

ORGANOMETALLICS

Volume 15, Number 17, August 20, 1996

© Copyright 1996
American Chemical Society

Communications

Formation of an Anionic Titanium(IV) Sulfido Dimer, $\{Na_2[CpTi(\mu-S)(S)]_2 \cdot 4THF\}_2$, by Elimination of CpH and H_2 from $Cp_2Ti(SH)_2$ upon Deprotonation with NaH

Penelope J. Lundmark, Gregory J. Kubas,* and Brian L. Scott

Chemical Science and Technology Division, Los Alamos National Laboratory,
MS C346, Los Alamos, New Mexico 87545

Received May 13, 1996[⊗]

Summary: A deprotonation reaction of $Cp_2Ti(SH)_2$ with NaH in THF yields $\{Na_2[CpTi(\mu-S)(S)]_2 \cdot 4THF\}_2$, generated by unexpected elimination of CpH. This anionic dimer is unique in that it is the first organometallic titanium species containing terminal sulfido ligands. The latter are stabilized by interactions with THF-solvated sodium cations, thus imposing a *syn* Ti=S configuration.

Organometallic hydrosulfido complexes are potentially valuable for study to develop an understanding of metal sulfide based catalysis, especially hydrogenation processes such as hydrodesulfurization. These species are still quite rare, however. One of the older examples, $Cp_2Ti(SH)_2$, was first synthesized by Köpf and Schmidt in 1965.¹ The preparation was improved in 1980 by McCall and Shaver,² but the reactivity of $Cp_2Ti(SH)_2$ in the literature is limited.³ Important questions are whether deprotonated anionic forms of hydrosulfide complexes are stable and whether they show higher reactivity than neutral sulfides with elec-

trophiles such as SO_2 .⁴ Previous work showed that SO_2 disproportionates to sulfur and SO_3 and also can undergo catalytic hydrogenation on certain sulfide-bridged Cr and Mo complexes,^{4b-e,5,6} and earlier metal sulfides may give similar or increased reactivity. In this paper, we report deprotonation of $Cp_2Ti(SH)_2$ by sodium hydride to give an anionic titanium sulfido species, $Na_2[CpTi(\mu-S)(S)]_2 \cdot 4THF$. Anionic titanium sulfur-containing complexes themselves are rare,⁷ and to our knowledge, this dimer is the first reported organometallic titanium species containing a terminal sulfido ligand.⁸ The elimination of CpH from a *bis*-Cp complex to form a *mono*-Cp-coordinated Ti is also noteworthy in that $[Cp_2Ti(S)(SH)]^-$ appears to be unstable, while the related $Cp^*_2Ti(O)L$ and $Cp^*_2Zr(S)L$ systems are isolable.⁹

(4) (a) Kubas, G. J.; Wasserman, H. J.; Ryan, R. R. *Organometallics* **1985**, *4*, 419, 2012. (b) Kubas, G. J.; Ryan, R. R. *Polyhedron* **1986**, *5*, 473. (c) Kubas, G. J.; Ryan, R. R.; Kubat-Martin, K. A. *J. Am. Chem. Soc.* **1989**, *111*, 7823. (d) Toupadakis, A.; Kubas, G. J.; Burns, C. J. *Inorg. Chem.* **1992**, *31*, 3810. (e) Kim, C. G.; Coucouvanis, D. *Inorg. Chem.* **1993**, *32*, 1881, 2232.

(5) Kubas, G. J.; Ryan, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 6138.

(6) Kubas, G. J. *Acc. Chem. Res.* **1994**, *27*, 183.

(7) (a) For Ti_2TiS_4 see: Maué, G. P.; Fenske, D. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1985**, *40B*, 229. (b) For $[Ph_4P][CpTi(1,2-S_2C_6H_4)_2]$ see: Köpf, H.; Lange, K.; Pickardt, J. *J. Organomet. Chem.* **1991**, *420*, 345. (c) For $Na[CpTi(SCH_2CH_2CH_2S)(SC_6H_5)_2]$ see: Nadasdi, T. T.; Huang, Y.; Stephan, D. W. *Inorg. Chem.* **1993**, *32*, 347. (d) For $(PPh_4)[TiSCl_4]$ and $(PPh_4)[Ti_3O(S_2)_3Cl_6]$, see: Müller, U.; Krug, V. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 293.

(8) The only other titanium complexes containing terminal sulfido ligands are $(PPh_4)[TiSCl_4]^{7d}$ and $[tmtaa][Ti=S]$: Goedken, V. L.; Ladd, J. A. *J. Chem. Soc., Chem. Commun.* **1982**, 142.

