

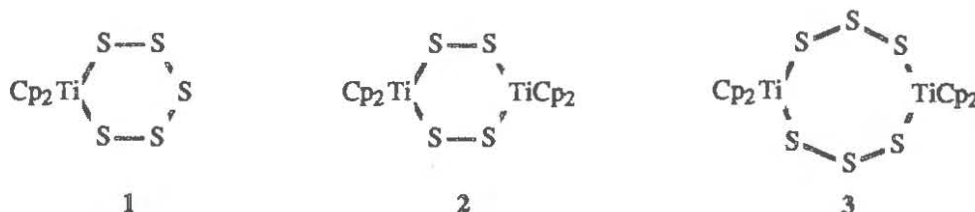
Synthesis and Reactivity of Some Organometallic Chalcogenide Complexes

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Final Seminar

July 22, 1986

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.



Compound 1 is rapidly desulfurized by tertiary phosphines to give dititanium polysulfides (1,4-[Cp₂Ti]₂S₄ (2) [4] and 1,5-[Cp₂Ti]₂S₆ (3) [5]). Our results indicate the Ti₂S₄/Ti₂S₆ product distribution arises from the competition between coupling of two (RC₅H₄)₂TiS₃ units and further desulfurization of (RC₅H₄)₂TiS₃ by PR₃. The synthesis of 1,4-[Cp₂Ti]₂S₄ from an intermediate perthiocarbonate compound, Cp₂TiCS₄, may occur as well from an unstable Cp₂TiS₂ species; which is probably also true for the oxidative-coupling of Cp₂Ti(SH)₂.

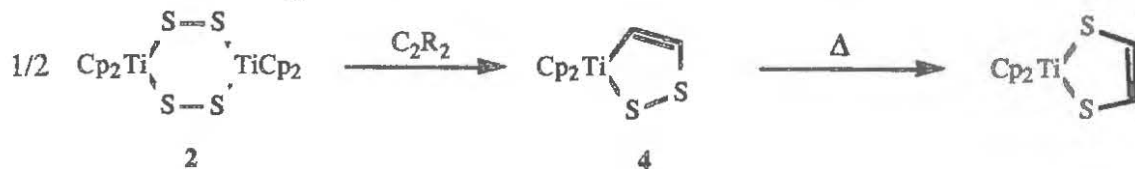
The presence or existence of reactive titanocene sulfides is suggested by the formation of dithiolene complex (Cp₂TiS₂C₂(CO₂CH₃)₂) by addition of PR₃ to a solution of 1 and CH₃O₂CC≡CCO₂CH₃ (DMAD). In this case, PR₃ probably reacts with 1 to give a polysulfido-phosphonium intermediate which upon reaction with the electrophilic acetylene gives the observed dithiolene product, even at -20°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 Cp₂TiS₅ (1) reacts with sulfide anion, S²⁻, to give 1,4-Cp₂TiS₄CR₂ heterocycles. Both the 1,3- and 1,4-Cp₂TiS₄CH₂ isomers are produced when CH₂Br₂ is used. The pathway for the substitution of a sulfur atom for a CR₂ unit into the cyclo-TiS₅ moiety is proposed to proceed via initial cleavage of the TiS₅ ring by an anionic sulfur nucleophile. The intermediate (C₅H₅)₂TiS_x²⁻ species would be capable of nucleophilic addition to ketones or substitution on alkyl halides.



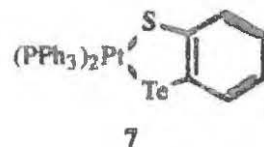
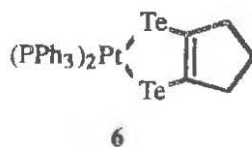
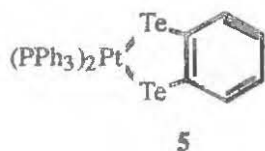
In the reactions of **1** with nucleophiles the titanium center functions as a template. Direct reaction at the titanium atom may not be mechanistically important. Rather, the Ti-S bonds provide stabilization of the reactive polysulfido compounds produced. We also suggest that the reaction is occurring predominantly at the S(2)-S(3) site.

