Synthesis of a Germylidenide Anion from the C-C Bond Activation of a Bis(Germylene)

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Supporting Information Placeholder

ABSTRACT: The synthesis of a germylidenide anion by the C-C bond activation of a bis(germylene) is described. The reaction of the 2,6-bis(imino)phenylbromide **1** with *n*BuLi, followed by reacting with $GeCl_2$.dioxane afforded the chlorogermylene [LGeCl] (**2**, L = 2,6-(HCN*t*Bu)$_2$C$_6$H$_3$). It was then reacted with 1 equivalent of lithium in tetrahydrofuran (THF), which proceeded through the reduction of the imine skeleton, along with the C-C bond formation, to afford the bis(germylene) [2-(HC-N*t*Bu)-6-(HC=N*t*Bu)C$_6$H$_3$Ge:]$_2$ (**3**). It was further reacted with 2 equivalents of lithium in THF, which proceeded through the reduction of the germanium(II) centres, followed by the homolytic cleavage of the C-C bond, to form the lithium germylidenide [LGeLi]$_2$ (**4**). Compounds **2** – **4** were characterized by NMR spectroscopy and X-ray crystallography. Their bonding natures were also investigated by theoretical studies.

INTRODUCTION

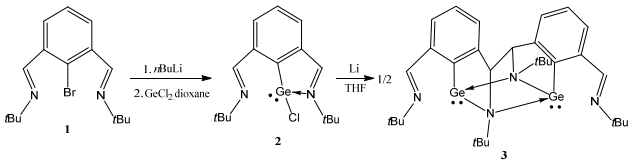
Germylidenide, stannylidenide, and plumbylidenide anions of composition [RË:]$^-$ (E = Ge, Sn, Pb; R = supporting ligands), which are low valent group 14 element anionic complexes comprising two lone pairs of electrons on the metal centers, have attracted much attention in the past few years due to their unique structures and potential application in metathesis reactions for the formation of metal-metal bonds.[1] The most magnificent example of such a complex is the germylidenide anion [:G̈e{C(R)C(H)C(R)N(Ar)}]$^-$ (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$, R = Me or *t*Bu), which was afforded by the reduction of the β-diketiminato germanium(II) chloride [HC{C(R)N(Ar)}$_2$G̈eCl] with two equivalents of lithium.[1b] It is proposed that a number of steps, which includes reductive ring contraction reactions, is involved in the mechanism of the formation of the complex. Then, our group showed that the 2,6-bis(imino)phenyl-stabilized heavier derivatives, stannylidenide, and plumbylidenide anions [{2,6-(HCNAr)$_2$C$_6$H$_3$}Ë:]$^-$ (E = Sn, Pb), were isolated by the reduction of the corresponding tin(II) and lead(II) halides with alkali metal.[2,1c] They can also be prepared by the reduction of the tin(I) or lead(I) dimer [{2,6-(HCNAr)$_2$C$_6$H$_3$}Ë]$_2$ with alkali metal. In addition, the reduction of the 2,6-bis(imino)phenyl germanium(II) chloride [{2,6-(HCNAr)$_2$C$_6$H$_3$}GeCl] with excess calcium afforded the dianion radical [{2,6-(HCNAr)$_2$C$_6$H$_3$}G̈e:]$^{\bullet-}$.[3,4] It is proposed that the reduction of [{2,6-(HCNAr)$_2$C$_6$H$_3$}ËX] (E = Ge, Sn, Pb; X = Cl or Br) with alkali metal proceeds through the formation of a group 14 element(I) radical intermediate [{2,6-(HCNAr)$_2$C$_6$H$_3$}Ë·], which subsequently either undergoes a further one-electron reduction to form the anion in the presence of excess alkali meal, or dimerizes in a head to head manner to form the group 14 element(I) dimer [{2,6-(HCNAr)$_2$C$_6$H$_3$}Ë]$_2$. This hypothesis drove us to investigate whether the radical intermediate can be stabilized or destabilized if the kinetic stabilization of the ligand backbone is increased or decreased, respectively.