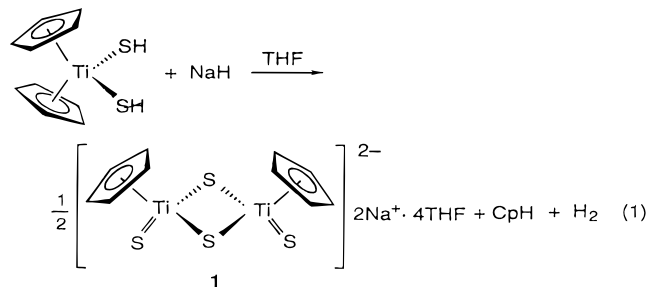
[⊗] Abstract published in *Advance ACS Abstracts*, July 15, 1996.

(1) Köpf, H.; Schmidt, M. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 953.

(2) (a) McCall, J. M.; Shaver, A. *J. Organomet. Chem.* **1980**, *193*, C37. (b) Shaver, A.; Marmolejo, G.; McCall, J. M. *Inorg. Synth.* **1990**, *29*, 65.

(3) (a) Ruffing, C. J.; Rauchfuss, T. B. *Organometallics* **1985**, *4*, 524. (b) Shaver, A.; McCall, J. M. *Organometallics* **1984**, *3*, 1823. (c) Bollinger, C. M.; Hoots, J. E.; Rauchfuss, T. B. *Organometallics* **1982**, *1*, 223. (d) Bottomley, F.; Day, R. W. *Can. J. Chem.* **1992**, *70*, 1250.

Titanocene bis(hydrosulfide) reacts with 1 equiv of NaH to produce the anionic titanium sulfido species $\text{Na}_2[\text{Cp}_2\text{Ti}(\mu\text{-S})_2] \cdot 4\text{THF}$ (**1**), according to eq 1. This



reaction occurs at room temperature with the solution changing color from red to green in 5 min.¹⁰ The color change is accompanied by the evolution of a gas. This reaction proceeds very slowly at low temperature. The green complex is crystallized by THF/hexanes diffusion in 63% yield,¹⁰ and an X-ray structure was obtained (see below). The THF molecules in the crystal lattice are extremely labile and can be removed in vacuo. The complex is thus best stored cold in the presence of THF vapor. **1** is also very air and moisture sensitive, and elemental analysis was not possible. **1** is soluble only in THF and will convert to a yellow-brown solid in other organic solvents such as hexanes, toluene, or Et₂O. The infrared spectra of **1** in KBr indicate the presence of both terminal (466 cm⁻¹) and bridging sulfide (394, 386 cm⁻¹) ligands.^{10,11}

When reaction 1 is performed on an NMR-tube scale in THF-*d*₈, a color change occurs within 2 min. During this time, the evolution of a gas is evident. A ¹H NMR spectrum of the resulting solution indicates the formation of H₂ (δ 4.54 ppm), CpH (δ 6.50 (m), 6.41 (m), 2.94 (s) ppm), and the product complex (δ 6.10 ppm). Over time a signal at δ 5.73 ppm, attributed to a decomposition product, appears in the NMR spectra.

In order to confirm that the CpH identified above by NMR is indeed a direct product of eq 1, a sample of the reaction mixture was filtered over alumina and the clear filtrate was collected. This filtrate was analyzed by GC/MS, and only CpH, [CpH]₂, and solvents were observed in the spectra. As a control experiment, isolated crystals of **1** were dissolved in THF and then filtered over alumina and analyzed by GC/MS. The spectrum showed no CpH, confirming that the CpH seen in the

reaction mixture is not a result of decomposition of the final product, e.g. on the alumina. We expected a 63% yield of CpH based on Ti, similar to the yield of **1**. Ferrocene was used as an internal standard to determine that the actual yield was 30%, probably as a result of side reactions involving the eliminated CpH.

