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The dimethylaminoethyl-tetramethylcyclopentadienyl ligand in germanium(II) chemistry: synthesis, properties and X-ray crystal structural data of $(Me_2NCH_2CH_2)Me_4C_5GeCl$ ☆

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Abstract

1-(Dimethylaminoethyl)-2,3,4,5-tetramethylcyclopentadienyl(chloro)germylene (**1**) is prepared from $GeCl_2 \cdot$ dioxane and 1-(dimethylaminoethyl)-2,3,4,5-cyclopentadienyllithium. In **1** the nitrogen atom of the side chain is coordinated to the Ge(II) center. As a consequence of N coordination, the Ge–Cl bond is one of the longest ever found, and the Ge–Cp interaction is in between π and σ bonding.

Keywords: Germanium; Cyclopentadienyl; Germylene; Intramolecular coordination

1. Introduction

Cyclopentadienyl ligands with the dimethylaminoethyl functionality have been introduced into the chemistry of the s, p, d and f block elements only recently [1–15]. The additional donor function in the side chain of a Cp fragment can drastically influence the structure and reactivity of the corresponding compounds. Thus the coordination of the amino group is able to reduce electron deficiency at the respective central atom; a non-coordinating group may exert substituent effects, influence the solubility and allow surface fixation of the cyclopentadienyl moiety.

In the chemistry of the Group 14 elements, merely a few dimethylaminoethyl cyclopentadienyl compounds with tetravalent silicon and tin have been described in the literature; they are potential reagents for Cp transfer [11]. Compounds with a divalent Group 14 element are unknown so far. In this paper, we describe the synthesis, the unexpected structure and some properties of the first germanium(II) compound possessing a dimethylaminoethyl–cyclopentadienyl ligand.

2. Synthesis, NMR data and X-ray crystal structure of 1

Reaction of the lithiated 1-(dimethylaminoethyl)-2,3,4,5-tetramethylcyclopentadiene ($Cp^{\wedge}Li$) with one equivalent of $GeCl_2 \cdot$ dioxane in tetrahydrofuran (THF) leads to the formation of 1-(dimethylaminoethyl)-2,3,4,5-tetramethylcyclopentadienyl(chloro)germylene ($(Me_2NCH_2CH_2)Me_4C_5GeCl$ ($Cp^{\wedge}GeCl$)) (**1**). Compound **1** is isolated with good yields as colourless crystals, which are very soluble in THF and $CHCl_3$, less soluble in benzene and toluene and only slightly soluble in aliphatic hydrocarbons. It is stable as a solid and in solution at room temperature and melts at 98 °C under decomposition. The stability against air is strongly increased compared with the stability of Me_5C_5GeCl (**2**); while **2** decomposes within seconds [16], **1** slowly decomposes only within some days.

The ^1H and ^{13}C NMR spectra of **1** are in accord with a highly fluxional structure in solution. Resonances for three sets of methyl groups and three types of ring carbon atom are observed at room temperature as well as at -60 °C. The ^1H NMR spectrum measured in $CDCl_3$ indicates the coordination of the nitrogen lone pair to the germanium atom by a low field shift of the CH_2N signals and the Me_2N signals in relation to the corresponding signals of $Cp^{\wedge}H$ [17] and other $Cp^{\wedge}$

☆ Dedicated to Professor Hideki Sakurai on the occasion of his retirement.

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compounds with a non-coordinating dimethylamino function [11]. Thus the fluxional behaviour of **1** resembles that observed for the aluminum compound $(Me_2NCH_2CH_2)Me_4C_5AlCl_2$ [8]; owing to steric constraints, only a "windshield-wiper"-type migration process takes place.

Crystals of **1** suitable for an X-ray crystallographic study have been obtained by crystallization in THF at −30 °C. Fig. 1 shows the molecular structure of **1** together with representative bond lengths and bond angles. Crystallographic data for **1** are summarized in Table 1 [18]; atomic coordinates are given in Table 2.

Table 1
Crystallographic data for **1**

Empirical formula	$C_{13}H_{22}ClGeN$
Space group	$P2_1$
Z	2
a (Å)	6.798(2)
b (Å)	11.661(3)
c (Å)	9.129(3)
β (°)	104.21(3)
V (Å^3)	701.5(4)
d_{calc} (g cm^{-3})	1.422
Crystal size (mm)	0.7×0.4×0.3
T (K)	158
Radiation	Mo Kα
Scan type	ω
μ (mm^{-1})	2.349
2θ range (°)	4–60
Number of reflections collected	4569
Number of reflections with $I > 2\sigma(I)$	3559
$F(000)$	312
R_F (%)	3.81
wR_{F^2} (%)	11.0