As such, we replaced the Ar substituents in the 2,6-bis(imino)phenyl ligand with *t*Bu substituents and then investigated the resulting effect. Herein, we report the synthesis of a germylidenide anion via a new mechanism, the C-C bond activation of a bis(germylene).

RESULTS AND DISCUSSION

Synthesis of the Chlorogermylene. The reaction of the 2,6-bis(imino)phenylbromide LBr[5] (**1**, L = 2,6-(HCN*t*Bu)$_2$C$_6$H$_3$) with *n*BuLi in THF at -78 °C, followed by reacting with $GeCl_2$·dioxane, afforded the chlorogermylene [LGeCl] (**2**, Scheme 1). It was isolated as an extremely air- and moisture-sensitive orange crystalline solid. Compound **2** is soluble in hydrocarbon solvents and was characterized by NMR spectroscopy. Its ^{1}H NMR spectrum displays a singlet at δ 1.36 ppm, a multiplet at δ 7.10 – 7.14 ppm, and a singlet at δ 8.01 ppm for the *t*Bu, Ph and HC=N protons respectively. These imply that the imino substituents are chemically equivalent in solution, whereas they are chemically inequivalent in the solid-state structure (see below).

Scheme 1. Synthesis of **2** and **3**



The molecular structure of **2** (Figure 1) is isostructural to the 2,6-bis(imino)phenyl germanium(II) chloride [{2,6-(HCNAr)$_2$C$_6$H$_3$}GeCl][3] with the Ar substituents at the N_{imine} atoms. The Ge1 atom adopts a distorted trigonal pyramidal geometry. The sum of the bond angles at the Ge1 atom (259.57°) is comparable to that in [{2,6-(HCNAr)$_2$C$_6$H$_3$}GeCl] (267.40°). This indicates that there is a stereoactive lone pair at the Ge1 atom. The Ge1–C1 (2.0004(19) Å) and Ge1–N1 (2.2981(17) Å) bonds are comparable to those in [{2,6-(HCNAr)$_2$C$_6$H$_3$}GeCl] (Ge–C: 2.028(3) Å, Ge–N, 2.247(3) Å). The Ge1···N2 distance (2.57(1) Å) is significantly longer than the Ge1-N1 bond length, but shorter than the sum of the van der Waals radii (ca. 3.55 Å). These results indicate that there is a weak interaction between the Ge1 and N1 atoms.

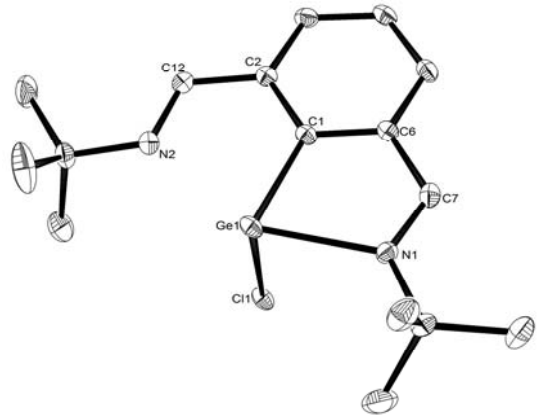


Figure 1. Molecular structure of **2** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1-C1 2.0004(19), Ge1-N1 2.2981(17), C7-N1 1.281(3), C6-C7 1.466(3), C1-C6 1.394(3), Ge1-Cl1 2.3477(5); C1-Ge1-N1 76.68(7), C7-N1-Ge1 111.41(13), N1-C7-C6 117.81(18), C7-C6-C1 115.92(18), C1-Ge1-Cl1 93.95(5), N1-Ge1-Cl1 88.94(4).

In order to understand the bonding nature, compound **2** was investigated by means of quantum chemical calculations.[6] The HOMO shows the lone pair orbital on the germanium atom (see the Supporting Information). The LUMO illustrates the π* orbitals on the ligand backbone. Accordingly, the natural-bond-orbital (NBO) analysis shows the lone pair electrons at the Ge atom being high in *s*-character with some directionality ($sp^{0.23}$, occupancy: 1.94).

