

π -Bonded Cyclopentadienyl Complexes of the p-Block Elements

Patrick Jeffries

Literature Seminar

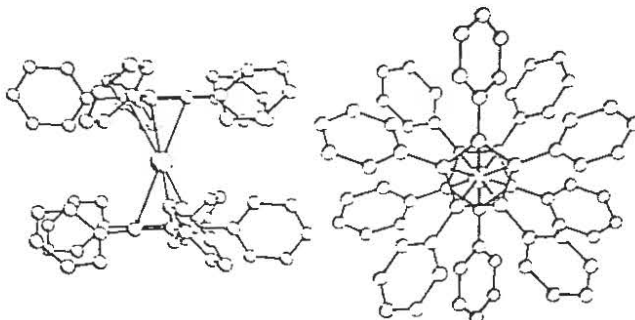
March 16, 1989

One of the largest classes of subvalent organometallic derivatives of the p-block elements consists of the π cyclopentadienyl complexes [1]. These complexes are intriguing structurally, and, unlike transition metal π cyclopentadienyl complexes, the d-orbitals do not participate significantly in the bonding.

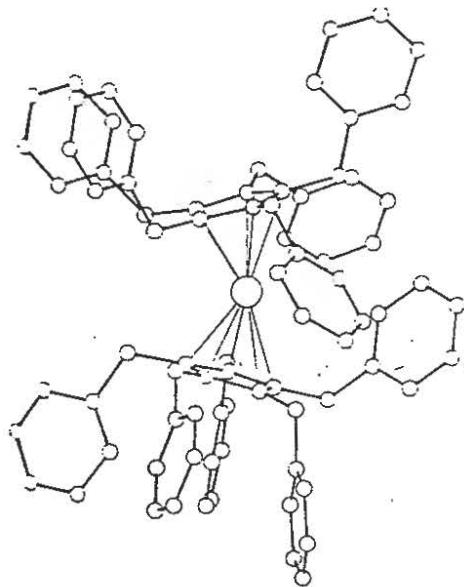
In 1956, E. O. Fischer and H. Grubert synthesized the first p-block π cyclopentadienyl complexes, stannocene, Cp_2Sn , and plumbocene, Cp_2Pb [2,3]. Germanocene, Cp_2Ge , was later prepared by J. V. Scibelli and M. D. Curtis in 1973 [4]. Whereas stannocene and germanocene are monomers in the solid and gas phases, plumbocene is polymeric in the solid phase and monomeric in the gas phase. The monomeric complexes adopt a bent sandwich structure with a stereochemically active "lone pair" of electrons which is consistent with the predictions of VSEPR theory. The bent structure is more stable than a parallel structure because the lower symmetry allows the filled s orbital to mix with an empty p orbital and stabilizes the "lone pair" [1]. The methylcyclopentadienyl (MeCp) and pentamethylcyclopentadienyl (Cp^*) derivatives of Si (Cp^* only), Ge, Sn, and Pb have been prepared and are monomeric [5]. A comparison of the structures yields two conclusions. First, molecules with less sterically demanding ligands are more severely bent. Second, for a given element the metal-ring distance does not change upon substituting the cyclopentadienyl ligand.

The bis(Cp^*) complexes of Ge, Sn, and Pb react with Brønsted acids (HX) with loss of Cp^*H to form CpEX or $[\text{CpE}]^+[\text{X}]^-$, depending on the nucleophilicity of X [6]. In contrast, attack occurs at the metal center in the Si complex to form $(\eta^1\text{-Cp})_2\text{SiHX}$ [7]. It has been predicted that because of the presence of the "lone pair" these complexes should behave as Lewis bases [8]. However, a Lewis acid-base adduct has not been conclusively identified. In fact, contrary to early reports, it has been shown that reactions with BF_3 and AlCl_3 do not lead to adduct formation [9].

Recently, the bis(pentaphenylcyclopentadienyl) complexes of Ge, Sn, and Pb have been prepared [10]. The crystal structure of the Sn complex has been solved and is shown in Figure 1. This molecule contradicts the predictions of VSEPR theory and has rare S_{10} symmetry. Calculations show that this parallel metallocene structure is controlled by steric factors. Theoretical investigations and Mössbauer studies have shown that the "lone pair" in these complexes is stabilized by mixing with the d_{z^2} orbital. Based on X-ray powder diffraction data and ^{13}C CPMA S NMR spectra, the Ge and Pb compounds are assumed to be isostructural with the Sn compound.



Attempts to use similarly bulky ligands to synthesize other molecules with parallel rings have been unsuccessful. The bis(1,2,4-tris(trimethylsilyl)cyclopentadienyl) complexes of Ge and Sn have been prepared [11]. The Cp(centroid)-E-Cp(centroid) angles are $\sim 170^\circ$ and 162° , respectively. A bent structure, shown in Figure 2, also is adopted by in the bis(pentabenzylcyclopentadienyl) compounds of Ge, Sn, and Pb which have angles 163° , 156° , and 153° , respectively [12]. NMR studies indicate that the Cp rings are rapidly rotating despite the steric bulk of the ligands [11,12].



