

π -Coordination to main-group elements—some new results

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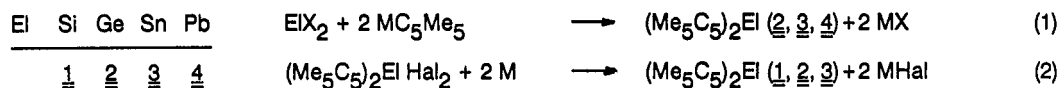
Abstract. Cyclopentadienyl complexes of p-block elements in their low-oxidation state are stabilized by permethylation of the cp ring. In this context, synthesis, structure, and bonding of the group 14 decamethyl metallocenes $(\text{Me}_5\text{C}_5)_2\text{El}$ with $\text{El}=\text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$ is described. Furthermore, synthesis, structure, and reactivity of the monomeric π -complexes $\text{Me}_5\text{C}_5\text{GeCR}(\text{SiMe}_3)_2$ with $\text{R}=\text{H}, \text{SiMe}_3$ is presented. - Half-sandwich cyclopentadienyl complexes of the type $(\text{Me}_4\text{C}_5\text{H})\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)\text{El}^+\text{X}^-$ with $\text{El}=\text{Ge}, \text{Sn}$ show an additional weak metal-olefin interaction; their metallocenophane-like structure is proved by crystal structure analysis. π -Carbollyl complexes of low-valent group 13, 14, and 15 elements show interesting structural features, which are discussed on the basis of NMR and x-ray crystal structure data.

INTRODUCTION

The π -coordination chemistry of s- and p-block elements has a long history; it came into focus in the late 1950's and once more during the last years. This chemistry is documented by compounds with diverse cyclopentadienyl (ref.1,2), carbollyl (ref.1,3), and arene (ref.1,4) ligands. Examples from the first two classes are presented.

THE DECAMETHYL METALLOCENES OF THE GROUP 14 ELEMENTS – A COMPARISON OF STRUCTURE AND BONDING

The decamethyl metallocenes of germanium, tin, and lead are synthesized 1) by reaction of divalent inorganic substrates with pentamethylcyclopentadienyl transfer agents (equ.1), and 2) by reduction of tetravalent precursors with appropriate leaving groups (equ.2,ref.1). Decamethyl silicocene, the first stable silicon (II) compound, is available by the second method only (ref.5).



The bonding of these hypervalent compounds is best understood on the basis of MO arguments. Calculations for the parent metallocenes have been performed on different levels of sophistication; bent structures are energetically preferred. Going from the parent to the decamethyl metallocenes, the inductive and steric effect of the incorporated methyl groups have to be taken into account. Data of solid state or gas phase structure determinations for the group 14 decamethyl metallocenes are presented in Table 1 together with MO energies derived from PES data. Important features of the bonding are:

- 1) In all metallocenes the HOMO is non-bonding with electron density concentrated at the cyclopentadienyl rings.
- 2) In decamethyl silicocene, the MO representing the lone-pair is of comparably higher energy (ca. 0.9 eV).

SYNTHESIS, STRUCTURE, AND REACTIVITY OF PENTAMETHYLCYCLO- PENTADIENYL(ALKYL)GERMYLENES

Reaction of pentamethylcyclopentadienylgermanium chloride or pentamethylcyclopentadienylgermanium tetrafluoroborate with the corresponding lithiumalkyls leads to the pentamethylcyclopentadienyl (alkyl) germylenes 5 and 6, resp. (equ.3,ref.6). These compounds are monomeric in the solid state, in solution, and

TABLE 1: Structure Data, Ionization Energies, and Orbital Assignments for 1-4

| | d ^{a)} [Å] | r(M-C) ^{b)} [Å] | δ ^{c)} [Å] | ∠C ₅ C ₅ ^{d)} [°] | HOMO πnb [eV] | MO πb [eV] | MO lone-pair [eV] |
|----------|--|-------------------------------|------------------------|---|---------------------|------------------|-------------------------|
| <u>1</u> | 2.11 ⁺ 2.12 ⁺ 2.129(12) [*] | 2.42(1) 2.42(6) 2.45(2) | 0 0.023 0.021 | 0 25.3 22.4(12) | 6.7 | 8.1 | 7.5 |
| <u>2</u> | 2.21(3) [*] | 2.52(3) | 0.015 | 23(3) | 6.6 | 7.9 | 8.4 |
| <u>3</u> | 2.39 ⁺ | 2.68 | 0.023 | 36.4 | 6.6 | 7.5 | 8.4 |
| <u>4</u> | 2.48 ⁺ | 2.79 | 0.029 | 43.0 | 6.3 | 7.4 | 8.9 |

⁺ X-ray; ^{*} GED; a) Distance from the central atom to the ring centroid; b) Mean distance; c) Mean value of the distance from the center of mass of each C₅ ring to the projection of the group 14 element into the ring plane; d) Interplane-angle;

in the gas phase; they show no ligand symmetrization or Ge=Ge double bond formation. X-ray crystal structure data indicate a ring slippage to lower hapticity, short germanium-carbon π-bonds, and a stereochemically active lone-pair at the germanium center. Fig. 1 shows the molecular structure of 5. In solution, the pentamethylcyclopentadienyl ligand is highly fluxional in 5 and 6.



X = Cl, BF₄; 5: R = H; 6: R = SiMe₃

The chemistry of the mixed gerylenes 5 and 6 is determined by 1) oxidative addition reactions at the germanium center, 2) nucleophilic substitution of the pentamethylcyclopentadienyl ligand, and 3) nucleophilic and electrophilic substitution of the alkyl ligand. This is documented by the following examples (equ.4-6).