Synthesis of the Bis(germylene). The reaction of **2** with 1 equivalent of lithium in THF at room temperature afforded the bis(germylene) [2-(HC-N*t*Bu)-6-(HC=N*t*Bu)C$_6$H$_3$Ge:]$_2$ (**3**, Scheme 1). Based on the LUMO of **2**, it is proposed that the reaction proceeds through the reduction of the imine moiety of the ligand backbone to form an imine radical anion intermediate, which then undergoes C-C coupling reaction and salt elimination of LiCl to afford compound **3**.

Compound **3** was isolated as an extremely air- and moisture-sensitive colourless crystalline solid. It is soluble in hydrocarbon solvents and was characterized by NMR spectroscopy. Its ^{1}H NMR spectrum displays two singlets at δ 1.10 and 1.35 ppm, which is consistent to two chemically nonequivalent *t*Bu substituents. It also displays a singlet at δ 3.80 ppm for the HC-N protons and a singlet at δ 8.48 ppm for the HC=N protons.

The molecular structure of **3** (Figure 2) shows that the germanium atoms adopt a distorted trigonal pyramidal geometry (sum of bond angles = 247.7, 248.4°), indicating that there is a lone pair of electrons on each of the germanium atom. The C1-Ge1 (1.991(3) Å) and C23-Ge2 bonds (1.995(3) Å) are comparable to that of **2**. The C17-N2 (1.490(4) Å) and C12-N1 bond lengths (1.489(4) Å), which are longer than the C3-N3 (1.265(4) Å) and C24-N4 bond lengths (1.256(4) Å), indicate that they are single bonds. In addition, the C12-C17 bond (1.562(4) Å) is a C-C single bond. The N-Ge bonds (2.081(2), 2.119(2), 2.127(2) and 2.082(2) Å) are significantly longer than those of the germanium(II) amido compound [{(Me$_3$Si)$_2$N}$_2$Ge] (1.873(5), 1.878(5) Å).[7] They are comparable to the N-Ge coordinative covalent bond (2.0634(18) Å) in the *N*-donor-stabilized chlorogermylene [{ArN=C(Me)C(Me)$_2$-N(Ar)}GeCl].[8] These indicate that compound **3** possesses resonance structures **3A** and **3B**, resulting in weak N_{amino}-Ge bonds (Scheme 2).

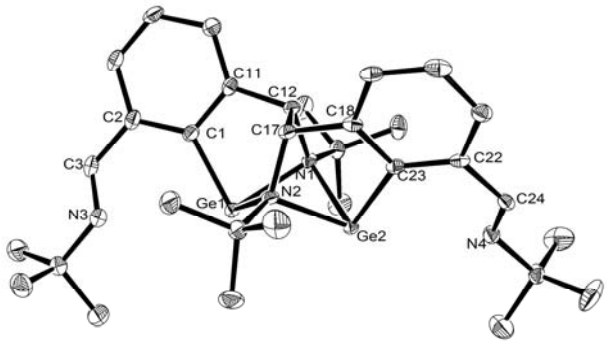
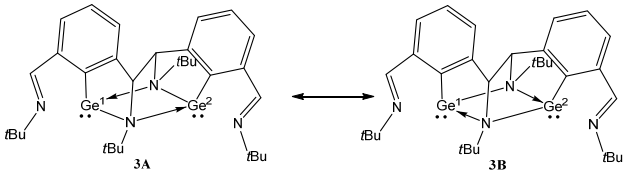


Figure 2. Molecular structure of **3** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1-C1 1.991(3), Ge1-N2 2.127(2), Ge2-N2 2.081(2), Ge2-N1 2.119(2), Ge1-N1 2.082(2), C12-N1 1.489(4), C17-N2 1.490(4), C12-C17 1.562(4), C12-C11 1.519(4), Ge2-C23 1.995(3), C17-C18 1.512(4);

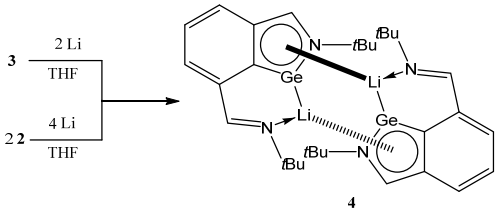
C1-Ge1-N2 93.37(11), C1-Ge1-N1 85.00(10), C12-N1-Ge1 99.36(15), N1-C12-C11 111.0(2), N2-C17-C12 103.8(2), C17-N2-Ge1, 111.28(16), N1-Ge1-N2 69.17(9), N2-Ge2-N1 69.33(8), Ge1-N1-Ge2 86.20(8), C17-N2-Ge2 98.82(17), C23-Ge2-N2 85.96(11), N2-C17-C18 111.5(2), C23-C18-C17 113.7(3).

