Synthesis and Structure of a Germylene Bearing a 1,8-Dimethoxyanthracene Ligand

Makoto Yamashita, Hiromi Murakami, Toshifumi Unrin-in, Atsushi Kawachi,
Kin-ya Akiba,† and Yohsuke Yamamoto*
Department of Chemistry, Graduate School of Science, Hiroshima University,
1-3-1 Kagamiyama, Higashi-Hiroshima 739-8526
†Advanced Research Center for Science and Engineering, Waseda University,
3-4-1 Ohkubo, Shinjuku-ku, Tokyo 165-8555

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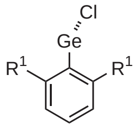
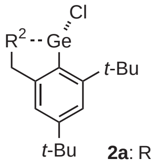
A novel chlorogermylene compound, (1,8-dimethoxy-9-anthracenyl)chlorogermylene, has been synthesized by the reaction of $GeCl_2$•dioxane and 9-lithio-1,8-dimethoxyanthracene. X-ray crystallographic study of the germylene revealed the bis-coordination of the oxygen atoms at the 1,8-positions to the germanium(II) center and the elongation of the Ge–Cl bond caused by the coordination.

Organochlorogermylenes (RGeCl) are intriguing species in low-valent germanium chemistry with regard to structure and bonding.[1] They are also important substrates for preparation of low-valent germanium derivatives with a Ge–Ge triple bond[1o,p] by reductive dehalogenation[1e,n] reactions. The structurally determined organochlorogermylenes reported so far include those bearing the sterically bulky aromatic ligands (R = C_6H_3-2,6-Mes_2[1g] (**1a**) and C_6H_3-2,6-$Trip_2$[1i,m] (**1b**)) and those having the ligands with a donor functionality to the germanium center (R^2 = Me_2N (**2a**)[1h] and *t*-BuO (**2b**)[1k]).



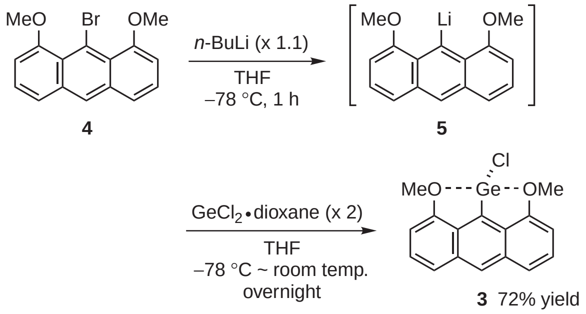
1a: $R^1 = C_6H_2$-2,4,6-Me (Mes)
1b: $R^1 = C_6H_2$-2,4,6-*i*-Pr (Trip)



2a: $R^2 = Me_2N$
2b: R^2 = *t*-BuO

We have investigated a 1,8-dimethoxy-9-anthracenyl ligand[2] in chemistry of low-valent derivatives of heavier group 14 elements and found that the ligand effectively stabilizes divalent germanium species by intramolecular bis-coordination of the two methoxy groups. We present here the first results concerning the synthesis and structure of intramolecular bis-coordinated germanium(II) compound, (1,8-dimethoxy-9-anthracenyl)chlorogermylene (**3**). This ligand was recently synthesized in our laboratory and successfully applied in the chemistry of hypervalent carbon[2a] and boron[2b] compounds. The lone pairs on the oxygen atoms at the 1,8-positions coordinate with the empty p orbital of the central carbon or boron atom at the 9-position to form a three-center-four-electron bond.

The introduction of the anthracenyl ligand to the germanium center was achieved as shown in Scheme 1. 1,8-Dimethoxy-9-bromoanthracene (**4**) was treated with *n*-BuLi (1.6 mol/L in hexane, 1.1 molar amt) in THF at −78 °C for 1 h.[2b] The resulting lithiated anthracene **5** in THF was added to the THF solution of $GeCl_2$•dioxane[3] (2.0 molar amt) at −78 °C, and the reaction mixture was allowed to warm to ambient temperature overnight. After the volatile materials were removed under reduced pressure, the residue was washed with 1,2-dichloroethane and then dichloromethane to afford almost pure chlorogermylene **3** in 72% yield as a yellow solid.[4] The germylene **3** is stable for exposure to the air. The bis(anthracenyl)germylene, the disubstituted compound, was not detected.



Scheme 1.

