

Molecular Structure in the Solid State of Bis(pentamethylcyclopentadienyl)germanium

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Summary: Decamethylgermanocene GeCp^*_2 ($\text{Cp}^* = \text{Me}_5\text{C}_5$) was synthesized starting from a solution of GeBr and was obtained as colorless crystals. The molecular structure of **1** was determined by X-ray diffraction, showing that **1** is monomeric in the solid state, featuring two pentahapto-bonded Cp^* ligands in a bent configuration with a bending angle of 162° .

Ferrocene-like sandwich molecules of the heavier group 14 elements (Si, Ge, Sn, and Pb) represent the most extensive series of isolated main group metallocenes.¹ Most of these metallocenes exhibit a bent structure, which can be attributed to a stereochemically active lone pair at the central atom (Figure 1).² This explanation has been widely adopted in interpreting the structures of group 14 metallocenes. Furthermore numerous theoretical calculations have been performed, showing that the bent structure is energetically favored, supporting the experimental results.³

However these theoretical calculations also reveal that the difference in energy between the parallel and the bent configuration for a group 14 metallocene is very small (ca. 0.3–3 kcal/mol for ECp_2).^{3f} Therefore, the stereochemical influence of the metal-centered lone pair is relatively slight, and thus it is not surprising that also metallocenes with a parallel configuration are known for all the heavier elements of group 14: Si,⁴ Ge,^{3e} Sn,⁵ and Pb.⁶

Consequently it is difficult to predict theoretically if a group 14 metallocene will exhibit a parallel or a bent structure. This uncertainty is best demonstrated in the case of decamethylsilicocene, the only structurally characterized metallocene of silicon, which assumes both forms, a parallel and a bent one ($\alpha = 25.4^\circ$, $\beta = 167.4^\circ$) in the same crystal structure,⁴ although the bent structure should be energetically favored according to theoretical calculations (for SiCp_2 the bent structure should be energetically favored by 3 kcal/mol).^{3f} As the bent structure is the dominant one in solution, the parallel structure seems to be the result of a packing effect in the solid state. On descending group 14,

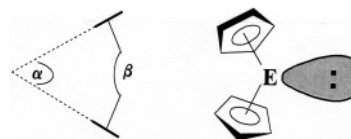


Figure 1. Model of the bent structure of a group 14 metallocene with the bending angle β and the angle between the planes α .

$\text{Cp}^*_2\text{Sn}^{3b}$ and Cp^*_2Pb^7 assume a bent structure in the solid state with an angle between the Cp planes of $\alpha = 36^\circ$ and 37° ($\beta = 155^\circ$ and 151°), respectively.

In the case of decamethylgermanocene no structural data about the solid state structure were available. The molecular structure was known only in the gas phase,⁸ having a bent structure with an angle between the Cp planes of 22° . However it was not certain if decamethylgermanocene exhibits a bent structure or a parallel one (or both) in the solid state. This question has now been answered as presented below: decamethylgermanocene exhibits only a bent structure in the solid state.

The most direct synthesis of decamethylgermanocene involves the reaction of a Ge(II) halide with a suitable Cp^* source, e.g., LiCp^* .^{3b} Another route, also reported by Jutzi and Hielscher in 1985, was based on the reduction of the tetravalent $\text{Cp}^*_2\text{GeCl}_2$ with potassium cyclooctatetraenide.⁹ We report here a third synthetic route, starting from a metastable solution of a Ge(I) halide, GeBr .¹⁰ Its reaction with LiCp^* gave GeCp^*_2 in 16% yield. This synthesis is based on the disproportionation of GeBr ,¹¹ as shown in eqs 1 and 2.



Decamethylgermanocene was isolated as colorless crystals, suitable for X-ray crystal structure analyses. It crystallizes in the monoclinic space group $C2/c$ with two independent molecules in the asymmetric unit, as is the case for decamethylsilicocene. Also the packing of the molecules inside the crystal, presented in Figure 2, is similar to that of SiCp^*_2 .

In contrast to decamethylsilicocene, in whose crystals two very different molecules were found (bent and parallel form), the two crystallographically different molecules in decamethylgermanocene exhibit nearly the same molecular structure

