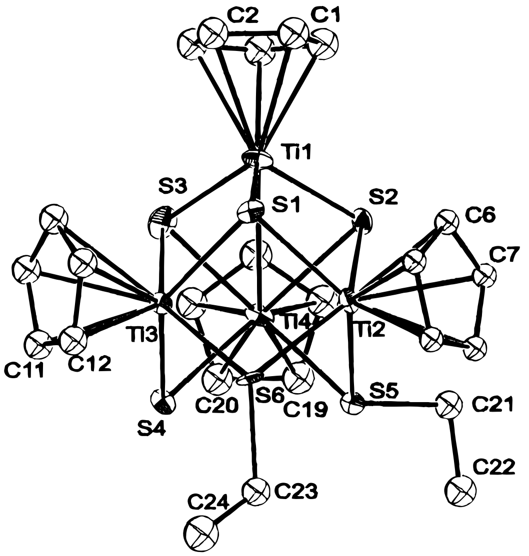

Figure 2. ORTEP drawing of **2**. 20% thermal ellipsoids are shown. Distance and angles: Ti1−S1 2.36(1), Ti1−S2 2.23(1), Ti1−S3 2.27(2), Ti2−S1 2.42(1), Ti2−S2 2.52(2), Ti2−S5 2.43(1), Ti2−S6 2.49(2), Ti3−S1 2.51(2), Ti3−S3 2.53(2), Ti3−S4 2.38(1), Ti3−S6 2.51(1), Ti4−S2 2.52(2), Ti4−S3 2.41(1), Ti4−S4 2.47(2), Ti4−S5 2.51(1) Å; S1−Ti1−S2 100.2(4), S1−Ti1−S3 102.4(5), S1−Ti2−S2 91.1(5), S1−Ti2−S5 135.6(6), S1−Ti2−S6 73.0(5), S2−Ti2−S5 79.9(5), S2−Ti2−S6 139.4(5), S5−Ti2−S6 86.1(5), S1−Ti3−S3 91.5(6), S1−Ti3−S4 138.4(5), S1−Ti3−S6 71.3(4), S3−Ti3−S4 79.3(5), S3−Ti3−S6 140.3(6), S4−Ti3−S6 90.2(4), S2−Ti4−S3 90.0(6), S2−Ti4−S4 137.5(5), S2−Ti4−S5 78.2(5), S3−Ti4−S4 80.0(5), S3−Ti4−S5 137.3(5), Ti1−S1−Ti2 83.4(4), Ti1−S1−Ti3 81.8(4), Ti2−S1−Ti3 83.3(5), Ti1−S2−Ti2 83.7(5), Ti1−S2−Ti4 82.2(5), Ti2−S2−Ti4 81.7(5), Ti1−S3−Ti3 82.9(5), Ti1−S3−Ti4 83.9(5), Ti3−S3−Ti4 −79.9(5), Ti3−S4−Ti4 81.8(5), Ti2−S5−Ti4 83.8(5), Ti2−S6−Ti3 81.8(5)°.

the known species $(CpTi)_5(\mu_3\text{-}S)_6$[1] by comparison of the unit cell parameters obtained X-ray diffraction methods to those reported by Bottomley and co-workers. While the other products were not identified, the success of this C−S bond cleavage approach in the formation of a known Ti−S cluster prompted the study of related mixtures in the hope of isolating new aggregates. To that end, the compound $CpTiMeCl_2$ was generated via the reaction of $CpTiCl_3$ and $ZnMe_2$ in hexane. Benzyl mercaptan and lithium hydroxide were added, and the mixture was heated to 80 °C for 12 h. Fractional crystallization afforded crystals of a new species, **1**, in low yield. Unfortunately, this yield could not be improved because the oxophilic nature of **1** precludes use of chromatographic methods for compound purification. A crystallographic study of this compound confirmed the formulation of **1** as $(CpTi)_6(\mu_3\text{-}S)_4(\mu_3\text{-}O)_4$ (Figure 1). In this cluster, six CpTi fragments form a pseudo-octahedral array in which four oxygen and four sulfur atoms cap each of the triangulated faces of the octahedron. The cluster is 2-fold symmetric, such that each of the chalcogenide atoms are triply bridging. Each Ti atom is bonded to two sulfur atoms, with two oxygen atoms completing the coordination geometry about the Ti centers. The S and O atoms are partially disordered (75:25). Nonetheless, structurally, the Ti−O distances in **1** are comparable to those seen in $(CpTi)_6(\mu_3\text{-}O)_8$[10] while the Ti−S distances are similar to those seen in $(CpTi)_5(\mu\text{-}S)_6$.[1] The pseudo-square-based-pyramidal coordination spheres of the Ti centers in **1** are somewhat flattened compared to those in $(CpTi)_6(\mu_3\text{-}O)_8$,[10] $(CpTi)_8(\mu_3\text{-}O)_{12}$,[11] and $(CpTi)_5(\mu_3\text{-}S)_6$,[1] as evidenced by the S−Ti−O angles of ca. 140° in **1**. It is presumably the presence of π-bonding to oxygen that elicits this distortion. This flattening of the Ti coordination spheres (Figure 3a) accommodates the inclusion of six metal centers in **1** whereas only five metal centers aggregate in $(CpTi)_5(\mu_3\text{-}S)_6$[1] in the absence of oxygen atom bridges.

