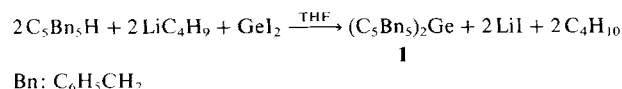


## Decabenzylgermanocene: Synthesis and Structure of a Monomeric, Air-Stable Germanocene\*\*

By Herbert Schumann,\* Christoph Janiak, Ekkehardt Hahn, Jörg Loebel, and Jerold J. Zuckerman\*

Decaphenylstannocene<sup>[1]</sup> has  $S_{10}$  symmetry with two parallel, staggered cyclopentadienyl rings and a stereochemically inert electron pair at Sn<sup>II</sup>. It has not yet been determined whether the corresponding compounds of Ge<sup>II(2)</sup> or Pb<sup>II(2)</sup> have similar structures. In the germanocenes studied up to now, ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ge,<sup>[3]</sup> ( $\eta^5$ -CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>Ge,<sup>[4]</sup> and ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ge,<sup>[5]</sup> on the other hand, the planes of the two cyclopentadienyl rings intersect at an angle of 34 to 50°; the compounds are very reactive.

We have now obtained decabenzylgermanocene, **1**, the first germanocene that, despite nonparallel cyclopentadienyl ring planes, is stable toward air. **1** is formed as large, pale yellow crystals by addition of germanium diiodide to a freshly prepared solution of pentabenzylcyclopentadienyllithium in tetrahydrofuran (THF).<sup>[6]</sup>



The X-ray structure determination<sup>[7]</sup> shows that **1** (Fig. 1) is monomeric, and that the two cyclopentadienyl rings are bonded in  $\eta^5$ -fashion to Ge<sup>II</sup>. The planes of the two cyclopentadienyl rings form an angle of 31°.

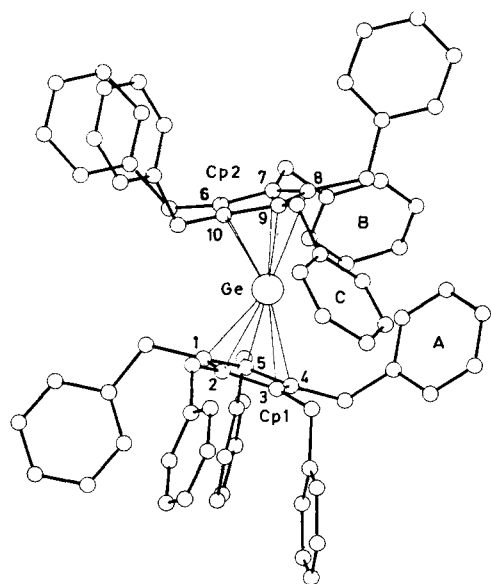


Fig. 1. Crystal structure of **1**. Selected bond lengths [Å] and bond angles [°]: Ge-Cp1 2.240(4), Ge-Cp2 2.288(4), Ge-C1 2.444(4), Ge-C2 2.429(3), Ge-C3 2.623(4), Ge-C4 2.636(4), Ge-C5 2.528(4), Ge-C6 2.489(4), Ge-C7 2.661(4), Ge-C8 2.723(4), Ge-C9 2.613(4), Ge-C10 2.441(4); Cp1-Ge-Cp2 163.1(1) (Cp: centroids of the cyclopentadienyl groups).

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[\*\*] This work was supported by the Fonds der Chemischen Industrie (H. S., C. J.), by the T.U.B.-O.U. Exchange Program (E. H., C. J., J. L.), and by the U.S. Office of Naval Research (J. J. Z.).

Of the ten benzyl (Bn) groups, seven are directed away from and three toward the central atom. The phenyl ring plane of Bn group A (distances: Ge-C<sub>ph</sub> 3.635 to 5.509 Å) is thereby intersected by the assumed vector of the lone pair of electrons on the germanium atom. The two Bn groups B and C (distances: Ge-C<sub>ph</sub> 4.107 to 5.847 and 3.739 to 5.554 Å, respectively) flank the space occupied by the lone pair electrons.

This arrangement of ligands explains the unexpected stability of **1** toward atmospheric oxygen. The Bn groups form a protective shield not only for the reactive positions of the cyclopentadienyl rings, but also, particularly, for the central germanium atom. A comparable interaction between the lone pair of electrons of a divalent element of the fourth main group and a phenyl group has been found in [(PhO)<sub>2</sub>PS<sub>2</sub>Sn]<sub>2</sub>.<sup>[8]</sup> In that case, too, a phenyl group is nearly perpendicular to the postulated vector of the lone pair electrons on tin, resulting also in unusual air-stability of the compound.

Received: May 3, 1985 [Z 1289 IE]  
German version: *Angew. Chem.* 97 (1985) 765

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[6] Experimental procedure: A solution of LiC<sub>5</sub>Bn<sub>5</sub> (2.90 mmol, freshly prepared from C<sub>5</sub>Bn<sub>5</sub>H [9] and LiC<sub>4</sub>H<sub>9</sub>) in 15 mL of THF at 0°C was added to a suspension of GeI<sub>2</sub> (0.47 g, 1.45 mmol) in 5 mL of THF. After stirring for 2 h, the THF was removed in vacuo, the oily brown residue was dissolved in 20 mL of benzene, the solution was decanted from insoluble matter, and the clear yellow-orange solution was concentrated until a precipitate began to appear. By addition of a layer of pentane, pale-yellow crystals were obtained. Total yield: 0.42 g **1** (26%). M.p. = 105°C (decomp.). Characterized by complete elemental analysis, IR, Raman, and mass spectra. <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>, 25°C): δ = 4.02 (s, 20H, CH<sub>2</sub>), 7.08 (m, 50H, C<sub>6</sub>H<sub>5</sub>).

[7] **1**: P<sub>2</sub>/n (non-standard arrangement of P<sub>2</sub>/c), a = 17.539(5), b = 23.329(4), c = 14.890(2) Å, β = 106.90(2)°, V = 5829.4 Å<sup>3</sup>, Z = 4, ρ<sub>calcd</sub> = 1.258 g/cm<sup>3</sup>; MoK<sub>α</sub> radiation, -105(3)°C, 1° ω-scans. Data reduction with Lorentz and polarization correction, no absorption correction (μ = 5.28 cm<sup>-1</sup>). Solution with Patterson techniques and refinement with Fourier techniques, 7602 independent reflections, 5456 reflections (I ≥ 2σ(I)) for calculation, R = 0.0438, R<sub>w</sub> = 0.0432. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, by quoting the depository number CSD 51372, the names of the authors, and the journal citation.

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## Synthesis of the Immunologically Essential Saccharide Sequence of the "Enterobacterial Common Antigen"

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Most bacterial surface antigens contain specific saccharide sequences as immunodeterminants, which permit the serological differentiation of the different species of a genus. In contrast, the "enterobacterial common antigen"

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