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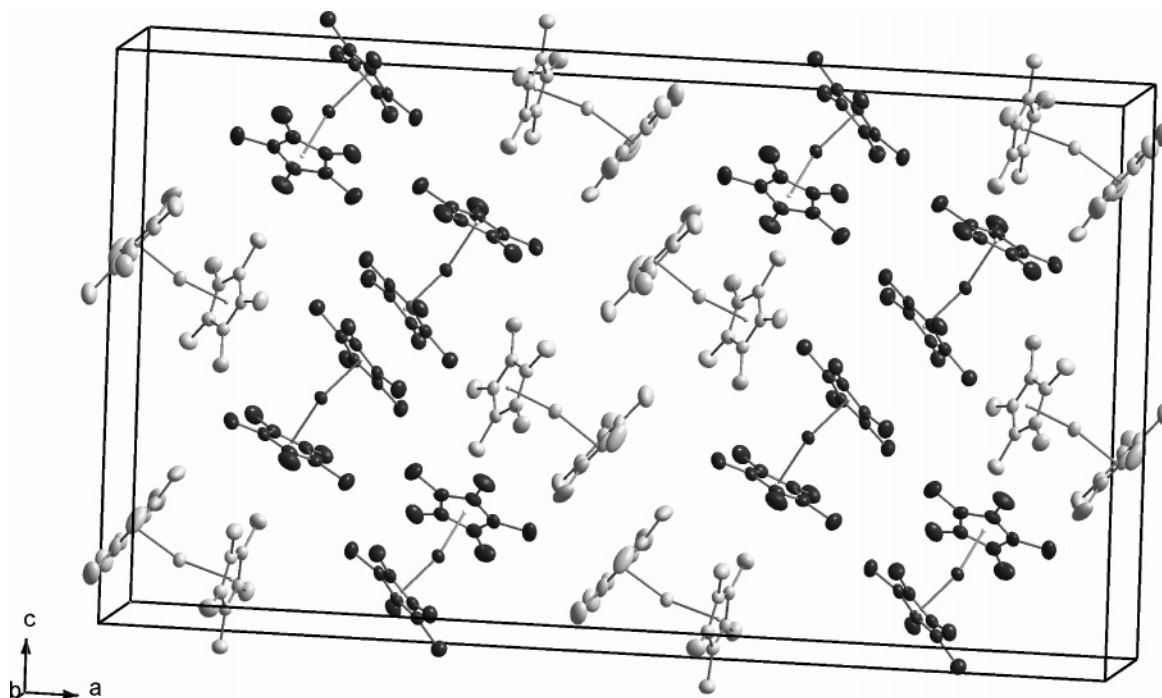


Figure 2. Packing of decamethylgermanocene in the crystal. The two different sites are marked by different shades of the molecules (hydrogen atoms are omitted for clarity).

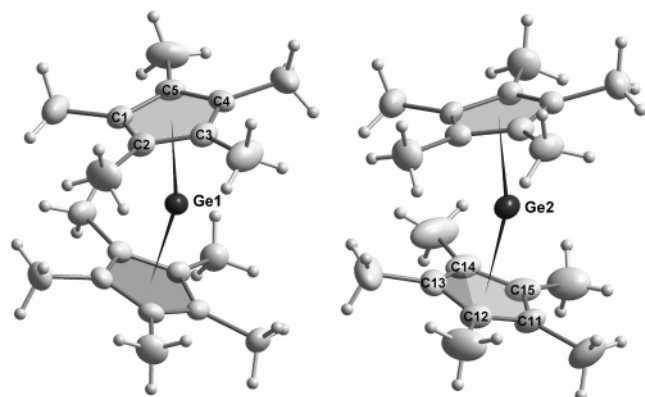


Figure 3. Molecular structure of the two independent molecules of decamethylgermanocene (the Cp ring planes are emphasized). Thermal ellipsoids with 50% probability. Selected bond length [Å] and angles [deg]: Ge1–C1: 2.414(4); Ge1–C2: 2.464(4); Ge1–C3: 2.605(4); Ge1–C4: 2.646(4); Ge1–C5: 2.533(4); Ge2–C11: 2.634(4); Ge2–C12: 2.525(4); Ge2–C13: 2.403(4); Ge2–C14: 2.427(4); Ge2–C15: 2.576(4); Ge1–Cp^c: 2.231; Ge2–Cp^c: 2.209; Cp^c–Ge1–Cp^c: 161.5; Cp^c–Ge2–Cp^c: 162.2.

(Figure 3), as the differences in bond distances and angles are about 0.04 Å and 1°, respectively (a situation similar to that as found in Cp^{*}₂Sn).¹²

This result may be rationalized in terms of packing effects that lead to two different structures (bent and parallel form) in the case of decamethylsilicocene, but lead only to small deviations in the case of decamethylgermanocene. Comparing the structural features of **1** in the solid state with those found in the gas phase (Table 1) shows that the average Ge–C distance and the Ge–Cp^{*}(centroid) distance are nearly identical, while the angle between the planes differs by 7° (25%), which might be the result of packing effects in the solid state.¹³

(12) Another difference from SiCp^{*}₂ is the fact that GeCp^{*}₂ exhibits no site symmetry; thus all atoms of both molecules in the crystal are independent. In SiCp^{*}₂ the silicon atom of the parallel form occupies a center of inversion.

Table 1. Comparison of the Structural Features of Decamethylgermanocene in the Crystal and the Gas Phase (distances are in Å and angles in deg)

| | Ge–Cp [*] _c | Ge–C (min.) | Ge–C (max.) | Ge–C (av) | α |
|-------------|---------------------------------|-------------|-------------|-----------|------|
| solid state | 2.213 | 2.397 | 2.645 | 2.514 | 28.8 |
| | 2.209 | 2.403 | 2.636 | 2.516 | 30.5 |
| gas phase | 2.21 | | | 2.51 | 22 |

The solid-state structure also reveals that the Cp^{*} rings in **1** have slipped, leading to different Ge–C distances, between 2.397 and 2.645 Å. This behavior has been observed in the corresponding decamethylsilicocene in the bent configuration (2.32–2.53 Å), decamethylstannocene (2.59–2.78 Å), and decamethylplumbocene (2.69–2.90 Å).