Compound **1** crystallizes in the space group $P2_1$. The nitrogen atom of the dimethylaminoethyl group is coordinated to the germanium atom. The Ge–N bond length is 2.286(3) Å; the Ge–Cl bond length is 2.369(1) Å. The cyclopentadienyl fragment is bonded to the Ge center in an asymmetric η^2 fashion. The Ge–C(4) distance is 2.180(3) Å and the Ge–C(5) distance is 2.402(3) Å; typical Ge–C σ bond distances in germanium(II) compounds vary between 1.98 and 2.14 Å [19]. Marked variations within the C–C bond lengths in the Cp unit are observed in **1**. Rather long distances are found for C(4)–C(5) (1.451(5) Å) and for C(4)–C(3) (1.450(5) Å), whereas the remaining C–C bonds are comparatively short. A deviation from planarity of the C_5 perimeter leads to an angle of 3.5° between the planes C(1)–C(2)–C(3)–C(5) and C(3)–C(4)–C(5); C(4) is oriented towards the Ge atom. A pronounced deviation of the methyl group at C(4) to the opposite side of the ring is indicated by an angle of 17.4° between the C–C bond vector and the plane C(3)–C(4)–C(5).

A comparison of the structural data for **1** with those of other cyclopentadienyl germanium(II) compounds such as Me_5C_5GeCl (**2**) [20], $Me_5C_5GeCH(SiMe_3)_2$ (**3**) [21], $Me_5C_5GeC(SiMe_3)_3$ (**4**) [19] and $Me_5C_5GeC_6H_2^tBu_3$ (**5**) [19] shows some differences worth mentioning. In **2**–**5**, the Cp ligands are η^2 bonded to the respective germanium atom; as a consequence, the Ge–C bonds are rather long (2.24–2.30 Å), and the C–C bond distances within the Cp ring vary only to a small extent, with the exception of those bonds between the carbon

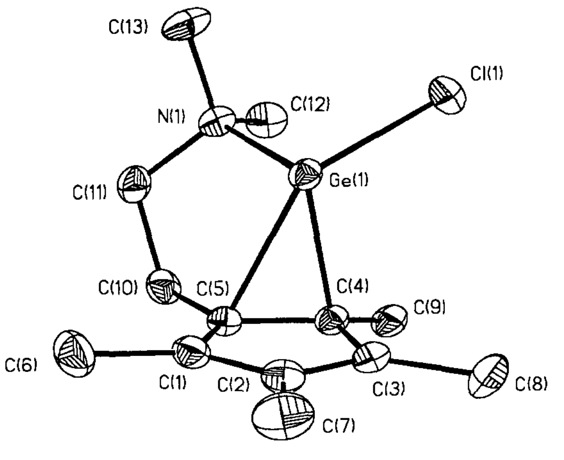

Fig. 1. Molecular structure of **1**. Selected bond lengths and angles are as follows: Ge–Cl, 2.369(1) Å; Ge–N, 2.286(3) Å; Ge–C(4), 2.180(3) Å; Ge–C(5), 2.402(3) Å; C(1)–C(2), 1.414(5) Å; C(2)–C(3), 1.396(5) Å; C(3)–C(4), 1.450(5) Å; C(4)–C(5), 1.451(5) Å; C(5)–C(1), 1.403(5) Å; C(4)–Ge–N, 95.6(1)°; C(4)–Ge–Cl, 98.4(1)°; C(5)–Ge–N, 77.5(1)°; C(5)–Ge–Cl, 129.1(1)°; N–Ge–Cl 89.7(1)°; C(1)–C(5)–Ge, 88.7(2)°; C(3)–C(4)–Ge, 86.3(2)°; C(1)–C(2)–C(3) 108.7(3)°; C(2)–C(3)–C(4), 108.1(3)°; C(3)–C(4)–C(5), 106.4(3)°; C(4)–C(5)–C(1), 107.4(3)°; C(5)–C(1)–C(2) 109.2(3)°.

Table 2
Atomic coordinates and isotropic displacement parameters U_{eq} for **1**

	x ($\times 10^{-4}$)	y ($\times 10^{-4}$)	z ($\times 10^{-4}$)	U_{eq} [a] ($\times 10^{-3}$ Å^2)
Ge(1)	3696(1)	7030(1)	2245(1)	19(1)
Cl(1)	5816(1)	7300(1)	4699(1)	32(1)
N(1)	1381(4)	6109(2)	3269(3)	23(1)
C(1)	1071(5)	7842(3)	−342(4)	24(1)
C(2)	2845(5)	8476(3)	−338(4)	25(1)
C(3)	3510(6)	9011(3)	1064(4)	25(1)
C(4)	2156(5)	8685(3)	1997(4)	21(1)
C(5)	581(5)	7982(3)	1053(4)	21(1)
C(6)	−59(5)	7071(6)	−1603(3)	35(1)
C(7)	3882(7)	8504(4)	−1621(5)	38(1)
C(8)	5280(6)	9809(4)	1559(5)	37(1)
C(9)	2009(8)	9333(4)	3409(5)	29(1)
C(10)	−1103(5)	7404(3)	1572(4)	26(1)
C(11)	−550(6)	6172(3)	2088(4)	28(1)
C(12)	1104(6)	6544(4)	4735(4)	31(1)
C(13)	2099(8)	4918(4)	3479(6)	36(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atoms involved in Ge–Cp π bonding. Also the deviations from planarity of the ring carbon atoms are very small. As a consequence of π bonding, the angles between the ring plane and the corresponding Ge–C vectors are about 70° (**3**, 71.1° and 69.6°; **4**, 71.4° and 68.1°; **5**, 70.7° and 70.4°).