The reaction could be quite complex mechanistically but most likely proceeds first by the deprotonation of one SH group of Cp₂Ti(SH)₂ by NaH to give H₂ and the 18e Na[Cp₂Ti(S)(SH)] species. This unobserved intermediate is presumably unstable and eliminates CpH, leaving an anionic "CpTiS₂" fragment which dimerizes. If the reaction is run with 2 equiv of NaH per Ti, the solution color becomes red-brown instead of green. Thus, stoichiometrically deprotonating both SH ligands with hydride apparently leads to a totally different product (as yet unidentified). This is a critical observation because most hydride reductions are carried out with excess reagent. Reaction of Cp₂Ti(SH)₂ with NaD in THF-*d*₈ as in eq 1 gave H₂ (δ 4.54 ppm), HD (δ 4.51 ppm (t, *J*_{HD} = 42 Hz)), CpH and CpD (δ 6.50 (m), 6.42 (m), 2.93 (t) ppm), a decomposition product (δ 5.73 ppm), and **1** (δ 6.10 ppm), as observed by ¹H NMR of the reaction mixture. The dissolved H₂ and HD were in a ratio of about 1:2, which along with the formation of both CpH and CpD suggests that some isotopic equilibration occurs during the course of the reaction. This equilibration might result from either secondary reactions (only HD and CpH would be expected according to the postulated mechanism) or a more complex pathway to **1**.

X-ray crystallographic analysis¹² of **1** shows that in the solid state this species exists as two dinuclear units stitched together by weak interactions of both terminal and bridging sulfide ligands with THF-solvated sodium cations (Figure 1). All Na-S distances (dotted lines) range from 2.825(1) Å in Na(2)-S(4a) to 2.981(2) Å in Na(1)-S(4). Each dimer contains two bridging sulfur atoms, and the dimensions of the nearly planar Ti₂(μ-S)₂ unit (Figure 2) are typical of those found in other μ-S titanium complexes (Ti-(μ-S) bond lengths range from 2.226 to 2.611 Å, and the Ti...Ti distances range from 3.140 to 3.597 Å).¹³ The distance between the Ti atoms is large (3.174(1) Å), indicating that no Ti-Ti bond is present, which would be consistent with the apparent d⁰ electronic configuration. This complex also contains two terminal sulfur atoms (Ti(1)-S(2) = 2.202

(9) (a) Howard, W. A.; Parkin, G. *J. Am. Chem. Soc.* **1994**, *116*, 606. (b) Howard, W. A.; Waters, M.; Parkin, G. *J. Am. Chem. Soc.* **1993**, *115*, 4917. (c) Polse, J. L.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 5393. (d) Smith, M. R.; Matsunaga, P. T.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 7049.

(10) In a He-filled glovebox, Cp₂Ti(SH)₂^{2b} (0.052 g, 21 mmol) and NaH (Aldrich, 0.005 g, 21 mmol) were mixed as solids. Dried THF (3 mL) was added to the solids. The resultant red-orange solution was stirred and periodically evacuated for 30 min since a small amount of gas, presumably H₂, was slowly evolved. The solution was then stirred at room temperature overnight, and the green solution was reduced in vacuo to a volume of ca. 1 mL. A THF/hexane diffusion was set up by placing the product solution in a small vial inside of a larger vial of hexanes. The THF in the inner vial diffused to the hexanes, leaving dark green crystals (45 mg) of **1** in a green-brown supernatant. IR (KBr): 1438, 1015, 801 (s), 466, 394, 386 cm⁻¹. ¹H NMR (THF-*d*₈): δ 6.10 (C₅H₅), 3.56, 1.76, 1.75, 1.74, 1.71 (C₄H₉O) ppm. The coordinated THF resonances are broad and overlap with the THF-*d*₈ resonances (δ 3.58, 1.73 ppm).

(11) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Wiley: New York, 1986, and references therein. ν(Ti=S) = 530 cm⁻¹ for (PPh₄)[TiSCl₄];^{7d} ν(Mo=S) = 479 cm⁻¹ for [Cp*Mo(S)(μ-S)]₂;^{14b} ν(Ti-(μ-S)) = 390, 370 cm⁻¹ for Cp₃Ti₂S₂Cl.^{13c}

(12) A dark green parallelepiped-shaped crystal (0.21 × 0.28 × 0.37 mm) was placed under a liquid N₂ stream on a Siemens P4/PC diffractometer at 173 K: Mo Kα radiation (λ = 0.710 73 Å); space group *P1*; *a* = 10.6300(10), *b* = 11.3700(10), *c* = 14.3960(10) Å; α = 83.960(6), β = 80.410(6), γ = 70.370(6)°; *V* = 1613.7(3) Å³ at 173 K; *D*_{calc} = 1.417 g/cm⁻³ for *Z* = 1; *R* = 3.15% for 4227 independent reflections with *I* ≥ 2σ(*I*) and 7.0 ≥ 2θ ≤ 45.0°; total number of data measured 5049; number of observed reflections 3599 (*F* > 4.0σ(*F*)). No absorption corrections were applied, due to the low absorption coefficient of this material. The structure was solved using Patterson techniques to reveal the Ti and S atom positions. The remaining atoms appeared in subsequent Fourier syntheses. All hydrogen atoms were fixed in positions corresponding to a C-H distance of 0.96 Å using the HFIX facility in SHELXTL PC. The final refinement included anisotropic thermal parameters on all non-hydrogen atoms. Hydrogen atoms had their isotropic temperature factors fixed at 0.08 Å².