Comparing the structural features of decamethylgermanocene with those found in the unsubstituted compound GeCp₂ (Cp = C₅H₅) **1a** shows that the Ge–C distances in **1a** spread over a wider range (2.35–2.73 Å) than those in **1** (Table 1). Additionally, **1a** exhibits a larger bending angle of 50.4°. This means that the sterically more demanding Cp^{*} ligand leads, as expected, to a less bent arrangement of the Cp planes, reducing additionally the spread in the Ge–C bond length. This behavior is further continued in GeCp^s₂ (Cp^s = C₅Me₄SiMe₃), in which a parallel arrangement of the Cp planes is observed (β = 180°), leading to small deviations in the Ge–C distances (2.50–2.53 Å).^{3e}

With the structural characterization of decamethylgermanocene as the last missing member of the group 14 ECp^{*}₂ family (E = C is left out, as carbocene prefers a classical dicyclopentadienylcarbene structure¹⁵), it is possible to compare

(13) Another reason for the observed differences might be the fact that the gas-phase structure is measured at 409 K, while the crystal structure is measured at 150 K. This temperature difference corresponds to an energy difference of ca. 0.5 kcal mol⁻¹ (*kT*), being in the region of the calculated differences between parallel and bent form (e.g., 0.83 kcal mol⁻¹ for GeCp₂^{3f}). Additionally the electron diffraction value for α represents a thermal average value which has not been corrected for ring–metal–ring bending vibrations.⁸

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Table 2. Structural Features of ECp*₂ Compounds of Group 14 (E = Si–Pb) (distances are in Å and angles in deg)

| E | E–Cp* ^c | E–C (min.) | E–C (max.) | Ge–C (av) | α | β |
|----|--------------------|------------|------------|-----------|----|-----|
| Si | 2.12 | 2.32 | 2.54 | 2.43 | 25 | 167 |
| Ge | 2.21 | 2.40 | 2.64 | 2.54 | 30 | 162 |
| Sn | 2.40 | 2.59 | 2.78 | 2.68 | 36 | 155 |
| Pb | 2.50 | 2.69 | 2.90 | 2.79 | 37 | 151 |

metallocenes of Si, Ge, Sn, and Pb bearing the same ligand that are in the same phase (Table 2) for the first time.

Consideration of structural features presented in Table 2 shows a consistent behavior in these metallocenes: the bending angle β shrinks from silicon to lead, while the angle between the Cp planes α simultaneously increases. This behavior now becomes clear with the availability of the data for GeCp*₂, and we now have a good base for further theoretical investigations.

Experimental Section

Fifteen milliliters of a 0.266 M solution of GeBr (4 mmol) in 1,2-difluorobenzene/*n*-Bu₃N (5:1)—synthesized via a co-condensation technique¹⁰—was added to 723 mg of LiCp* (5 mmol) at –40 °C. The reaction mixture was slowly warmed to room temperature to give a nearly black solution, which then was heated at 55 °C for 1 h. Evaporating of the solvent in vacuo gave a black residue, which after extraction with pentane gave a yellow pentane extract. On

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concentrating the pentane extract, decamethylgermanocene crystallized in the form of colorless needles (ca. 300 mg, 0.87 mmol, 22%). Recrystallization from THF gave colorless crystals suitable for X-ray diffraction (221 mg, 0.64 mmol, 16%). ¹H NMR (250 MHz, C₆D₆): δ 1.95 (s, 15H, CH₃). ¹³C NMR (62 MHz, C₆D₆): δ 11.0 (CH₃), 118.9 (C). RAMAN (crystals): ν 2083, 1427, 592, 314, 153 cm⁻¹.

Crystal data for 1: C₂₀H₃₀Ge, fw 343.03, space group *C2/c*, *a* = 39.707(8) Å, *b* = 8.470(2) Å, *c* = 22.556(5) Å, β = 90.54°, *V* = 7590(5) Å³, *Z* = 16, *D*_{calc} = 1.201 g cm⁻³, *T* = 150(2) K, Mo K α radiation, graphite monochromator, Stoe-IPDS area detector, 22 934 reflections, 6573 unique (*R*_{int} = 0.0707), structure solution by direct methods, refinement on *F*² ($2\theta_{\max}$ = 49.98°), H atoms calculated, 419 parameters, *R*1 (*I* > 2 σ (*I*)) = 0.0431, *wR*2 (all data) = 0.0895, GOF (*F*²) = 1.022; computer programs SHELXS-97, SHELXL-97, Stoe IPDS software.

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Note Added in Proof. The same molecular structure of the title compound has been reported simultaneously by Weidenbruch et al.: Schöpper, A.; Saak, W.; Weidenbruch, M. *J. Organomet. Chem.* **2006**, *691*, 809.

Supporting Information Available: Crystallographic information for **1** (cif format) is available free of charge via the Internet at <http://pubs.acs.org>.

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