The group 13 compounds CpTl and Cp*Tl have been synthesized and in the solid state form polymeric zig-zag chains [13]. Again, the Cp-Tl-Cp units in the chains are bent to allow mixing of the s and p orbitals [14]. Monomers exist in the gas phase with C_{5v} symmetry [15]. The pentabenzylcyclopentadienyl complex of thallium has been synthesized [16]. Slow crystallization yields a head to head dimer and rapid crystallization yields a head to tail linear polymer. The Tl to nearest bonded ring distance is the same in both complexes, 2.49Å. Interactions between the Tl and ortho carbon atoms of the benzyl groups are observed by ^{13}C NMR spectroscopy [17].

The CpIn, MeCpIn, and Cp*In complexes have been prepared and characterized. CpIn and MeCpIn form polymeric zig-zag chains in the solid state [18]. In contrast, Cp*In forms an electron deficient close structure consisting of an octahedron of In atoms with π -bonded Cp* ligands at each vertex [19]. The average In-In distance in Cp*In is 3.953Å which is close to In-In distance between separate chains in CpIn and MeCpIn, 3.986Å [18,19]. This indicates that In-In interactions are probably present in these compounds. In the gas phase these compounds exist in C_{5v} monomeric forms. The In to ring distance decreases in the order Cp > MeCp > Cp* [18,19,20].

The interesting features of these compounds have sparked studies of the p-block elements with other π donating ligands such as arenes and carboranes [1].

References

1. Jutzi, P., " π bonding to Main-Group Elements," Adv. Organomet. Chem. 1986, 36, 217.
2. Fischer, E. O.; Grubert, H., "Di-cyclopentadienyl-zinn," Z. Naturforsch., Teil B 1956, 11, 423.
3. Fischer, E. O.; Grubert, H., "Di-cyclopentadienyl-blei," Z. Anorg. Allg. Chem. 1956, 286, 327.
4. Scibelli, J. V.; Curtis, M. D., "Bis(π -cyclopentadienyl)germanium(II)," J. Am. Chem. Soc. 1973, 95, 924.
5. (a) Jutzi, P.; Hielscher, B., "Preparation of Tin and Germanium Metallocenes from Tetravalent Precursors," Organometallics 1986, 5, 1201.
 (b) Jutzi, P.; Kohl, F.; Hofmann, P.; Krüger, C.; Tsay, Y., "Bis(pentamethylcyclopentadienyl)germanium und -zinn sowie (Pentamethylcyclopentadienyl)-germanium- und -zinn-Kationen: Synthese, Struktur und Bindungsverhältnisse," Chem. Ber. 1980, 113, 757.
 (c) Jutzi, P.; Kanne, D.; Krüger, C., "Decamethylsilicocen-Synthesis and Structure," Angew. Chem. Int. Ed. Engl. 1986, 25, 164.
 (d) Bonny, A.; McMaster, A. D.; Stobart, S. R., "Bis(methylcyclopentadienyl) Derivatives of Germanium(II), Tin(II), and Lead(II): ^1H and ^{13}C NMR Properties and Comparison with those for Analogues Formed by Univalent Metals (Li, K, and Ti)," Inorg. Chem. 1978, 17, 95.
6. (a) Jutzi, P.; Kohl, F.; Krüger, C., "Synthesis and Structure of the nido-Cluster $(\text{CH}_3)_5\text{C}_5\text{Sn}^+$," Angew. Chem. Int. Ed. Engl. 1979, 18, 59.
 (b) Jutzi, P.; Hampel, B., "Electrophilic Attack at Pentamethylcyclopentadienyl-Substituted Germylenes," Organometallics 1986, 5, 730.
7. Jutzi, P.; Holtmann, U.; Bögge, H.; Müller, A., "Protonation of Decamethylsilicocene [Bis(pentamethylcyclopentadienyl)silicon]," J. Chem. Soc., Chem. Comm. 1988, 305.
8. Harrison, P. G.; Richards, J. A., "Derivatives of Bivalent Germanium, Tin and Lead XIV. The Reactions of Cyclopentadienyltin(II) Compounds with Some Main Group Lewis Acids," J. Organomet. Chem. 1976, 108, 35.
9. (a) Kohl, F. X.; Jutzi, P., "Kovalente und ionische (Pentamethylcyclopentadienyl)zinn(II)-Verbindungen," Chem. Ber. 1981, 114, 488.
 (b) Dory, T. S.; Zuckermann, J. J., "Do Subvalent Main-Group Compounds Form Adducts with Main-Group Acceptors? The BF_3 Adduct of Stannocene, A Revision. The Crystal and Molecular Structure of $\{[\text{BF}_4](\mu\text{-}\eta^5\text{-C}_5\text{H}_5)_2\text{-Sn}[\mu\text{-}\eta^5\text{-C}_5\text{H}_5\text{Sn}]^+\text{THF}\}_n$," J. Organomet. Chem. 1985, 281, C1.
10. (a) Heeg, M. J.; Janiak, C.; Zuckerman, J. J., "Decaphenylstannocene, $[\eta^5\text{-}(\text{C}_6\text{H}_5)_5\text{C}_5]\text{Sn}^{\text{II}}$: The First Symmetrical Main-Group Sandwich Compound," J. Am. Chem. Soc. 1984, 106, 4259.
 (b) Williamson, R. L.; Hall, M. B., "The Nature of the Tin Lone Pair and Phenyl Ring Packing in Decaphenylstannocene," Organometallics 1986, 5, 2142.