Recrystallization of **3** from dichloromethane (ca. −18 °C) gave the yellow crystals suitable for X-ray crystallographic analysis.[5] The analysis revealed that the germanium(II) center in **3** is bis-coordinated[6] to the two oxygen atoms at the 1,8-positions in an almost symmetrical manner, as shown in Figure 1. Some features deserve comments. (i) The atomic distances between the germanium atom and the oxygen atoms (Ge1–O1 = 2.386(5) Å; Ge1–O2 = 2.357(5) Å) are longer than the covalent Ge–O bond (1.65 Å)[7] but shorter than the atomic distances between the corresponding ipso carbons (C9–C1 = 2.46 Å; C9–C8 = 2.46 (Å). (ii) Furthermore the exo bond angles at the 1,8-positions (O1–C1–C11 = 112.1(6)°; O2–C8–C14 = 112.1(6)°) are smaller than the expected angle of 120°, displaying that both of the methoxy groups tilt to the germanium center. These features clearly showed the existence of the attractive interaction between the germanium atom and the oxygen atoms. (iii) The geometry around the oxygen atoms are planar (the sum of the one C–O–C and the two C–O–Ge is 360°), which may indicate their oxonium character. (iv) The atoms Ge1, O1, and O2 are located on the same plane defined by the anthracene skeleton. (v) Because of the electron-donation by the coordination, the Ge1–Cl1 bond length (2.311(2) Å) is elongated compared to that in the noncoordinated **1b** (2.2026(19) Å) and close to that in the nitrogen-coordinated **2a** (2.3283(4) Å). The bond angle Cl1–Ge1–C9 (96.44(19)°) is also similar to that in **2a** (94.04(4)°) and smaller than that in **1b** (101.31(15)). Thus the lone pairs on the oxygen atoms at the 1,8-positions interact with the empty p orbital of the germanium(II) center at the 9-position to form a three-center-four-electron bond. The geometry around the

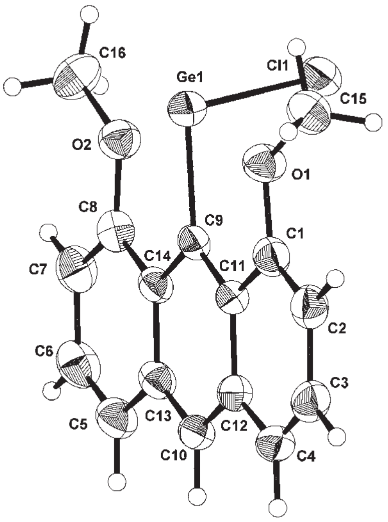


Figure 1. Crystal structure of **3** with 30% probability ellipsoids. Selected bond lengths (Å) and angles (°): Ge1–Cl1 = 2.311(2), Ge1–O1 = 2.386(5), Ge1–O2 = 2.357(5), Ge1–C9 = 1.992(7), O1–C1 = 1.386(8), O1–C15 = 1.439(9), O2–C8 = 1.384(9), O2–C16 = 1.441(9), Cl1–Ge1–C9 = 96.44(19), O1–Ge1–O2 = 148.79(18), O1–Ge1–C9 = 74.2(2), O2–Ge1–C9 = 74.6(2), Ge1–O1–C1 = 112.5(4), Ge1–O2–C8 = 113.0(4), C15–O1–C1 = 118.6(6), C16–O2–C8 = 118.9(6), O1–C1–C11 = 112.1(6), O2–C8–C14 = 112.1(6).

germanium atom may be formally regarded as a distorted trigonal bipyramid if including the lone pair on the germanium atom.

The coordination of the methoxy groups to the germanium center is supported by the ^{1}H NMR spectra. The ^{1}H NMR chemical shift of the methyl groups bonded to the coordinating oxygen atoms is shifted to the downfield (δ 4.34) from the corresponding methyl groups in **4** (δ 4.04) and in the 1,8-dimethoxyanthracene (δ 4.09). This means the electron deficiency of the oxygen atoms in **3**.

In this way we synthesized a novel chlorogermylene **3** with the bis-coordination mode, which has been rare compared to the monocoordination mode in the low-valent chemistry of heavier Group 14 elements.

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4 Spectral data for **3**: mp 192–193 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.34 (s, 6H), 6.88 (d, 2H, $J = 7.6$ Hz), 7.42 (dd, 2H, $J = 7.6$ and 8.4 Hz), 7.68 (d, 2H, $J = 8.4$ Hz), 8.32 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (ar. = aromatic; quat. = quaternary) δ 56.59 (OCH_3), 102.80 (ar. CH), 122.25 (ar. CH), 125.37 (ar. CH), 125.50 (ar. CH), 127.57 (ar quat C), 132.63 (ar quat C), 156.25 (ar quat C) (Although four peaks should appear as aromatic quaternary carbons, only three peaks were observed.).

5 Crystal data for **3**: $C_{16}H_{13}ClGeO_2$, fw 345.30, monoclinic, $P2_1/a$ (No. 14), $a = 14.867(1)$, $b = 10.589(1)$, $c = 9.0960(6)$ Å, $\beta = 91.013(7)°$, $V = 1431.7(2)$ Å^3, $Z = 4$, $D_{calcd} = 1.602$ g cm^{-3}, $R = 0.0625$ for 2846 observed reflections (183 parameters) with $I > 2\sigma(I)$, $R_w = 0.2199$ for all data, GOF = 1.198 (CCDC No. 264359). The data were collected at 150 K on a Mac Science DIP2030 imaging plate equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å).

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