In an analogous reaction, ethanethiol and triethylamine were added to a solution of $CpTiMeCl_2$ in hexane. Following

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(10) Heshmatpour, F.; Wocadlo, S.; Massa, W.; Dehnicke, K.; Bottomley, F.; Day, R.W. *Z. Naturforsch.* **1994**, *49B*, 827.

(11) Huffman, J. C.; Stone, J. G.; Krusell, W. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1977**, *99*, 5829.

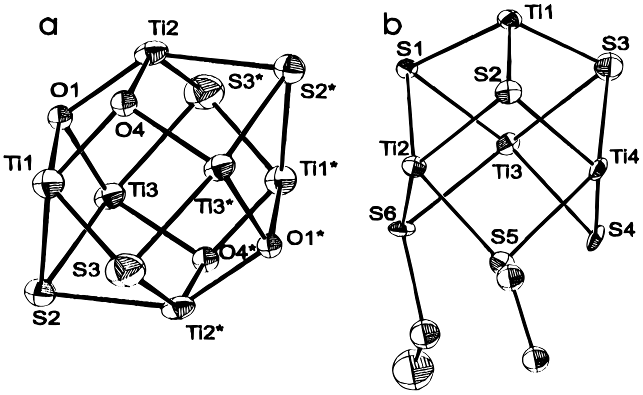

Figure 3. ORTEP drawing of the cores of (a) **1** and (b) **2**.

filtration to remove triethylammonium chloride, the solvent was removed, the residue extracted into benzene, and the extract heated to 80 °C for 12 h. The solvent was subsequently removed in vacuo and the residue extracted into hexane. NMR spectroscopy revealed a complex mixture of products. The oxophilic nature of the Ti complexes precluded a chromatographic separation; however, when the mixture was allowed to stand for several days in an inert atmosphere, crystals of one of the new compounds, **2**, were obtained in low yield (~5%). Similar to those for **1**, chromatographic separations of this cluster were precluded by its oxophilicity. This compound was paramagnetic, exhibiting an EPR signal centered at a g value of 1.998. Hyperfine coupling to titanium was also evident. An X-ray crystallographic study of **2** established the molecular structure as $(CpTi)_4(\mu_3\text{-S})_3(\mu_2\text{-S})(\mu_2\text{-SEt})_2$ (Figure 2). The metal atom core of this species is a pseudotetrahedral arrangement of four CpTi fragments. Three S atoms are triply bridging three of the triangular faces of the metal atom tetrahedron. On the remaining triangular face, one sulfur atom and two ethanethiolate ligands are doubly bridging along each of the edges. Thus, the coordination geometry of the three titanium atoms (Ti2, Ti3, Ti4) in the basal plane is best described as pseudo square-based pyramidal whereas the titanium atom (Ti1) in the axial position is appropriately likened to a "three-legged piano stool" (Figure 3b). The Ti1−S distances average 2.29(2) Å, slightly shorter than those of the remaining Ti−S bonds, consistent with the greater Lewis acidity of the Ti1 center. The remaining Ti−S distances range from 2.38(2) to 2.52(2) Å. These distances fall within the range of Ti−S distances seen in $(CpTi(\mu\text{-S}))_5(\mu\text{-S}_2)(\mu\text{-O})$,[2] $(MeCpTi(\mu\text{-S}))_4$,[3] and $(CpTi)_5(\mu\text{-S})_6$[1] and are significantly longer than the terminal Ti−S distances seen in $[CpTiS(\mu\text{-S})]_2^{2-}$ and $[TiSCl_4]^{2-}$.[4,6] Unlike those in the diamagnetic cubane cluster $(MeCpTi(\mu\text{-S}))_4$,[3] the Ti−Ti distances in **2** do not reflect significant metal−metal interactions, consistent with the observed paramagnetism.

Related S−C bond scission/reduction reactions mediated by early metals have been described by Coucouvanis and coworkers. In those cases, the Zr aggregates $Zr_3S_3(S\text{-}t\text{-Bu})_2(BH_4)_4$, $Zr_6S_6(S\text{-}t\text{-Bu})_2(BH_4)_8$, and $Zr_3S(S\text{-}t\text{-Bu})_{10}$ were obtained.[12] The present work demonstrates that thermolysis of C−S bonds of phenylmethane- and ethanethiol can provide the novel Ti−sulfide aggregates **1** and **2**. Current studies are targeting the utilization of such C−S cleavage in desulfurization chemistry as well as the interception of reactive aggregate precursors.

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Supporting Information Available: Tables of crystallographic data, positional parameters, thermal parameters, and bond distances and angles (13 pages). Ordering information is given on any current masthead page.

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(12) (a) Coucouvanis, D.; Hadjikyriacou, A.; Kanatzdis, M. G. *J. Chem. Soc., Chem. Commun.* **1985**, 1224. (b) Coucouvanis, D.; Lester, R. K.; Kanatzdis, M. G.; Kessissoglou, D. P. *J. Am. Chem. Soc.* **1985**, *107*, 8279.