Distorted Germyllithium Induced by Intramolecular Coordination of an Amino Group: Synthesis and Structures of {Tris[2-(dimethylamino)phenyl]germyl}lithium

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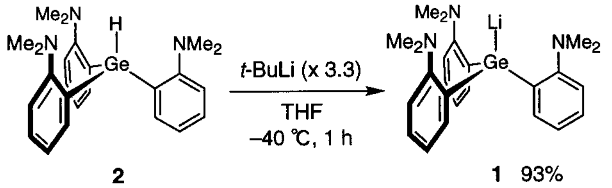
{Tris[2-(dimethylamino)phenyl]germyl}lithium (**1**) has been prepared. The X-ray analysis shows that **1** exists as a monochelated monomer in the solid state, where the lithium atom is coordinated to one of the amino groups and two THF molecules. The interaction between the lithium atom and the amino group induces the distortion of the geometry around the germanium atom. In solution, however, two species exist as evidenced by ^{1}H-, ^{7}Li-, and ^{13}C-NMR spectra. The temperature-dependent behavior of these two species has been analyzed by variable-temperature NMR studies.

Introduction

Among a variety of Group-14 element−alkali metal compounds, germyllithium compounds have been well studied from the synthetic point of view,[1] but structural studies are still scarce; only six structures of germyllithium compounds have been determined by X-ray analysis[2] and the substituents have been limited to the tris(trimethylsilyl)silyl group and germole skeletons. We report here the preparation of {tris[2-(dimethylamino)phenyl]germyl}lithium (**1**) and its structure in the solid state and in solution, focusing on the interaction between the lithium atom and the amino group[3] as well as on the germanium−lithium bonding character.

Results and Discussion

The germyllithium **1** was prepared by deprotonation of the hydrogermane[4] **2** with *tert*-butyllithium (3.3 equiv.) in THF at −40°C in 93% yield, as shown in Scheme 1; the yield was estimated by quenching with D_2O. When **2** was treated with a deficient amount of *tert*-butyllithium (1.2 equiv.), **1** could be isolated as pale yellow crystals in 33% yield after recrystallization from toluene at −20°C.



2

1 93%

Scheme 1

Structure in the Solid State

X-ray analysis of the crystal reveals that **1** has a monomeric structure in the solid state, as shown in Figure 1. The selected bond lengths, bond angles, and torsion angles are listed in Table 1. The most striking feature is the highly distorted geometry around Ge(1) due to the unsymmetrical interaction of Li(1) with the amino group. Li(1) bonded to Ge(1) is coordinated to N(1) of one of the three NMe_2 groups, forming a five-membered chelate ring consisting of Li(1), Ge(1), C(1), C(2), and N(1). Li(1) is also coordinated to O(1) and O(2) of two THF molecules arising from the reaction solvent. The Li(1)−Ge(1) bond length [2.598(9) Å] is the shortest among those of the characterized germyllithium compounds [2.613(3)−2.759(24) Å].[2] The Li(1)−N(1) bond length [2.15(1) Å] is longer than the sum of the covalent radii (Li 1.23 Å; N 0.70 Å),[5] but normal as coordinative Li−N bonds (2.01−2.17 Å).[3] The intramolecular coordination of N(1) to Li(1) reduces the angle of Li(1)−Ge(1)−C(1) to 83.9(3)°. As a result, Li(1), Ge(1), C(9), and C(17) are almost coplanar; the sum of the three angles of Li(1)−Ge(1)−C(9), Li(1)−Ge(1)−C(17), and C(9)−Ge(1)−C(17) is 359.5°. In spite of the distorted geometry, however, there are no significant differences among the three Ge−C bonds [2.042(6), 2.030(5), and 2.054(5) Å] and the three C−Ge−C angles [96.8(2), 99.2(2), and 98.4(2)°]. It is also noted that the sum of the latter (294.4°) is strongly reduced from the sp^3 tetrahedral value (328°). Thus, the geometry of **1** may be designated pyramidal rather than distorted tetrahedral.