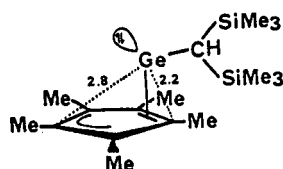
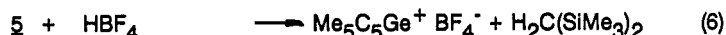
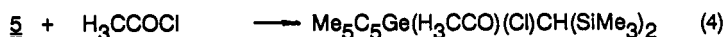
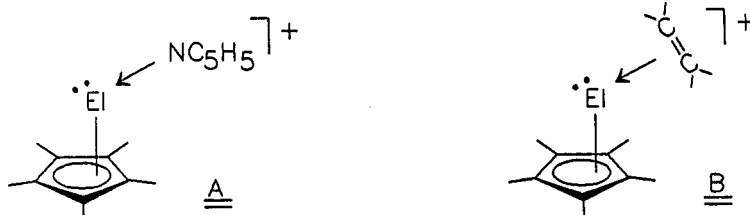


Fig. 1: Solid-state structure of 5

ALKENE COORDINATION TO GROUP 14 ELEMENTS

Half-sandwich cyclopentadienyl complexes of germanium, tin, and lead form 1:1 adducts A with nitrogen ligands which possess π-acceptor qualities. This prompted us to search for comparable compounds of type B with an alkene molecule as π-acceptor.



Protonation of the metallocenes 7, 8, or 9 with tetrafluoroboric or trifluoromethanesulfonic acid leads under ligand abstraction to the ionic species 10a,b, 11a,b, or 12a,b (equ.7). The complex 10c is prepared by chloride elimination with GeCl_2 from the corresponding chlorogermylene precursor. Crystal structure investigations confirm metallocene-like structures, in which the central atom is pentahapto bonded to the cyclopentadienyl ring and furthermore weakly dihapto bonded to one of the double bonds of the cyclopentadiene ligand (ref.7).



| EI \ X | - | BF_4 | CF_3SO_3 | GeCl_3 |
|--------|----------|---------------|--------------------------|-----------------|
| Ge | <u>7</u> | <u>10a</u> | <u>10b</u> | <u>10c</u> |
| Sn | <u>8</u> | <u>11a</u> | <u>11b</u> | |
| Pb | <u>9</u> | <u>12a</u> | <u>12b</u> | |

CARBOLLYL AND CYCLOPENTADIENYL COMPLEXES – A COMPARISON

The first compounds with p-block elements in their low oxidation state π -complexed to the open face of nido-carborane anions were published by the groups of Todd (ref.8), Rudolph (ref.9), and Stone (ref.10) already twenty years ago. Recently, increased interest in this area has developed (ref.1,4). We refer to the isolobal and isoelectronic relationship of the 6π anions Me_5C_5^- and $\text{H}_9\text{B}_9\text{Me}_2\text{C}_2^{2-}$. Comparable π -complexes with low-valent group 13, 14, and 15 elements as central atoms are presented in Table 2.

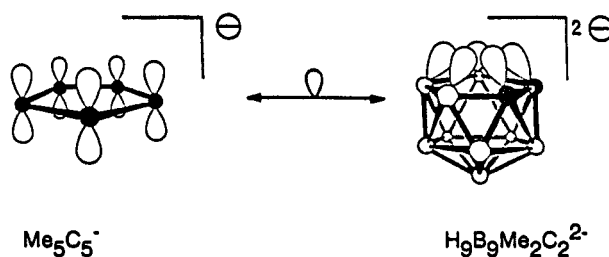
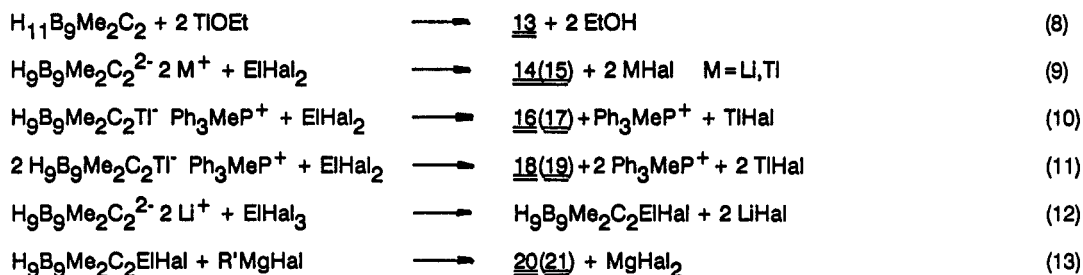


TABLE 2: Comparable Complexes containing Me_5C_5 or $\text{H}_9\text{B}_9\text{Me}_2\text{C}_2$ ligands

| Ligand R | π -Complex | | | | |
|---|---|------------------------------|-----------------------------------|--|--------------------------------|
| Me_5C_5 | RTI | REI^+ | REIHal | R_2EI | REIR'^+ |
| $\text{H}_9\text{B}_9\text{Me}_2\text{C}_2$ | $\text{RTI}^+ \text{TI}^+$ <u>13</u> | REI <u>14,15</u> | REIHal^- <u>16,17</u> | R_2EI^{2-} <u>18,19</u> | REIR' <u>20,21</u> |
| | | $\text{EI} = \text{Ge, Sn}$ | $\text{EI} = \text{Ge, Sn}$ | $\text{EI} = \text{Ge, Sn}$ | $\text{EI} = \text{P, As}$ |

In 13-21 the relevant p-block element is either η^5 -bonded to the planar face of the B_9C_2 carborane ligand or in a slightly slipped (η^3) bonding situation.

The preparation and synthetic utility of the amorphous complex 13 has already been described (ref.10). A crystalline material is obtained by an alternative synthesis (equ.8). The π -complexes 14-21 are synthesized by salt-elimination procedures according to equations 9-13.



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