Scheme 2. Resonance structures of **3**



Compound **3** was investigated by means of quantum chemical calculations. The HOMO shows the lone pair orbitals on the germanium atoms. The LUMO illustrates the π* orbitals on the ligand backbone and the C-Ge bonds.

Scheme 3. Synthesis of **4**



Synthesis of the Germylidenide Anion by the C-C Bond Activation of 3. The reaction of **3** with two equivalents of lithium in THF afforded the lithium germylidenide $[LGeLi]_2$ (**4**, Scheme 3). Based on the LUMO of **3**, the reaction appears to proceed through the reduction of the germanium(II) centres in **3**, followed by the homolytic cleavage of the C-C bond to form **4**. Compound **4** can also be synthesized by the reaction of **2** with four equivalents of lithium in THF, which proceeds through the reduction of **3**.

Compound **4** was isolated as an extremely air- and moisture-sensitive dark green crystalline solid, which is stable at the solid state, under room temperature and inert atmospheric conditions. Its ^{1}H NMR spectrum displays a singlet at δ 1.49 ppm for the *t*Bu substituents and 8.03 ppm for the HC=N protons. This shows that the two imino substituents are equivalent in solution.

Compound **4** was characterized by X-ray crystallography (Figure 3). The Li1 atom is η^1-coordinated to the N2 atom, η^1-coordinated to the Ge1 atom, and η^5-coordinated to the GeCCCN ring of another molecule. The Li1-Ge1 bond (2.680(7) Å) is comparable to those in the dianionic germole complex $[(\mu\text{-}\eta^5\text{-}GeC_4Ph_4)\{Li(dioxane)_2\}_2]$ (average Ge-Li bond length: 2.706 Å),[9] but the Ge1-Li1A bond is longer than the latter. Comparing the Ge1–C1 (1.946(4) Å), C1–C6 (1.463(5) Å), C6–C7 (1.401(6) Å), C7–N1 (1.380(5) Å), and Ge1–N1 (1.939(3) Å) bond lengths of compound **4** with those in compounds **2**, it suggests that the negative charge on the geranium centre is stabilized by an electron delocalization in the GeCCCN five membered ring.

The bonding nature of compound **4** was investigated by means of quantum chemical calculations. The HOMO and HOMO-2 precisely show that each germanium atom comprises two lone pair orbitals being perpendicular to and lie on the same plane as the germanium-containing five-membered ring. The HOMO also illustrates the π-delocalization. In addition, the negative nucleus independent chemical shift[10] (NICS(1): -12.8 ppm) of the germanium-containing five-membered ring and the natural charge of the germanium atoms (0.75) show that the negative charge at the germanium atom is stabilized by an aromatic delocalization in the germanium-containing five-membered ring.

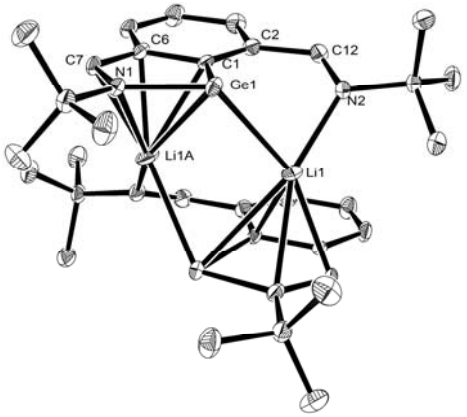


Figure 3. Molecular structure of **4** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1-N1 1.939(3), C7-N1 1.380(5), C6-C7 1.401(6), Ge1-C1 1.946(4), C1-C6 1.463(5), Ge1-Li1A 2.897(8), Ge1-Li1 2.680(7), Li1-N2 2.101(9); C7-N1-Ge1 115.1(3), N1-Ge1-C1 83.31(16), C6-C1-Ge1 112.1(3), C7-C6-C1 114.0(4), N1-C7-C6 115.0(4), N1-Ge1-Li1 126.1(2), N1-Ge1-Li1A 59.35(18), N2-Li1-Ge1 157.2(4).