(13) For structural data for complexes containing the Ti₂(μ-S)₂ unit, see refs 3d and 7d and: (a) Zank, G. A.; Jones, C. A.; Rauchfuss, T. B.; Rheingold, A. L. *Inorg. Chem.* **1986**, *25*, 1886. (b) Bottomley, F.; Egharevba, G. O.; White, P. S. *J. Am. Chem. Soc.* **1985**, *107*, 4353. (c) Darkwa, J.; Lockmeyer, J. R.; Boyd, P. D. W.; Rauchfuss, T. B.; Rheingold, A. L. *J. Am. Chem. Soc.* **1988**, *110*, 141. (d) Krug, V.; Koellner, G.; Müller, U. *Z. Naturforsch., B* **1988**, *43*, 1501. (e) Maue, G. P.; Fenske, D. *Z. Naturforsch., B* **1988**, *43*, 1213.

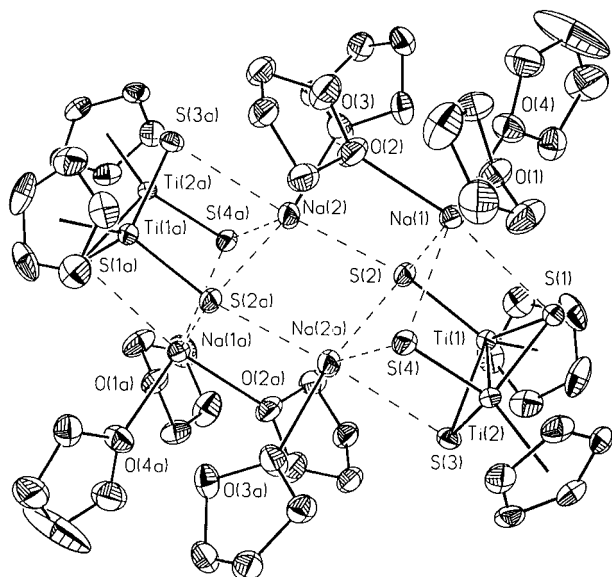


Figure 1. ORTEP diagram of $\{\text{Na}_2[\text{CpTi}(\mu\text{-S})(\text{S})]_2 \cdot 4\text{THF}\}_2$ (**1**). The inversion center makes the two dimers equivalent. Na(2) has one coordinated THF (Na(2)–O(3) = 2.322(3) Å), and Na(1) has three (Na–O = 2.352(3)–2.405(2) Å).

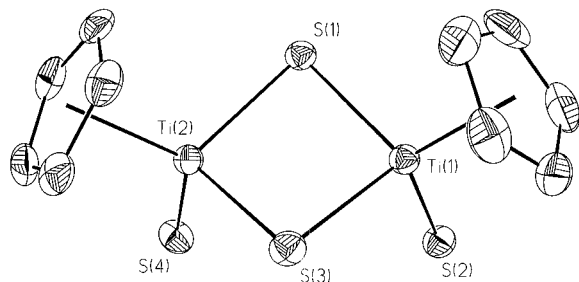


Figure 2. ORTEP diagram of the dinuclear center of **1**. Selected bond lengths (Å): Ti(1)–S(1), 2.335(1); Ti(1)–S(3), 2.343(1); Ti(2)–S(1), 2.348(1); Ti(2)–S(3), 2.360(1); Ti(1)–S(2), 2.202(1); Ti(2)–S(4), 2.187(1). Selected bond angles (deg): Ti(1)–S(1)–Ti(2), 85.3(1); Ti(1)–S(3)–Ti(2), 84.9(1); S(1)–Ti(2)–S(3), 92.4(1); S(1)–Ti(1)–S(3), 93.1(1).

