

Note

Molecular structure of decamethylgermanocene in the solid state [☆]

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Abstract

The low temperature X-ray structure analysis of decamethylgermanocene reveals two independent molecules in the unit cell, both of which have a bent sandwich structure with angles between the planes of the two C₅Me₅ rings of 31.26(0.09)° and 31.55(0.10)°, respectively. The perpendicular germanium to ring distances are 220 pm, corresponding to Ge–C bond lengths ranging from 240 to 266 pm. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

In 1980 Jutzi et al. [2] isolated the molecules Cp₂*Ge (1) and Cp₂*Sn (2) as the first representatives of bis(pentamethylcyclopentadienyl) compounds with elements of group 14. The synthesis of the corresponding lead compound Cp₂*Pb (3) followed just one year later [3]. The series was completed in 1986 with the synthesis of Cp₂*Si (4) [4], perhaps the most interesting compound in the series. Although X-ray crystallographic analyses of the compounds 2–4 have been carried out, the germanium compound 1 has only been characterised by electron diffraction in the gas phase [5]. Because of the uncertainties that sometimes accompany this method as well as to realise a direct comparison with the X-ray structures of the other Cp₂*M metallocenes of group 14, we now report on the structure of 1 in the solid state.

2. Results and discussion

Compound 1 was prepared according to the method of Jutzi et al. [2] by reaction of pentamethylcyclopentadienyllithium with the dioxane adduct of germanium dichloride.



Crystals suitable for X-ray diffraction analysis were obtained by twofold crystallisation from *n*-hexane at –20 °C in the form of long, pale yellow needles, mp = 202 °C. The unit cell contains 2 independent molecules of 1 which, however, differ from one another only insignificantly; thus, the following discussion of the bonding situation refers to the molecule 1 (Fig. 1).

The structure determination carried out at 153 K revealed that 1 possesses a bent sandwich structure with angles between the planes of the two C₅Me₅ rings of 31.26(9)° and 31.55(10)°, respectively. These values differ markedly from those derived from the gas phase structure [5] of 1 which amounted to 22(2)°. However, the difference in energy between the linear and bent forms for the heavier metallocenes of Group 14 is very small, and the stereochemical influence of the metal-centre lone pair of electrons is relatively small. The fact that the heavier metallocenes are still bent even though there is little energetic push from the metal-centred lone pair suggests that other bending mechanisms, such as core polarisation, should be considered for these molecules [6–9].

In spite of these minor differences in the degree of bending compound 1 fits well in the series of metallocenes Cp₂*Si, 1, Cp₂*Sn. While the silicon compound exhibits both a parallel and a bent arrangement of the rings (25.3°) in the

[☆] See [1].

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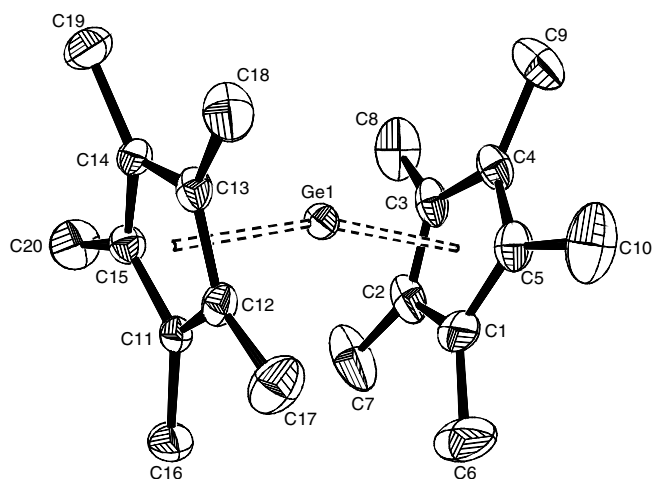


Fig. 1. Molecule of **1** in the crystal (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability.

Table 1
Selected bond lengths (pm) of **1**

Ge–C(1)	239.8(2)	Ge–C(11)	241.9(2)
Ge–C(2)	242.2(2)	Ge–C(12)	244.6(2)
Ge–C(3)	258.1(2)	Ge–C(13)	257.0(2)
Ge–C(4)	263.9(2)	Ge–C(14)	264.1(2)
Ge–C(5)	251.8(2)	Ge–C(15)	253.2(2)

solid state [4], the angle in the corresponding tin compound is somewhat enlarged to 36° , presumably due to the larger Sn–C bond length [2]. The distances from the germanium atom in **1** to the planes of the Cp* rings amount to 220 pm (molecule 1) and 222 pm (molecule 2), respectively. As a result of the bending the Ge–C separations also differ between 240 and 264 pm (Table 1), the higher values being found in the proximity of the free electron pair. The observed Ge–C bond lengths are not reflected in the C–C bonds of the staggered rings that are approximately equal at 141 pm.

3. Experimental

3.1. Preparation of **1**

Compound **1** was prepared by a slight modification of the literature procedure. An equimolar amount of a solution of *n*-BuLi (40 mL, 64.5 mmol) in hexane was added dropwise at -18°C to $\text{C}_5\text{Me}_5\text{H}$ (8.78 g, 64.5 mmol) in THF (30 mL) and the mixture stirred at room temperature for 15 h until completion of the reaction. The resultant white suspension was cooled to -78°C and half an equivalent of $\text{GeCl}_2 \cdot \text{dioxane}$ (7.47 g, 32.3 mmol) in THF (150 mL) was slowly added dropwise. After removal of the solvents under vacuum, the solid was extracted with

n-hexane and the obtained pale-yellow long needles were crystallised twice from *n*-hexane. This provided pale-yellow needles (8.29 g, 75% yield, [2]: 78%), mp = 202°C , that were suitable for an X-ray crystallographic analysis. ^1H NMR (C_6D_6): δ 1.93 (s, CH_3); ^{13}C NMR (C_6D_6): δ 10.17 (s, CH_3), 118.15 (C_5Me_5).

3.2. X-ray structure analysis of **1**

A pale-yellow crystal of **1** was mounted in an inert oil. Data collection was performed with a STOE IPDS area detector using graphite monochromated Mo $\text{K}\alpha$ radiation (71.073 pm). The structure was solved by direct phase determination and refined by full-matrix least-squares techniques against F^2 with the SHELXL-97 program package [10]. Hydrogen atoms were placed in the calculated positions, and all other atoms were refined anisotropically.

$\text{C}_{20}\text{H}_{30}\text{Ge}$, formula weight 343.03, crystal dimensions: $0.60 \times 0.35 \times 0.27 \text{ mm}^3$, temperature 153(2) K, monoclinic, space group $C2/a$, $a = 3979.12(15)$, $b = 845.36(2)$, $c = 2254.66(10)$ pm, $\beta = 90.445(5)^\circ$, $V = 7584.0(5) \times 10^6 \text{ pm}^3$, $D_{\text{calcd}} = 1.202 \text{ g cm}^{-3}$, $Z = 16$, $2\theta_{\text{max}} = 52^\circ$, collected reflections 39381, observed reflections 5852, $\mu = 1.609 \text{ mm}^{-1}$, $R1 = 0.0281$, $wR2$ (all data) = 0.0706 for 399 parameters, GOF = 0.938 [11].

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