An Anionic Dimer of Cyclopentadienyl-Titanium (IV) Sulfide: A Potential Precursor for Heterometallic Assemblies

Abstract

Reaction of Cp,Ti(SH)₂ with lithium salts in THF yields the cluster Li₂[CpTi(μ-S₂)₂]₂·6THF, generated by elimination of CpH. This anionic dimer is unique that during the preparation none of the sulfur atoms of the precursor has been eliminated and the Ti-S-H groups are completely converted to Ti-S-Li bonds. The crystal structure indicates the presence of all Ti-S single bonds in bridging positions of the titanium cluster.

Keywords: Heterobimetallic; Titanium; Cluster; Sulfide; Precursor

Introduction

Transition metal complexes with bridging sulfide ligands have a broad interest ranging from widely studied biological systems and applied industrial processes, such as hydrosulfurization and catalysis, to novel chemistry of molecular systems [1]. Particularly, complexes having two widely divergent metals, one a Lewis-acid early transition metal and the other an electron-rich late transition metal are promising candidates for new stoichiometric and catalytic reactions [2,3] and they serve as models for studying the role of the support in heterogeneously catalyzed reactions [4]. Multimetallic systems of various main group and transition metals bridged by oxygen, carbon, nitrogen and halides have been reported [5-9]. Properties such as multifunctionality and cooperative effects have been studied [10]. Nevertheless, the problems found to meet the different coordination environments of both metals in close proximity could be as great as the expectations, and thus synthetic strategies leading to new complexes are highly desirable. Although a variety of tetrathiometalates have been very effective in preparing mixed-metal complexes, organometallic early main group metal complexes are relatively uncommon, and efforts to develop their chemistry have been reported recently [11]. Moreover, hydrosulfide complexes that are considered as inorganic equivalents of thiols, can be potential building blocks for the synthesis of sulfur-bridged complexes [12-15] Indeed, most of the hydrosulfide complexes of group 4 transition metals such as [Cp₂M(SH)] (Cp) μ³-C₅H₅, M = Ti, Zr) react with late transition metal complexes to afford hydrosulfide- or sulfide-bridged complexes. They have described [16] the dimeric species [CpTi(μ-S₂)₂]₂ while Ref. [17] reported comound (PhC(NSiMe₃))₂Ti(S)₃.

With the exception of these two salts, synthetic pathways to these terminal sulfide complexes involve oxidation of a M(II) species by sulfur. C-S bond cleavage is an alternative route to M-S bond formation. The research groups of Ref. [18,19] have produced TiS and TiS₂ films from titanium thiolate precursors. However, the synthetic approach is not very effective and there is a need for a new synthetic route to prepare sensitive metal thiols. The successful synthesis of terminal hydrides of Zr, Al, Ge and terminal sulfides of Al, from our group allowed a rational design to assemble novel hetero-bimetallic systems with predictable composition and properties [20-24]. We also reported the lithium salts by reacting hydrides of Al with Li[N(SiMe₃)]₂ to afford the novel trimeric lithium-organoaluminate [25]. The utility of this lithium-organoaluminate can be envisaged as alternative precursor, to those of aluminum hydrides towards the assembly of soluble heterometallic oxides in reactions with metal halides. Similar examples for sulfide complexes are rare compared to those of hydrides, and in fact no lithium-titanium compounds containing sulfides are known to the best of our knowledge. Organometallic hydrosulfide complexes are potentially valuable...
to study the development and understanding of metal sulfide based catalysis, especially hydrogenation processes such as hydrodesulfurization. One of the older examples, Cp₂Ti(SH)₂, was first synthesized by Köpf and Schmidt in 1965 [26]. The preparation was improved in 1980 by Ref. [27,28] but the reactivity studies of Cp₂Ti(SH), in the literature are limited. In our continuing study on the synthesis and reactivity of oxygen/sulfur bridged multimetallic complexes containing titanium [5-9] we have now found that the hydrosulfide complex of a titanium [Cp₂Ti(SH)] reacts with lithium amide or methyl lithium to form the lithium salt under elimination of CpH. The resulting compound was characterized by spectroscopic and X-ray diffraction studies. In this paper, we report on the deprotonation of Cp₂Ti(SH), by lithium amide to produce an anionic titanium sulfide species of composition Li₆[Cp₂Ti(S₂)]·6THF (2). Anionic titanium sulfur containing complexes are rare, and to our knowledge, this dimer is the first reported organometallic lithium-titanium species showing during the preparation the transformation of the terminal Ti-S-H groups to bridging Ti-S-Li bonds. The elimination of CpH from a bis-Cp complex to form a mono-Cp-coordinated Ti is also noteworthy in that [Cp₂Ti(S₂)(SH)] appears to be unstable, while the related Cp₄Ti(S₂)L₄ [L = Py, 4-phenylpyridine, alkylene, alkine] systems are isolable [29-33]. The precursor Cp₂Ti(SH), is prepared as published in literature [27,28]. Titanocenebis(hydrosulfide) (1) reacts with 1 equiv of LiNMe₂ or methyl lithium in THF to produce the anionic titanium sulfide species of composition Li₆[Cp₂Ti(S₂)]·6THF (2), according to Scheme 1 [For experimental details, see Supporting Information].

