

Reaction of Dilithiosilane R_2SiLi_2 and Dilithiogermene R_2GeLi_2 ($R = SiMe^tBu_2$) with $MesBCl_2$ ($Mes = 2,4,6$ -trimethylphenyl): Evidence for the Formation of Silaborene $R_2Si=BMe$ and Germaborene $R_2Ge=BMe$

Norio Nakata, Rika Izumi, Vladimir Ya. Lee, Masaaki Ichinohe, and Akira Sekiguchi*

Department of Chemistry, Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba 305-8571

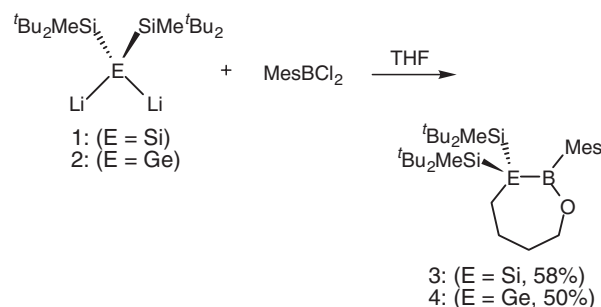
(Received January 5, 2005; CL-050014)

1,1-Dilithiosilane and -germane, R_2SiLi_2 and R_2GeLi_2 ($R = SiMe^tBu_2$) reacted with $MesBCl_2$ to give the unexpected seven-membered ring products, [1,3,2]oxasila- and -germaborepanes, through the intermediate formation of $>Si=B-$ and $>Ge=B-$ doubly bonded species.

Until very recently, the chemistry of compounds having a double bond between elements of Groups 13 and 14 was limited to the examples of boraalkenes $R_2C=BR'$; that is, compounds featuring a $>C=B-$ bond, which have been intensively studied over the past two decades.¹ In contrast, the heavy analogues of boraalkenes of the type $R_2E=BR$ ($E = Si, Ge$) were unknown, partially because of the relative weakness of the $>Si=B-$ bond, which was calculated to be only half as strong (26.0 kcal/mol) as the corresponding $>C=B-$ π -bond (51.8 kcal/mol).² Meanwhile, we have recently synthesized very effective coupling reagents, 1,1-dilithiosilane **1**³ and 1,1-dilithiogermene **2**,⁴ interaction of which with 1,1-bifunctional electrophiles resulted in the very fast and clean formation of a variety of doubly bonded derivatives containing heavier Group 14 elements.⁵ Using this synthetic approach, quite recently we succeeded in the synthesis and characterization of 1,3-disila-2-gallata- and -indataallenic anions, representing the first examples of double bonds between the heavier Group 13 and 14 elements.⁶ Here we report the rather unusual reaction of 1,1-dilithiosilane and -germane **1** and **2** with $MesBCl_2$ in THF, leading to the formation of novel seven-membered ring compounds through the intermediate formation of the silaborene $>Si=B-$ and germaborene $>Ge=B-$ species.

The reaction of **1** with an equivalent amount of $MesBCl_2$ ⁷ ($Mes = 2,4,6$ -trimethylphenyl) in dry THF immediately afforded a pale yellow reaction mixture, the ¹H NMR spectrum of which showed four distinct resonances for methylene protons at 1.19, 1.61, 1.83, and 4.51 ppm, as well as signals due to the ^tBu₂MeSi- and mesityl groups. After evaporation of solvent, the reaction mixture was separated by HPLC equipped with a recycling reverse phase ODS column to give the seven-membered ring compound **3**, 2-(2,4,6-trimethylphenyl)-3,3-bis[di-*tert*-butyl(methyl)silyl][1,3,2]oxasilaborepane, as colorless crystals in 58% yield (Scheme 1).⁸ The cyclic compound **4**, 2-(2,4,6-trimethylphenyl)-3,3-bis[di-*tert*-butyl(methyl)silyl][1,3,2]oxagermaborepane, was also obtained in 50% yield by reaction of dilithiogermene **2** with $MesBCl_2$ under similar conditions (Scheme 1).⁹

The structures of both **3** and **4** were unambiguously determined by NMR spectral data and X-ray crystallography. Thus, the ²⁹Si NMR spectrum of **3** displayed two signals at -63.0 and 12.3 ppm, of which the high field signal (-63.0 ppm) was assigned to the endocyclic silicon atom in the seven-membered



Scheme 1.