Å and Ti(2)–S(4) = 2.187 Å). The terminal titanium–sulfur bonds have nearly double-bond character, since the Ti–S distances are only slightly longer than that for $\text{Ti}_2\text{TiCl}_4\text{S}$ (Ti=S = 2.111 Å).^{7d} The *syn* configuration of the terminal sulfido ligands may be stabilized by the sulfide– Na^+ interactions. Apparently the $\text{Na}^+(\text{THF})$ network also maintains the integrity of the complex in solution, because decomposition occurs in solvents other than THF. Each Ti(IV) atom of **1** is six-coordinate but is formally electronically unsaturated (14 electrons).

Related sulfido complexes include $[\text{CpM}(\mu\text{-S})(\text{S})]_2$ (M = Mo, W),¹⁴ $[\text{Cp}_2\text{Nb}(\mu\text{-S})]_2$,¹⁵ $[\text{Li}(\text{THF})]_2[\text{Cp}^*\text{TaS}_3]$ (which has S– Li^+ interactions),¹⁶ $\text{Li}_3[\text{VS}_4] \cdot 2\text{DMF}$,¹⁷ and $(\text{Cp}')_2\text{V}_2(\mu\text{-S})_2(\mu\text{-S}_2)$.¹⁸ The number of terminal metal–sulfido compounds in existence is limited because of the tendency of the sulfur ligands to bridge metal centers. As a result, the chemistry of the M=S bond has not been extensively developed.¹⁹ We intend to determine if the nucleophilic sulfides of **1** can be protonated, alkylated, or coordinated to other metal centers for heterometallic cluster building. Preliminary evidence for protonation with acetic acid and reaction with Cp_2ZrCl_2 has been obtained. As in our previous studies of SO_2 disproportionation and catalytic hydrogenation on similar sulfides of Cr and Mo,⁶ we will also determine the reactivity of **1** and its derivatives with SO_2 . Reaction²⁰ of SO_2 with $\text{Cp}_2\text{Ti}(\text{SH})_2$ led to formation of the well-known metalla-cyclosulfane Cp_2TiS_5 , but reaction with **1** in THF produced an intractable white precipitate, indicating that modifications of **1** will be necessary to obtain homogeneous reaction systems.

Acknowledgment. The research was funded by the U.S. Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences.

Supporting Information Available: Text giving the experimental procedure and tables of crystal data, atomic coordinates, and bond distances and angles for $\{\text{Na}_2[\text{CpTi}(\mu\text{-S})(\text{S})]_2 \cdot 4\text{THF}\}_2$ (12 pages). Ordering information is given on any current masthead page.

OM960358X

(14) (a) Danzer, W.; Fehlhammer, W. P.; Lui, A. T.; Thiel, G.; Beck, W. *Chem. Ber.* **1982**, *115*, 1682. (b) Brunner, H.; Meier, W.; Wachter, J.; Guggolz, E.; Zahn, T.; Zeigler, M. L. *Organometallics* **1982**, *1*, 1107. (c) Rakowski DuBois, M.; DuBois, D. L.; Vanderveer, M. C.; Haltiwanger, R. C. *Inorg. Chem.* **1981**, *20*, 3064.

(15) Skripkin, Y. V.; Eremenko, I. L.; Pasynskii, A. A.; Struchkov, Y. T.; Shklover, V. E. *J. Organomet. Chem.* **1984**, *267*, 285.

(16) (a) 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. (b) Tatsumi, K.; Inoue, Y.; Nakamura, A.; Cramer, R. E.; VanDoorne, W.; Gilje, J. W. *J. Am. Chem. Soc.* **1989**, *111*, 782.

(17) Zhang, Y.; Holm, R. H. *Inorg. Chem.* **1988**, *27*, 3875.

(18) (a) Bollinger, M. C.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1982**, *104*, 7313. (b) Bollinger, M. C.; Weatherill, T. D.; Rauchfuss, T. B.; Rheingold, A. L.; Day, C. S.; Wilson, S. R. *Inorg. Chem.* **1986**, *25*, 634. (c) Bollinger, M. C.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1983**, *105*, 6321. (d) Herberhold, M.; Schrepfermann, M.; Darkwa, J. *J. Organomet. Chem.* **1992**, *430*, 61. (e) Herberhold, M.; Kuhnlein, M.; Schrepfermann, M.; Ziegler, M. L.; Nuber, B. *J. Organomet. Chem.* **1990**, *398*, 259.

(19) Housmekerides, C. E.; Ramage, D. L.; Kretz, C. M.; Shontz, J. T.; Pilato, R. S.; Geoffroy, G. L.; Rheingold, A. L.; Haggerty, B. S. *Inorg. Chem.* **1992**, *31*, 4453 and references therein.

(20) Lundmark, P. J.; Kubas, G. J., unpublished results.