CONCLUSION

In conclusion, the germylidenide anion **4** was prepared by the reduction of the bis(germylene) **3**, in which the reaction proceeds through the reduction of the germanium(II) centres in **3**, along with the homolytic cleavage of the C-C bond.

EXPERIMENTAL SECTION

General Procedure. All manipulations were carried out under an inert atmosphere of argon gas using standard Schlenk techniques. THF, toluene and Et_2O were dried over and distilled over Na/K alloy prior to use. CH_2Cl_2 was dried over and distilled over CaH_2 prior to use. LBr was prepared as described in the literature.[5] The ^{1}H, ^{13}C, and ^{7}Li NMR spectra were recorded on a JEOL ECA 400 spectrometer. The chemical shifts (δ) are relative to $SiMe_4$ for ^{1}H and ^{13}C and LiCl for ^{7}Li. Elemental analyses were

performed by the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured in seal glass tubes and were not corrected.

Synthesis of **2**. *n*BuLi (2.0 M in cyclohexane, 2.75 mL, 5.5 mmol) was added dropwise to a solution of **1** (1.62 g, 5.00 mmol) in THF (50 mL) at -78 °C. The reaction mixture was stirred for 3 hours. A solution of $GeCl_2$·dioxane (1.27 g, 5.50 mmol) in THF (5 mL) was then added to the reaction mixture at -78 °C. The resulting reddish brown solution was gradually warmed to room temperature and stirred overnight. Solvent was removed under vacuum, and the residue was extracted with dichloromethane. LiCl was filtered off and the reddish brown filtrate was concentrated to afford orange crystals of **2** (0.824 g, 47 %). Mp.: 163 °C (dec.). Elemental analysis for $C_{16}H_{23}N_2GeCl$: C, 54.68; H, 6.60; N, 7.97. Found: C, 54.30; H, 6.58; N, 7.80. ^{1}H NMR (395.9 MHz, C_6D_6, 25 °C): δ 1.36 (s, 18H, C(CH_3)$_3$), 7.10 – 7.14 (m, 3H, Ph), 8.01 (s, 2H, C*H*=N). ^{13}C{^{1}H} NMR (99.5 MHz, C_6D_6, 25 °C): δ 30.53 (*C*H$_3$), 59.30 (*C*(CH$_3$)$_3$), 130.20, 141.38, 157.69, 158.14 (Ph), 166.82 ppm (*C*=N–C).

Synthesis of **3**. THF (20 mL) was added to a mixture of compound **2** (0.351g, 1.00 mmol) and lithium metal (0.00694g, 1.00 mmol) at 0°C. The resulting red reaction mixture was gradually warmed to room temperature and stirred for 15 hours. Solvent was removed under vacuum, and the dark green residue was extracted with Et_2O. LiCl was filtered off and tmeda (0.15 mL, 1.00 mmol) was added at 0 °C. The resulting green solution was stirred at room temperature for 2 hours. The solution was then filtered and concentrated, affording dark green crystals of compound **3** (0.156g, 49%). Mp.: 218 °C (dec.). Elemental analysis for $C_{32}H_{46}Ge_2N_4$: C, 60.81; H, 7.33; N, 8.87. Found: C, 60.72; H, 7.14; N, 8.67. ^{1}H NMR (395.9 MHz, C_6D_6, 25 °C): δ 1.10, (s, 18H, C(CH_3)$_3$), 1.35 (s, 18H, C(CH_3)$_3$), 3.80 (s, 2H, C*H*-N), 7.16 – 7.24 (m, 4H, Ph), 7.39 (d, $^3J_{HH}$ = 6.79 Hz, 2H, Ph), 8.48 (s, 2H, C*H*=N). ^{13}C{^{1}H} NMR (99.5 MHz, C_6D_6, 25 °C): δ 30.21 (*C*H$_3$), 31.33 (*C*H$_3$), 55.86 (*C*(CH$_3$)$_3$), 57.87 (*C*(CH$_3$)$_3$), 73.46 (H*C*-N), 122.43, 127.11, 142.60, 155.82, 159.01 (Ph), 159.33 ppm (*C*=N–C).