The reaction is slow at low temperature but proceeds very fast at room temperature under changing the color from red to green within 2 min. The color change is accompanied by hydrogen evolution. The complex can be best stored under N₂ atmosphere with cooling in the presence of THF. Cp₂Ti(SH), reacts with methyl lithium and LiNMe₂, respectively to give compound 2 within 2 min. Both the reactions did not proceed when toluene was used instead of THF at room temperature. However, the reaction was very slow (takes 3 h) and gave a light green product with Li₂N(SiMe₃)₂. Compound 2 was formed, however not in a pure form and is extremely air and moisture sensitive and elemental analysis gave no convincing results. The ¹H NMR pattern is similar to that of the sodium compound Na₂[Cp₂Ti(S₂)(SH)],·4THF reported by Ref. [16] although the coordination environment of sulfur at the central titanium is different. The latter exhibits two Ti=S bonds, while compound 2 has only bridging Ti-S-Li units. The NMR-tube scale reaction in THF-d₈ showed the color change within a min. During this period, vigorous effervescence was observed indicating the evolution of a gas. A ¹H NMR spectrum of the resulting solution exhibits the formation of H₂ (δ 4.58 ppm) (similar peak at δ 4.54 ppm, was reported by Ref. [16]). After some time a resonance around δ 6.00 ppm was observed, this can be attributed to an unknown decomposition product. Furthermore, to confirm the evolution of CpH 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 solvent molecules were observed in the spectrum. 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 obtained 81% yield based on Titanium. In conclusion for the preparation of compound 2 the Lewis base THF seems to be important for the stabilization of the Li cations to compensate the negative charges on the anion. Moreover it is obvious that the deprotonation of Cp₂Ti(SH), is faster in polar THF when compared with that in toluene.

### Molecular structure of [Cp₂Ti(S₂)Li]·6THF

The green complex crystallizes from THF at -30°C. The THF molecules in the crystal lattice are extremely labile and can be removed in vacuo. The compound crystallizes in the monoclinic P2₁/n space group [see Supporting Information]. X-ray structural analysis of 2 shows that the species exists as dimer in the solid state and binuclear units are arranged together by weak interactions of bridging sulfide ligands with THF-solvated lithium cations (Figure 1). Selected bond lengths and angles of 2 are shown in the caption of Figure 2. Unlike the reported sodium titanium cluster [16] compound 2 contains no terminal sulfur atoms which are concurrent with the tendency of the sulfur ligands to bridge metal centers. All the three sulfur atoms are bridged to titanium with Ti-S bond distances of 2.291 Å (av). A comparison of the Ti-S bond lengths of 2 with those of reported Ti-S bond lengths (2.413(2) Å) [8] showed a distinct shortening of the former one. However, these Ti-S distances are slightly longer than the corresponding Ti-S (2.249 Å) [av] bond lengths in the homometallic complex [Cp₂TiCl₂(CîC₆H₅)]₃ [34]. The Li-S (2.463 Å) distance in 2 is comparable with those found in for homometallocyclics (2.401 Å) [av] [35]. The average distance between two metal centers of titanium and lithium is 3.020 Å and the mean bond angle of Ti-S-Li is 79.20°. The Li...Li separation within the Li₆ ring in 2 (av 2.77 Å) is similar to the Li...Li separation within the Li₂ ring in [Li₂(MeO)₆Li] [10]. Apparently the Li⁺(THF) network also maintains the integrity of the complex in solution, because decomposition occurs in
solvents other than THF. Each Ti(IV) atom of 2 is six-coordinate but is formally electronically unsaturated. The lithium ion centers are arranged in distorted cube similar to those of methyl lithium [35]. Heterobimetallic sulphide clusters like \([\text{CpTi}(\mu-S)_2\text{Ir}(\mu^{-}\text{CO})(\text{CO})_3(P\text{(OMe)})_5]_3\), have two long (3.121 Å (mean)) and one short (2.815 Å (mean)) Ti-Ir distances [1]. However, in compound 2 distance between the Ti atoms is large indicating that there is no Ti-Ti bond is present, which would be consistent with the apparent d⁰ electronic configuration. The unit cell packing shows the importance of THF molecule that fills up the channel between the Ti-S-Li cluster. Recrystallization other than THF was not occurred and decomposition of 2 was observed in toluene. Crystal Packing without THF molecule shows the fewer Ti-S-Li clusters exposing the huge gap between each molecule (see Supporting Information). The \([\text{Li}_{5}\text{CpTi}(\mu-S)_2]_3\)·6THF cluster was successful isolated and shows in the X-ray single crystal structure the presence of all Ti-S-Li single bonds in bridging positions. Complex 2 provides a rare example of a lithium titanium-sulfide complex with a cyclopentadienyl ligand on each of the titanium atoms. The cyclopentadienyl ligands as well as the THF coordinate lithium ions makes this cluster soluble in THF and therefore might be prone for further reactions under smooth conditions.

