Synthesis and Reactivity of Some Organometallic Chalcogenide Complexes

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The research reported today has been motivated by a desire to understand the reaction chemistry of polysulfido complexes [1]. The polysulfide ligands contain catenated sulfur atoms, and as such resemble elemental sulfur. The question being addressed is whether these ligands exhibit chemistry similar to that of the element. The reaction of sulfur with nucleophiles (such as phosphines and sulfide anion) is a classic reaction [2]. Under vigorous conditions sulfur and electrophilic acetylenes react in the vapor phase [3]. Our studies into analogous reactivity have centered upon the titanocene pentasulfide (1) complex.

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\begin{align*}
\text{Cp}_2\text{Ti} & \quad \text{S} & \quad \text{S} \\
\text{S} & \quad \text{S} & \quad \text{S} \\
\text{S} & \quad \text{S} & \quad \text{S}
\end{align*}
\]

Compound 1 is rapidly desulfurized by tertiary phosphines to give dititanium polysulfides \(1,4-\left[\text{Cp}_2\text{Ti}\right]_2\text{S}_4\) \(2\) [4] and \(1,5-\left[\text{Cp}_2\text{Ti}\right]_2\text{S}_6\) \(3\) [5]. Our results indicate the \(\text{Ti}_2\text{S}_4/\text{Ti}_2\text{S}_6\) product distribution arises from the competition between coupling of two \((\text{RC}_5\text{H}_4)_2\text{TiS}_3\) units and further desulfurization of \((\text{RC}_5\text{H}_4)_2\text{TiS}_3\) by \(\text{PR}_3\). The synthesis of \(1,4-\left[\text{Cp}_2\text{Ti}\right]_2\text{S}_4\) from an intermediate perthiocarbonate compound, \(\text{Cp}_2\text{TiCS}_4\), may occur as well from an unstable \(\text{Cp}_2\text{TiS}_2\) species; which is probably also true for the oxidative-coupling of \(\text{Cp}_2\text{Ti}(\text{SH})_2\).

The presence or existence of reactive titanocene sulfides is suggested by the formation of dithiolene complex \(\text{Cp}_2\text{TiS}_2\text{C}_2(\text{CO}_2\text{CH}_3)_2\) by addition of \(\text{PR}_3\) to a solution of 1 and \(\text{CH}_3\text{O}_2\text{CECCO}_2\text{CH}_3\) (DMAD). In this case, \(\text{PR}_3\) probably reacts with 1 to give a polysulfido-phosphonium intermediate which upon reaction with the electrophilic acetylene gives the observed dithiolene product, even at \(-20^\circ\text{C}\). The reaction of a tertiary phosphine and 1 is similar to the reaction of sulfide in that both involve an initial ring opening step to afford ionic open chain intermediates.

In the presence of unhindered ketones \(\text{Cp}_2\text{TiS}_5\) \(1\) reacts with sulfide anion, \(\text{S}^{2-}\), to give \(1,4-\text{Cp}_2\text{TiS}_4\text{CR}_2\) heterocycles. Both the 1,3- and 1,4-\(\text{Cp}_2\text{TiS}_4\text{CH}_2\) isomers are produced when \(\text{CH}_2\text{Br}_2\) is used. The pathway for the substitution of a sulfur atom for a \(\text{CR}_2\) unit into the cyclo-\(\text{TiS}_5\) moiety is proposed to proceed via initial cleavage of the \(\text{TiS}_5\) ring by an anionic sulfur nucleophile. The intermediate \(\text{C}_5\text{H}_5\text{TiS}_4\text{S}^{2-}\) species would be capable of nucleophilic addition to ketones or substitution on alkyl halides.
In the reactions of 1 with nucleophiles the titanium center functions as a template. Direct reaction at the titanium atom may not be mechanistically important. Rather, the Ti-S bonds provide stabilization of the reactive polysulfido compounds produced. We also suggest that the reaction is occurring predominantly at the S(2)-S(3) site.