In order to obtain information about the electronic structure, we performed an ab initio calculation of $\mathbf{1}\cdot(THF)_2$ at HF level using the 6-311+G* basis set on Li and Ge atoms and the 6-31G basis set on H, C, N, and O atoms,[6] based on the geometry of the crystal structure. The natural bond orbital analysis reveals that the anionic electrons on Ge(1) have a considerably higher s character (s 57.3%; p 42.6%; d 0.1%) than the sp^3-hybrid orbitals,[7] whereas the three Ge−C bonds have a higher p character [Ge(1)−C(1), 86.7%; Ge(1)−C(9), 84.0%; Ge(1)−C(17), 85.2%]. These p

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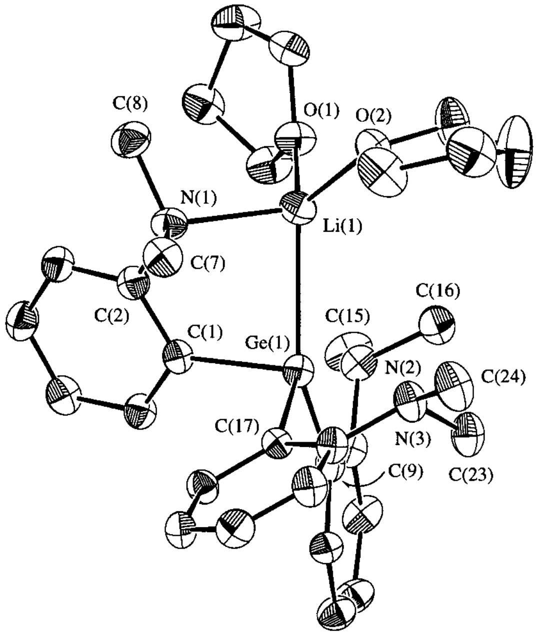


Figure 1. Molecular structure of **1**·(THF)$_2$ with 30% probability ellipsoids (H atoms omitted for clarity); selected bond lengths [Å] and angles [°]: Ge(1)−Li(1) 2.598(9), Ge(1)−C(1) 2.042(6), Ge(1)−C(9) 2.030(5), Ge(1)−C(17) 2.054(5), Li(1)−N(1) 2.15(1), Li(1)···N(2) 4.11(1), Li(1)···N(3) 4.43(1), Ge(1)−Li(1)−N(1) 83.7(3), Li(1)−Ge(1)−C(1) 83.9(3), Li(1)−Ge(1)−C(9) 138.3(3), Li(1)−Ge(1)−C(17) 122.8(3), C(1)−Ge(1)−C(9) 96.8(2), C(1)−Ge(1)−C(17) 99.2(2), C(9)−Ge(1)−C(17) 98.4(2)

Table 1. Selected bond lenghts [Å], bond angles [°], and torsion angles [°] for **1**·(THF)$_2$

Ge(1)−C(1)	2.598(9)
Ge(1)−C(9)	2.042(6)
Ge(1)−C(17)	2.030(5)
Li(1)−N(1)	2.15(1)
Li(1)···N(2)	4.11(1)
Li(1)···N(3)	4.43(1)
Li(1)−Ge(1)−C(1)	83.9(3)
Ge(1)−Li(1)−N(1)	83.7(3)
Li(1)−Ge(1)−C(9)	138.3(3)
Li(1)−Ge(1)−C(17)	122.8(3)
C(9)−Ge(1)−C(17)	98.4(2)
C(1)−Ge(1)−C(9)	96.8(2)
C(1)−Ge(1)−C(17)	99.2(2)
Li(1)−Ge(1)−C(1)−C(2)	−23.5(4)
Li(1)−Ge(1)−C(9)−C(10)	−9.1(7)
Li(1)−Ge(1)−C(17)−C(18)	−66.1(5)
Ge(1)−C(1)−C(2)−N(1)	−10.4(6)
Ge(1)−C(9)−C(10)−N(2)	6.1(8)
Ge(1)−C(17)−C(18)−N(3)	−5.8(7)

characters are almost equivalent to each other, in agreement with the similarity of the Ge−C bond lengths. The molecular orbital analysis of the anionic electrons (HOMO) indicates that the lithium atom is located not along the vector of the anionic electrons but aside from it, as shown in Figure 2. This may be represented as an intramolecular separated ion pair, which is not unusual if the Ge−Li interaction is weak while the N−Li coordinative interaction is relatively strong.