**Experimental Details**

**General procedures**

All experimental manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques or using a dry box unless otherwise specified. All chemicals used were of reagent grades and were purified by standard purification procedures. \(\text{Cp}_2\text{Ti(SH)}_2\) was prepared as reported elsewhere [1].

**Crystallographic analysis**

All measurements were made on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite-monochromated Mo Kα radiation. All structures were solved by direct methods and expanded using Fourier techniques [5-9] and the non-hydrogen atoms were refined anisotropic ally. Hydrogen atoms were included but not refined. All calculations for complexes 2 were performed using the crystal structure crystallographic software package [15]. Selected crystal collection parameters are summarized in Table 1, and the detailed structure reports including their CIF files shown in the Supporting Information.

**Synthesis of 2**

5 mmol (1.220 g) of titanocene bis(hydrosulfide) (Scheme 1) and 1 equiv of (5 mmol, 0.255 g) LiNMe₂, were placed in a Schlenk flask with stirrer in a glove box. THF solvent (20 mL) is added and the mixture is stirred at room temperature with the solution changing color from red to green in two min. The color change is accompanied by the evolution of a gas (effervescence). This reaction proceeds very slowly at low temperature. The complex can be best stored under cooling in the presence of THF vapor. Compound 2 is extremely air and moisture sensitive. Yield 0.99 g (81% based on \(\text{Cp}_2\text{Ti(SH)}_2\)), H NMR.

**Supplementary Material**

Appendix A, CCDC 1430445 2 contain the supplementary crystallographic data for this paper. Supplementary data to this article can be found online at these data include Experimental details, crystallographic files.

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Table 1 Crystal Data and Structure Refinement for Compound Li₆[CpTi(μ-S)₃]₂·6THF (2).

| Property                              | Value                     |
|---------------------------------------|---------------------------|
| **Empirical formula**                 | C₃₄H₅₈O₆Li₆Ti₂S₆          |
| **Formula weight**                    | 892.60                    |
| **Temperature**                       | 100(2) K                  |
| **Colour**                            | Green                     |
| **Wavelength (Å)**                    | 1.54178                   |
| **Crystal System**                    | Monoclinic                |
| **Space group**                       | P21/n                     |
| **a [Å]**                             | 19.4757(10)               |
| **b [Å]**                             | 10.6671(5)                |
| **c [Å]**                             | 32.4375(15)               |
| **α [deg]**                           | 90.00                     |
| **β [deg]**                           | 96.96(2)                  |
| **γ [deg]**                           | 90.00                     |
| **V [Å³]**                            | 6689.0(6)                 |
| **Z**                                 | 15                        |
| **Density (calculated) Mg m⁻³**       | 1.385                     |
| **Absorption coefficient (mm⁻¹)**     | 4.635                     |
| **F (000)**                           | 2906                      |
| **θ range for data collection (deg)** | 2.52 to 58.79             |
| **Index ranges**                      | -21 ≤ h ≤ 21, -11 ≤ k ≤ 11, -35 ≤ l ≤ 35 |
| **No. of reflections collected/unique** | Total: 58391 Unique: 9514 (R_w=0.1783) |
| **Refinement method**                 | Full-matrix least-squares on F² |
| **Goodness-of-fit on F²**             | 1.067                     |
| **Final R indices (I>2σ(I))**         | R1=0.0699, wR2=0.1188     |
| **R indices (all data)**              | R1=0.1379, wR2=0.1392     |
| **Largest diff peak/hole [e Å⁻³]**    | -0.381/+0.636             |
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