ring. The X-ray crystallographic analysis revealed that **3** and **4** are isomorphous, with very similar molecular geometries (Figure 1).¹⁰ The seven-membered rings of both **3** and **4** adopt a twist boat-like conformation, in contrast to oxacycloheptane,¹¹ which has a twist chair-like conformation. The Si1-B1 bond length (2.1249(18) Å) of **3** is significantly longer than that of lithium silylborenes $[Li(Ph_2RSi-BH_3)]$; $R = Ph, ^tBu$ (1.984–1.993 Å),¹² while the Ge1-B1 bond length (2.1647(17) Å) of **4** is close to those of lithium germylborenes $[Li(Et_3Ge-BPh_3)]$ (2.145–2.152 Å),¹³ which can be explained by the different degree of steric crowding around the E-B bond.

The formation of **3** and **4** can be reasonably explained by the

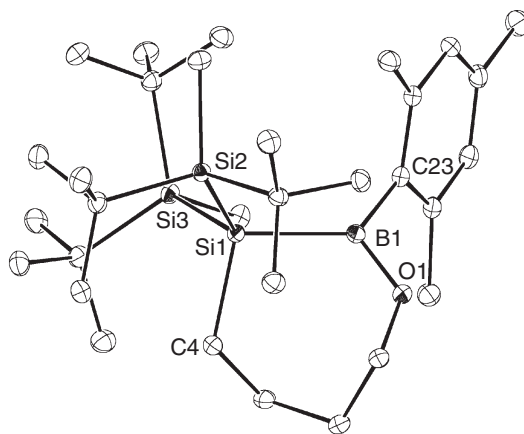
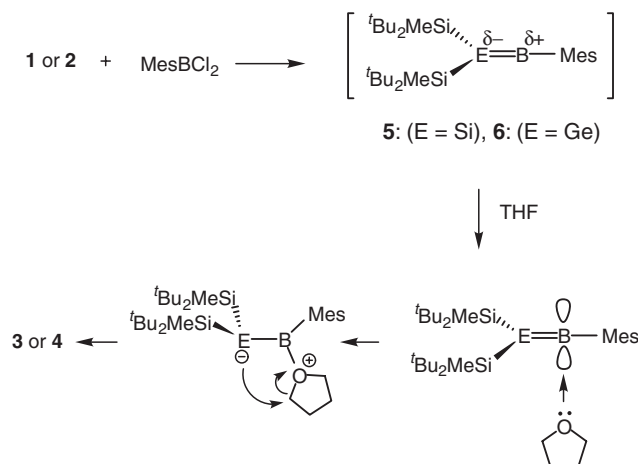


Figure 1. ORTEP drawing of **3** (30% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1-B1 = 2.1249(18), Si1-Si2 = 2.4726(6), Si1-Si3 = 2.4611(6), Si1-C4 = 1.9409(16), B1-O1 = 1.362(2), Si2-Si1-Si3 = 121.01(2), Si2-Si1-C4 = 106.49(5), Si3-Si1-B1 = 104.63(5), C4-Si1-B1 = 102.55(7), Si1-B1-O1 = 120.08(12), Si1-B1-C23 = 128.16(12), O1-B1-C23 = 111.23(14).



Scheme 2.

initial formation of silaborene **5** or germaborene **6** as the key reactive intermediates, which are stabilized by the coordination of a THF molecule to the vacant 2p_z-orbital on the B atom (Scheme 2). Because of the different substitution pattern around the doubly bonded atoms—the electron donating ^tBu₂MeSi group on Si (or Ge) atoms and the electron withdrawing Mes group on B atoms of intermediates **5** and **6**—both >Si=B– and >Ge=B– double bonds are greatly polarized: >E^{δ⁻}=B^{δ⁺}– (E = Si, Ge). Consequently, the nucleophilic Si and Ge atoms attack the α-carbons of a coordinated THF molecule accompanied with the cyclic C–O bond cleavage to form finally the seven-membered ring products **3** and **4**, respectively (Scheme 2).¹⁴ Indeed, the appreciable polarization of the >E=B– bond was clearly demonstrated by NPA (natural population analysis) calculations on the model compounds, (Me₃Si)₂E=BPh [E = Si (**7**), Ge (**8**)], which revealed the accommodation of a large part of the electron density on the Si (–0.246) and Ge (–0.335) atoms, whereas the B atom has a positive charge (+0.286 for **7**, +0.295 for **8**, respectively).¹⁵

This work was supported by a Grant-in-Aid for Scientific Research (Nos. 147078204, 16205008, 16550028) from the Ministry of Education, Culture, Sports, Science and Technology and COE (Center of Excellence) program.