- (c) Heeg, M. J.; Herber, R. H.; Janiak, C.; Zuckerman, J. J.; Schumann, H.; Manders, W. F., "Decaphenylgermanocene, -stannocene, and -plumbocene, $[\eta^5-(C_6H_5)_5C_5]E^{II}$ (E = Ge, Sn, Pb) and the X-ray crystal and molecular structure of pentaphenylstannocene, $(C_6H_5)_5C_5SnC_5H_5-\eta^5$," J. Organomet. Chem. 1988, 346, 321.
11. Jutzi, P.; Schlüter, E.; Hursthouse, M. B.; Arif, A. M.; Short, R. L., "Synthesis of Trimethylsilylated Germanocenes; X-ray Structure of and Steric Effects of Hexakis(trimethylsilyl)Germanocene," J. Organomet. Chem. 1986, 299, 285.
 12. Schumann, H.; Janiak, C.; Hahn, E.; Kolax, C.; Loebel, J.; Rausch, M. D.; Zuckerman, J. J.; Heeg, M. J., "Decabenzylgermanocen, -stannocen und -plumbocen. Synthese und Struktur von luftstabilen Metallocenen der 4. Hauptgruppe des Periodensystems der Elemente," Chem. Ber. 1986, 119, 2656.
 13. (a) Werner, H.; Otto, H.; Kraus, H. J., "Die Kristallstruktur von TlC_5Me_5 ," J. Organomet. Chem. 1986, 315, C57.
(b) Frasson, E.; Menegus, F.; Panattoni, C., "Chain Structure of the Cyclopentadienils of Monovalent Indium and Thallium," Nature 1986, 199, 1087.
 14. Canadell, E.; Eisenstein, O.; Rubio, J., "Theoretical Analysis of Bonding in Monomeric and Polymeric C_5H_5M Compounds," Organometallics 1984, 3, 759.
 15. (a) Tyler, J. K.; Cox, A. P.; Sheridan, J., "Molecular Symmetry in Cyclopentadienyl Thallium and Some Related Substances from their Microwave Spectra," Nature, 1959, 183, 1182.
(b) Blom, R.; Werner, H.; Wolf, J., "The Molecular Gas Phase Structure of $Tl(C_5Me_5)$," J. Organomet. Chem. 1988, 354, 293.
 16. (a) Schumann, H.; Janiak, C.; Pickardt, J.; Börner, U., "Pentabenzylcyclopentadienylthallium(I): Synthesis and Structure of a "Dimeric" Organothallium Compound with Tl-Tl Interaction," Angew. Chem. Int. Ed. Engl. 1987, 26, 789.
(b) Schumann, H.; Janiak, C.; Khan, M. A.; Zuckerman, J. J., "Eine zweite ungewöhnliche Kristallmodifikation von Pentabenzylcyclopentadienylthallium(I), $(PhCH_2)_5C_5Tl$," J. Organomet. Chem. 1988, 354, 7.
 17. Schumann, H.; Janiak, C.; Khani, H., "Cyclopentadienylthallium(I) Compounds with Bulky Cyclopentadienyl Ligands," J. Organomet. Chem. 1987, 330, 347.
 18. Beachley, O. T.; Pazik, J. C.; Glassman, T. E.; Churchill, M. R.; Fettinger, J. C.; Blom, R., "Synthesis, Characterization, and Structural Studies of $In(C_5H_4Me)$ by X-ray Diffraction and Electron Diffraction Techniques and a Reinvestigation of the Crystalline State of $In(C_5H_5)$ by X-ray Diffraction Studies," Organometallics 1988, 7, 1059.
 19. Beachley, O. T.; Blom, R.; Churchill, M. R.; Faegri, K.; Fettinger, J. C.; Pazik, J. C.; Victoriano, L., "(Pentamethylcyclopentadienyl)indium(I) and -indium(III) Compounds. Synthesis, Reactivities, and X-ray Diffraction and Electron Diffraction Studies of $In(C_5Me_5)$," Organometallics 1989, 8, 346.
 20. Shibata, S.; Bartell, L. S.; Gavin, R. M., "Molecular Structure and Bonding of $In(C_5H_5)$," J. Chem. Phys. 1964, 41, 717.