Synthesis of **4**. Method A: THF (40 mL) was added to a mixture of compound **3** (0.253g, 0.40 mmol) and lithium granules (0.0028g, 0.40 mmol) at 0°C. The resulting red reaction mixture was gradually warmed to room temperature and stirred for 15 hours to afford a dark green solution. Solvent was removed under vacuum, and compound **4** was obtained quantitatively.

Method B: THF (40 mL) was added to a mixture of compound **2** (1.41g, 4.00 mmol) and lithium granules (0.0555g, 8.00 mmol) at room temperature. The red reaction mixture turned blue initially and became dark green after 15 hours of stirring. Solvent was removed under vacuum, and the residue was extracted with toluene. LiCl was filtered off and the filtrate was concentrated to form dark green crystals of compound **4** (0.349g, 27%).

Mp.: 249 °C (dec.). Elemental analysis for $C_{32}H_{46}Ge_2Li_2N_4$: C, 59.51; H, 7.18; N, 8.67. Found: C, 59.32; H, 6.97; N, 8.44. ^{1}H NMR (399.5 MHz, C_6D_6, 25 °C): δ 1.49, (s, 36H, C(CH_3)$_3$), 6.67 (t, $^3J_{HH}$ = 7.55 Hz, 2H, Ph), 6.78 (d, $^3J_{HH}$ = 7.35 Hz, 4H, Ph), 8.03 (s, 4H, CH=N). ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6, 25 °C): δ 32.55 (*C*H$_3$), 57.46 (*C*(CH$_3$)$_3$), 120.42, 125.41, 136.53 (Ph), 160.15 ppm (*C*=N–C). ^{7}Li{^{1}H} NMR (155.3 MHz, C_6D_6, 25 °C): δ -2.27 ppm.

X-ray Data Collection and Structural Refinement. Intensity data for compounds **2–4** were collected using a Bruker APEX II diffractometer. The crystals of **2–4** were measured at 103(2) K. The structures were solved by direct phase determination (SHELXS-97) and refined for all data by full-matrix least-squares methods on F^2.[11] All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride on their respective parents atoms; they were assigned appropriate isotopic thermal parameters and included in the structure-factor calculations. Selected X-ray crystallography data of **2–4** are summarized in Table S1 (see Supporting Information).

Theoretical Studies. Compounds **2** – **4** were investigated using DFT B3PW91 method with the 6-31+G(d) level.[6] All calculations were carried out using the Gaussian 09 packages. The NBO analyses were performed using the NBO 5.0 program at the same level. The optimized geometries are in good agreement with the X-ray crystallographic data of **2** – **4**.

ASSOCIATED CONTENT

Supporting Information

CIF files giving X-ray data for **2–4**, a table giving selected crystallographic data of **2–4** and molecular orbitals of **2** – **4**. These materials are available free of charge via the Internet at http://pubs.acs.org.

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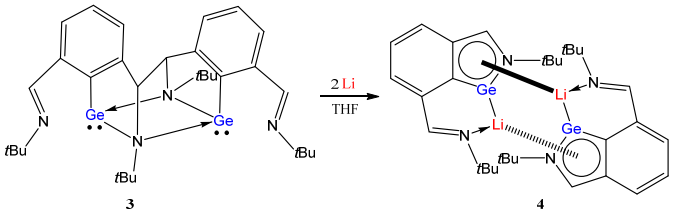
Table of Contents Graphic



3 4

The bis(germylene) **3** was reacted with 2 equivalents of lithium in THF, which proceeded through the reduction of the germanium(II) centres, followed by the homolytic cleavage of the C-C bond, to form the lithium germylidenide **4**