The compounds $(RC_5H_4)_2TiE_5$ ($R=H, CH_3$; $E=S, Se$) [6] have been reported to react with the activated acetylene DMAD to afford alkenedichalcogenide (dithiolene and diselenene) complexes. Through studies on $1,4-[(MeCp)_2Ti]_2S_4$ we have found that these reactions occur via the intermediacy of a vinyl disulfide compound, $Cp_2TiSC_2(CO_2CH_3)_2S$ (**4**). This intermediate undergoes an intramolecular



rearrangement to afford the dithiolene. The reason that the vinyl disulfide had not previously been identified in the pentasulfide chemistry is attributable to the high activation energy associated with the addition of DMAD to the poorly nucleophilic $(RC_5H_4)_2TiS_5$. Another example of a migration reaction is found in the rearrangement of $(C_5H_5)_2TiS_5$ to $(C_5H_5)TiS_5C_5H_5$. 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 $(RC_5H_4)_2TiE_2C_2R_2$ ($E = S, Se$) 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 $Pt(II)(PPh_3)_2$ system. Using reported procedures the ligands $o-C_6H_4(TeLi)_2$ [8] and $1,2-C_5H_6(TeLi)_2$ [9] were prepared, and found to react readily with $Pt(PPh_3)_2Cl_2$ to provide $Pt(PPh_3)_2(Te_2C_6H_4)$ (**5**) and $Pt(PPh_3)_2(Te_2C_5H_6)$ (**6**), respectively. We have also found $o-C_6H_4(SLi)Li$ [10] to be a precursor to $Pt(PPh_3)_2(TeSC_6H_4)$ (**7**). Compound **5** was structurally characterized.



Soluble and reactive anionic main group sulfides can be prepared by the reaction of sulfide anion, S^{2-} , and main group sulfides. In this way numerous examples of group IV ($M_xS_y^{z-}$ and $R_2MS_2^{2-}$, $M = Ge$ and Sn) [11] and group V (ES_3^{3-} and RES_3^{2-} , $E = P$ and As) [12] sulfide anions can now be found in the literature. We have found sila-1,1-dithiolate ($Me_2SiS_2^{2-}$) complexes can be conveniently prepared by treating a solution of $(Me_2SiS)_3/Li_2S$ with metal dichlorides. Using this methodology the complexes $Cp_2MS_2SiMe_2$ ($M = Ti$ (**8**) and V) and $Pt-(S_2SiMe)_2(PPh_3)_2$ were prepared from their respective chlorides.

The titanium compound, $\text{Cp}_2\text{TiS}_2\text{SiMe}_2$, 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 Cp_2TiCl_2 (>90%) without the formation of Me_2SiCl_2 , 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 $(\text{Me}_3\text{Si})_2\text{S}$ to effect such a transfer with oxometallates has been explored by several research groups [13,14,15]. However the synthetic utility of $(\text{Me}_3\text{Si})_2\text{S}$ is hampered by reduction (and silylation) and declusterification. We have examined the reactivity of $\text{Cp}_2\text{TiS}_2\text{SiMe}_2$ with oxometallates and observed a sulfiding reaction without reduction. Using **8** we were able to convert $\text{WO}_x\text{S}_{4-x}^{2-}$ ($x = 4,3,2$) and $\text{TaW}_5\text{O}_{19}^{3-}$ to WS_4^{2-} and $\text{TaW}_5\text{O}_{18}\text{S}^{3-}$, respectively.

References

1. Draganjac, M. D.; Rauchfuss, T. B. Angew. Chem. Int. Ed. Engl. **1985**, 24, 742.
2. Davies, R. E. in Survey of Progress in Chemistry; Scott, A., Ed.; Academic Press: New York, 1964; vol 2, 189.
3. Davidson, A.; Shawl, E. T. Inorg. Chem. **1970**, 9, 1820.
4. Bolinger, C. M.; Rauchfuss, T. B.; Wilson, S. R. J. Am. Chem. Soc. **1981**, 103, 5620.
5. Bolinger, C. M.; Hoots, J. E.; Rauchfuss, T. B. Organometallics **1982**, 1, 223.
6. Bolinger, C. M.; Rauchfuss, T. B. Inorg. Chem. **1982**, 21, 3947.
7. Bolinger, C. M.; Rauchfuss, T. B. Inorg. Chem. **1982**, 21, 3947.
8. Lerstrup, K.; Talham, D.; Bloch, A.; Poehler, T.; Cowan, D. J. Chem. Soc., Chem. Commun. **1982**, 336.
9. Wudl, F.; Aharon-Shalom, E. J. Am. Chem. Soc. **1982**, 104, 1154.
10. Figuly, G. A. Ph.D. Thesis, University of Illinois at Urbana-Champaign, 1981, p. 103.
11. Krebs, B. Angew. Chem. Int. Ed. Engl. **1983**, 22, 113.
12. (a) Zank, G. A.; Rauchfuss, T. B. Organometallics **1984**, 3, 1191.
(b) Zank, G. A.; Rauchfuss, T. B.; Wilson, S. R.; Rheingold, A. L. J. Am. Chem. Soc. **1984**, 106, 7621.
13. Do, Y.; Simhon, E. D.; Holm, R. H. Inorg. Chem. **1985**, 24, 2827.

14. Money, J. A.; Huffman, J. C.; Cristou, G. Inorg. Chem. **1985**, 24, 3297.
15. Klemperer, W. G.; Schwartz, C. Inorg. Chem. **1985**, 24, 4459.