A quite different situation is found for **1**. Here, the germanium atom is in between π and σ bonding. Strongly differing C–C bond distances and a marked deviation of the methyl group at C(4) indicate that a cyclopentadiene compound with a germanium(II) unit σ bound to an allylic carbon atom is preformed. On the contrary, the germanium atom is still positioned within the π cloud of the C_5 perimeter (the angle between the C(3)–C(4)–C(5) plane and the C(4)–Ge vector is smaller than 90°, i.e. 78.0°). According to the usual terminology [1], a π bond situation is still given.

Another significant feature in the structure of **1** is the extremely long Ge–Cl bond. The Ge–Cl bond length of 2.369 Å is much larger than those found for $GeCl_2$(g) (2.183(4) Å) [22], Me_5C_5GeCl (g) (2) (2.258(12) Å) [20], $GeCl_2 \cdot$ dioxane (s) (2.25 and 2.28 Å) [23], $GeCl_2 \cdot$ benzothiazole (s) (2.254(1) and 2.262(1) Å) [24], (2,4,6-tri-tert-butylphenyl)chlorogermylene (s) (2.28(1) Å) [25], $RbGeCl_3$ (s) (2.307(4) and 2.319(5) Å) [26], *trans*-$GeCl_4$(pyridine)$_2$ (s) (2.27(3) Å) [27] or Cs_2GeCl_6 (s) (2.35 Å) [28]. A similar Ge–Cl bond length (2.374(1) Å) is present in $Me_2Si(N^tBu)(N^tBuH)GeCl$ [29], another compound with intramolecular N coordination.

As can be seen from the above discussion, the intramolecular coordination of the amino group in **1** induces some marked structural changes within the CpGeCl unit. As a consequence of coordination, the degree of π bonding between the Ge atom and the Cp unit is reduced, and the Ge–Cl bond is drastically weakened. It is not possible to coordinate a nitrogen donor to the respective germanium center in Cp germanium(II) compounds of the type CpGeR. In the case of **1** the intramolecular N donor cannot be replaced by excess pyridin [30]. Thus there is no doubt that the observed coordination is mainly due to a pronounced chelate effect.

Future work will concentrate on the substitution chemistry of **1** utilizing the weakness of the Ge–Cl bond.

3. Experimental section

All manipulations were performed in an atmosphere of dried oxygen-free argon using Schlenk-type flasks. Solvents and reagents were appropriately dried and purified. The following instruments were used: melting-point measurements, Büchi 5010 capillary melting-point apparatus; ^{1}H NMR spectroscopy, Bruker AM 300 (300.1 MHz) spectrometer; ^{13}C spectrum, Bruker AM 300 (75.5 MHz, ^{1} decoupled); mass spectroscopy (MS), Autospec, Sison's instruments. The elemental analysis was carried out by the analytical laboratory of the Universität Bielefeld.

1-(Dimethylaminoethyl)-2,3,4,5-tetramethylcyclopentadiene was prepared as described before [17].

3.1. *1-(Dimethylaminoethyl)-2,3,4,5-tetramethylcyclopentadienyl(chloro)germylene(1)*

Within 5 min, 13.5 ml of 1.6 M solution of butyllithium in hexane is added to a solution of 4.08 g 1-(dimethylaminoethyl)-2,3,4,5-tetramethylcyclopentadiene (21.1 mmol) in 15 ml of THF at −60 °C. The mixture is stirred for another 5 min and is then dropped slowly into a solution of 4.89 g $GeCl_2 \cdot$ dioxane (21.1 mmol) in 15 ml of THF at the same temperature. Within 1 h the mixture is allowed to warm to room temperature. Storage of the solution at −30 °C for some days yields 4.56 g of **1** (72%) as colourless crystals. Anal. Found: C, 51.95; H, 7.27; N, 4.67. $C_{13}H_{22}ClGeN$ (*M* = 300.37) calc.: C, 51.98; H, 7.38; N, 4.66%. Melting point, 98 °C MS (electron impact): *m/z* (%) (only base peak and maxima of Ge containing fragments): 301 (3) [M^+], 266 (6) [$M^+ - Cl$], 58 (100) [$Me_2NCH_2^+$]. ^{1}H NMR (C_6D_6): δ 1.85 (s, 6H, CH_3), 1.87 (s, 6H, CH_3), 2.02 (s, 6H, $N(CH_3)_2$), 2.07 (m, 4H, CH_2CH_2) ppm. ^{1}H NMR ($CDCl_3$): δ 1.94 (s, 6H, CH_3), 1.98 (s, 6H, CH_3), 2.35 (s, 6H, $N(CH_3)_2$), 2.57 (m, 4H, CH_2CH_2) ppm, ^{13}C NMR (C_6D_6): δ 10.56, 10.66 (CH_3), 21.29 (CH_2), 43.82 ($N(CH_3)_2$), 58.97 (NCH_2), 109.19, 118.83, 128.79 (ring C) ppm.

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