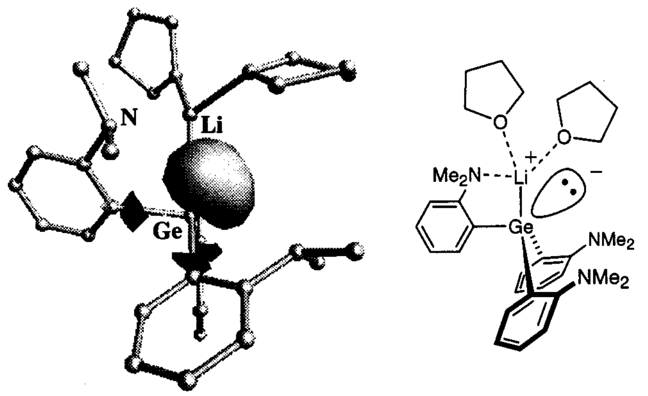


Figure 2. HOMO of **1**·(THF)$_2$ calculated at HF level using the 6-311+G* basis set on Li and Ge atoms and the 6-31G basis set on H, C, N, and O atoms; geometry is based on the crystal structure; its schematic representation is also shown

Structures in Solution

In contrast to the single structure in the solid state, the structure of **1** in solution is not simple. Crystalline **1** involving two solvated THF molecules was dissolved in [D$_8$]toluene, and the behavior was examined by variable-temperature ^{1}H-, ^{7}Li-, and ^{13}C-NMR spectroscopy. The results of the latter two analyses are shown in Figure 3. The analysis of the spectra reveals that **1** exists as a mixture of two species in the solution and their integral ratio reversibly changes as the temperature changes. Thus, the ^{7}Li-NMR spectra display two distinct signals at $\delta = 1.20$ and $\delta = 2.88$. The ^{13}C-NMR spectra show two kinds of signals at $\delta = 46.1$ and $\delta = 47.0$ for the NMe$_2$ carbon atoms. The ^{1}H-NMR spectra also show two kinds of signals at $\delta = 2.31$ and $\delta = 2.59$ for the NMe$_2$ protons, analogously to the ^{13}C-NMR signals.

Based on the temperature-dependent behavior of these two species, we assumed that the monomer **1a**, arising from the crystals, dimerizes to the dimer **1b** and they are in equilibrium in the solution, as shown in Scheme 2. Whereas the monomer **1a** is favored at higher temperatures in terms of the entropy effect,[3g] the dimer **1b** is favored at lower temperatures in terms of the electrostatic interaction,[8] through which the anionic electrons are efficiently stabilized by the two lithium cations. Based on this assumption, the thermodynamic parameters for the monomer−dimer equilibrium between **1a** and **1b** were estimated from a series of ^{1}H-NMR spectra. The equilibrium is described as K_{eq} = [**1b**]/[**1a**]^2 according to Scheme 2. From a van't Hoff plot of $\ln(K_{eq})$ vs $1/T$, we obtained $\Delta H° = -34.5 \pm 1.7$ kJ/mol, $\Delta S° = -135 \pm 7$ J/mol·K, $\Delta G°_{293} = 5.1 \pm 3.8$ kJ/mol, and $\Delta G°_{213} = -5.8 \pm 3.2$ kJ/mol. These thermodynamic data, especially the large negative entropy, strongly support the proposed monomer−dimer equilibrium and formation of the dimer at lower temperatures.

To confirm the monomer/dimer assignment and rule out other assignments for the higher aggregate, we performed a variable concentration study.[9] A plot of log[dimer] vs log[monomer] (integration of ^{1}H-NMR spectra at 233 K) has a slope of 2.1 ± 0.2, confirming that the two species