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- Dilithiosilane **1** (0.10 mmol) was reacted with dichloro-(2,4,6-trimethylphenyl)borane (15 mg, 0.072 mmol) in dry THF (1.0 mL) for 15 min at room temperature to form a pale yellow solution. After removal of the solvent in vacuo, the reaction mixture was separated by HPLC equipped with a reverse phase ODS column (eluent: MeOH:^tBuOMe = 1:1) to afford colorless crystals of **3** (23 mg, 58%); mp 199–202 °C (dec.), ¹H NMR (C₆D₆) δ 0.31 (s, 6 H), 1.11 (s, 18 H), 1.18 (s, 18H), 1.19 (m, 2H), 1.61 (m, 2H), 1.83 (m, 2H), 2.13 (s, 3H), 2.44 (s, 6H), 4.51 (m, 2H), 6.74 (s, 2H); ¹³C NMR (C₆D₆) δ –2.0, 11.1, 21.2, 22.8, 23.7, 24.8, 29.8, 31.0, 31.2, 67.3, 128.3, 137.7, 140.1; ²⁹Si NMR (C₆D₆) δ –63.0, 12.3. The ipso carbon atom in the ¹³C NMR spectrum was not observed, probably due to coupling with the ¹¹B nucleus, leading to broadening of the peak.
- 4**: mp 214–215 °C (dec.), ¹H NMR (C₆D₆) δ 0.31 (s, 6 H), 1.10 (s, 18 H), 1.17 (s, 18H), 1.40 (m, 2H), 1.65 (m, 2H), 1.99 (m, 2H), 2.13 (s, 3H), 2.44 (s, 6H), 4.52 (m, 2H), 6.74 (s, 2H); ¹³C NMR (C₆D₆) δ –1.9, 13.2, 21.2, 23.0, 23.7, 25.6, 30.0, 30.8, 30.9, 67.6, 128.3, 137.8, 139.9; ²⁹Si NMR (C₆D₆) δ 19.7. The ipso carbon atom in the ¹³C NMR spectrum was not observed.
- Crystal data for **3**: C₃₁H₆₁BOSi₃, MW = 544.88, monoclinic, space group P2₁/c (No. 14), *a* = 11.3740(3), *b* = 18.0810(9), *c* = 16.8290(9) Å, β = 103.517(3)°, *V* = 3365.1(3) Å³, *Z* = 4, *D*_{calc} = 1.076 g cm^{–3}, *R*₁ (*I* > 2σ(*I*)) = 0.0409, *wR*₂ (all data) = 0.1113 for 7535 reflections and 342 parameters, GOF = 0.968. **4**: C₃₁H₆₁BGeOSi₂, MW = 589.38, monoclinic, space group P2₁/c (No. 14), *a* = 11.4140(2), *b* = 18.1010(6), *c* = 16.8330(5) Å, β = 103.588(2)°, *V* = 3380.44(16) Å³, *Z* = 4, *D*_{calc} = 1.158 g cm^{–3}, *R*₁ (*I* > 2σ(*I*)) = 0.0318, *wR*₂ (all data) = 0.0851 for 7977 reflections and 342 parameters, GOF = 1.045. Selected bond lengths (Å) and angles (deg) for **4**: Ge1–B1 = 2.1647(17), Ge1–Si1 = 2.5001(4), Ge1–Si2 = 2.4914(4), Ge1–C4 = 2.0279(15), B1–O1 = 1.359(2), Si1–Ge1–Si2 = 121.375(15), Si1–Ge1–C4 = 106.57(4), Si2–Ge1–B1 = 104.56(5), C4–Ge1–B1 = 101.51(6), Ge1–B1–O1 = 120.06(11), Ge1–B1–C23 = 127.34(11), O1–B1–C23 = 112.13(13).
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- The possibility of the initial formation of R₂ELi–BClMes (THF) (E = Si, Ge) followed by the intramolecular THF ring-opening to form finally **3** (or **4**) seems unfavorable, since coordination of THF to B atom attached to an anionic E-center, is unlikely due to the preferential interaction of anionic center to B empty *p*-orbital. Instead, β-elimination of LiCl would rather take place resulting in the formation of >E=B– bond.
- The calculations were carried out using the Gaussian 98 program at the B3LYP/6-31G(d) level.