The compounds (RC₅H₄)₂TiE₅ (R=H, CH₃; E=S, Se) [6] have been reported to react with the activated acetylene DMAD to afford alkenedithiolo genide (dithiolene and diselenene) complexes. Through studies on 1,4-[(MeCp)₂Ti]₂S₄ we have found that these reactions occur via the intermediacy of a vinyl disulfide compound, Cp₂TiSC₂(CO₂CH₃)₂S (4). This intermediate undergoes an intramolecular rearrangement to afford the dithiolene. The reason that the vinyl disulfide had not previously been identified in the penta sulfide chemistry is attributable to the high activation energy associated with the addition of DMAD to the poorly nucleophilic (RC₅H₄)₂TiS₅. Another example of a migration reaction is found in the rearrangement of (C₅H₅)₂TiS₅ to (C₅H₅)TiS₅C₅H₅. This reaction also provides a third example of structural isomers in titanium sulfide chemistry.

One goal in this project was the synthesis and characterization of the tellurium (ditellurene) analogs of dithiolenes. Interest in this class of coordination compounds can be traced to the recent synthesis of the tetratellurafulvalenes [8,9]. The compounds (RC₅H₄)₂TiE₂C₂R₂ (E = S, Se) have been observed to transfer their chelate to other metal centers [6] and it seems plausible that the tellurium derivatives would behave similarly. However, our attempts to synthesize titanocene telluride complexes failed. We were able to produce the first examples of ditellurene complexes by turning to the robust Pt(II)(PPh₃)₂ system. Using reported procedures the ligands o-C₆H₄(TeLi)₂ [8] and 1,2-C₆H₄Te₂- (TeLi)₂ [9] were prepared, and found to react readily with Pt(PPh₃)₂Cl₂ to provide Pt(P(Ph₃)₃)(Te₂C₆H₄) (5) and Pt(P(Ph₃)₂(Te₂C₆H₆) (6), respectively. We have also found o-C₆H₄(SiLi)Li [10] to be a precursor to Pt(P(Ph₃)₂(TeSC₆H₄) (7). Compound 5 was structurally characterized.

Soluble and reactive anionic main group sulfides can be prepared by the reaction of sulfide anion, S₂²⁻, and main group sulfides. In this way numerous examples of group IV (M₂S₂²⁻ and R₂MS₂²⁻, M = Ge and Sn) [11] and group V (ES₃²⁻ and RES₂²⁻, E = P and As) [12] sulfide anions can now be found in the literature. We have found sila-1,1-dithiolate (Me₂SiS₂²⁻) complexes can be conveniently prepared by treating a solution of (Me₂SiS)₂/Li₂S with metal dichlorides. Using this methodology the complexes Cp₂MS₂SiMe₂ (R = Ti (8) and V) and Pt-(S₂SiMe)₂(PPh₃)₂ were prepared from their respective chlorides.
The titanium compound, Cp₂TiS₂SiMe₂, is particularly interesting because it contains two potentially reactive sites: the Ti-S and Si-S bonds. The reaction of 8 with transition metal (or main group) dichlorides affords Cp₂TiCl₂ (90%) without the formation of Me₂SiCl₂, indicating that reaction at titanium is preferred.

There has been recent interest in S-for-O exchange reactions within the coordination sphere of transition metals. The ability of (Me₃Si)₂S to effect such a transfer with oxometallates has been explored by several research groups [13,14,15]. However the synthetic utility of (Me₃Si)₂S is hampered by reduction (and silation) and declusterification. We have examined the reactivity of Cp₂TiS₂SiMe₂ with oxometallates and observed a sulfiding reaction without reduction. Using 8 we were able to convert WₓS₄⁻ₓ⁻ₓ (x = 4, 3, 2) and TaW₅O₁₉⁻³ to W₅S₄²⁻ and TaW₅O₁₈S₃⁻, respectively.

References
12. (a) Zank, G. A.; Rauchfuss, T. B. Organometallics 1984, 3, 1191.