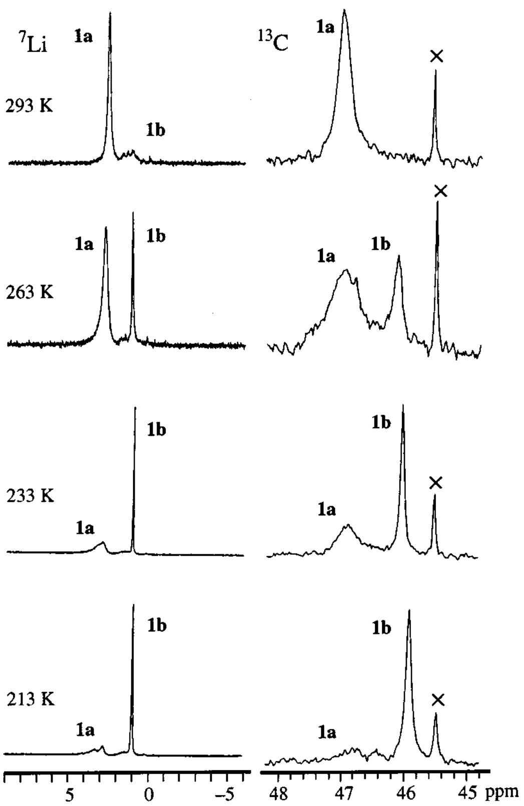
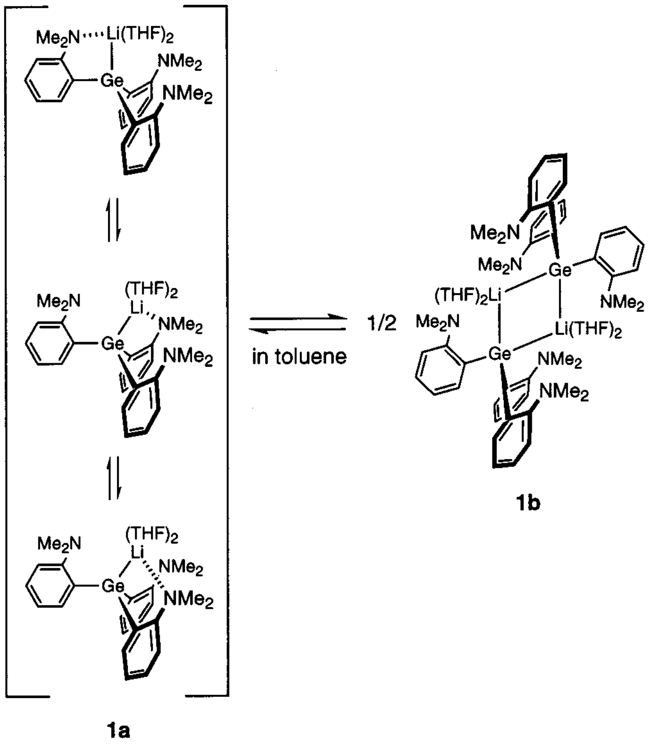


Figure 3. ^{7}Li- and ^{13}C-NMR spectra of **1** in [D$_8$]toluene at different temperatures; peaks marked with × are due to the hydrogermane **2**



Scheme 2

differ in aggregation state by a factor of 2. It is also found that the ^{7}Li-chemical shift of **1a** (δ = 2.88) is consistent with the GIAO calculated shift of **1**·(THF)$_2$ (δ = 3.06), based on the geometry of the crystal structure.[6,10,11] Thus, the two species **1a** and **1b** are represented as monomer and dimer, respectively.

Accordingly, the signals at δ = 2.88 (^{7}Li) and δ = 47.0 (^{13}C) can be attributed to **1a** while the signals at δ = 1.20 (^{7}Li) and δ = 46.1 (^{13}C) can be attributed to **1a** at 263 K in Figure 3. Some aspects require a comment: (i) In the hydrocarbon solvent, the monomer **1a** is expected to be chelated by the NMe$_2$ group(s), as observed in the crystal structure. However, the NMe$_2$ groups might equilibrate on the NMR time scale, because they appear as a broad ^{13}C resonance upon cooling to 213 K. (ii) In the dimer **1b**, the NMe$_2$ groups may not interact with the lithium atom, because they appear as a sharp ^{13}C resonance upon cooling to 213 K. (iii) The smaller line width of the ^{7}Li resonance[3g,12] of **1b** than that of **1a** may reflect the more symmetrical environment around the lithium atom in the former.

In conclusion we have revealed the structure of the germyllithium **1** in the solid state and in solution. While in the solid state the intramolecular coordination of the amino group induces the distorted geometry of the monomeric **1a**, **1a** tends to dimerize in solution.

Experimental Section

General: ^{1}H (270 MHz), ^{7}Li (105.01 MHz), and ^{13}C (67.94 MHz) NMR spectra were recorded with a JEOL EX-270 spectrometer. ^{1}H- and ^{13}C-chemical shifts were referenced to internal [D$_8$]toluene (^{1}H: δ = 2.10; ^{13}C: δ = 20.40), [D$_6$]benzene (^{1}H: δ = 7.20), and CDCl$_3$ (^{13}C: δ = 77.00). ^{7}Li-chemical shifts were referenced to external lithium chloride (δ = 0) in methanol. − Mass spectra were measured at 70 eV with a JEOL JMS-700 mass spectrometer equipped with an MS-SEPU data processing system. − Melting points were measured with a Yanaco-MP-S3 apparatus and are uncorrected. − Infrared spectra were recorded with a JASCO IR-810 spectrophotometer. − *tert*-Butyllithium in pentane was purchased from Kanto Chemical Co., Inc. THF was distilled under nitrogen from sodium benzophenone ketyl and then lithium aluminium hydride or sodium potassium alloy. Toluene was distilled under nitrogen from sodium. All reactions were carried out under an inert atmosphere.

Preparation of {Tris[2-(dimethylamino)phenyl]germyl}lithium (1) and Trapping with D$_2$O. − Formation of Tris[2-(dimethylamino)phenyl]-deuteriogermane (3): To a solution of tris[2-(dimethylamino)phenyl]hydrogermane (**2**)[4] (217 mg, 0.50 mmol) in THF (1.0 mL) was added *tert*-butyllithium in pentane (1.64 M, 1.0 mL, 1.64 mmol) at −40°C. The reaction mixture was stirred at −40°C for 1 h to give a yellow suspension of **1**. To the suspension was added deuterium oxide (0.3 mL, 17 mmol) at −40°C and the mixture was stirred at room temperature for 4 h. After the solvent was removed under reduced pressure, the residue was diluted with benzene (10 mL) and filtered. The filtrate was concentrated to give **3** as a solid. The yield was estimated by means of NMR analysis (93%) using mesitylene as the internal standard. Recrystallization of the solid from hexane (0.4 mL) gave **3** as colorless crystals (178 mg, 82% yield based on **2**), m.p. 96.5−97.0°C. − ^{1}H NMR ([D$_6$]benzene): δ = 2.57 (s, 18 H), 6.94−6.99 (m, 3 H), 7.07−7.10 (m, 3 H), 7.20−7.25 (m, 3 H), 7.40−7.43 (m, 3 H). − ^{13}C NMR (CDCl$_3$): δ = 45.68, 119.30, 123.40, 129.49, 135.53, 136.57, 159.44. − IR (KBr): $\tilde{\nu}$ = 1530 cm^{-1} (Ge−D). − MS (70 eV); m/z (%): 436 (2) $[M^+]$, 434 (1) $[M^+ - D]$, 314 (85) $[(Me_2NC_6H_4)_2Ge]$, 194 (56) $[Me_2NC_6H_4Ge]$, 120 (100) $[Me_2NC_6H_4]$.

Table 2. Summary of X-ray diffraction data for **1**·(THF)$_2$

Empirical formula	$C_{32}H_{46}GeLiN_3O_2$
Formula mass	584.27
Color	pale yellow
Crystal size [mm]	0.4 × 0.30 × 0.30
Crystal system	monoclinic
Space group	$P2_1/c$ (no. 14)
a [Å]	16.222(2)
b [Å]	10.1011(9)
c [Å]	20.715(2)
β [°]	111.897(3)
V [Å^3]	3149.5100
Z	4
D(calcd.) [g/cm^3]	1.232
μ (Mo-K_α) [$^{-1}$]	10.03
$2\theta_{max}$ [°]	55.3
Temp. [K]	173
No. of reflections collected	6355
No. of obsd. reflections, $I > 3\sigma(I)$	4370
No. of variables	353
R	0.093
R_w	0.121
Goodness of fit	1.68
Max/min peak in final diff. map [e/Å^3]	1.13/−1.17

Crystals of 1·(THF)$_2$: To a solution of **2** (210 mg, 0.49 mmol) in THF (1.4 mL) was added *tert*-butyllithium in pentane (1.56 M, 0.38 mL, 0.59 mmol) at −40°C. The reaction mixture was stirred at −40°C for 1 h. The solvent was removed under reduced pressure at 0°C to give a yellow solid. Recrystallization of the solid from toluene (0.5 mL) at −20°C gave **1**·(THF)$_2$ as pale yellow crystals (92 mg, 33% yield based on **2**), m.p. 270.0−271.0°C (sealed tube, decomp.).

X-ray Structure Determination for 1·(THF)$_2$: All crystal data and refinement parameters are summarized in Table 2. The crystal was sealed in a capillary tube under argon. Data were collected with a Rigaku RAXIS-IV imaging plate area detector with filtered Mo-K_α radiation. The structure was solved by direct methods (SIR92)[13] and expanded using Fourier techniques (DIRDIF94)[14] and refined on $|F|^2$. Empirical absorption corrections based on azimuthal scans of several reflections were applied**.** The non-hydrogen atoms were anisotropically refined. All hydrogen atoms were located at the expected positions by a geometrical calculation and fixed at these positions. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary no. CCDC-102693. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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