

Stabilization of a Transient Diorganogermylene by an N-Heterocyclic Carbene

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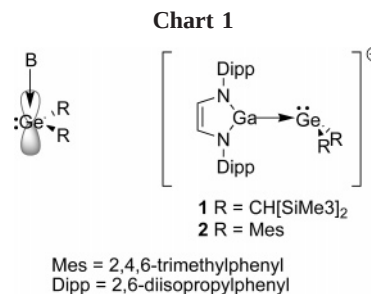
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Summary: The synthesis of a carbene-stabilized transient germylene is presented; the resulting complex liberates free germylene upon heating, forms a stable adduct with BH_3 , and reacts with MeLi to displace the carbene.

Germynes, divalent germanium(II) compounds, are highly reactive species and, unless stabilized by extreme steric bulk or electronic effects, are short-lived.¹ The reactivity of germynes can be moderated by the introduction of a Lewis base, which results in the formation of a donor–acceptor complex by the transfer of electron density from the base into the empty π orbital on germanium. Many examples of intramolecularly base-stabilized germynes are known, and their reactivity has been well studied;^{1e} however, far less is known about intermolecularly stabilized germynes, particularly diorganogermynes. Most intermolecularly base-stabilized $:\text{GeR}_2$ compounds are short-lived and are difficult to characterize.^{1a,e,2} On the other hand, stable inorganic germanium(II) derivatives, such as $\text{GeCl}_2 \cdot (\text{dioxane})$, have proven to be versatile reagents for the preparation of a variety of germanium compounds.¹ We believe that isolable, intermolecularly base-stabilized diorganogermynes will have useful applications as ligands in coordination chemistry,^{1f,3} as new thermal precursors for germynes, and in the novel synthesis of germanium polymers.

Recently, two groups reported the synthesis of anionic gallium carbenoid–germanium(II) complexes. The first example, **1**, was with Lappert's stable germylene $\text{Ge}[\text{CH}(\text{SiMe}_3)_2]_2$ ^{4,5} and the second, **2**, with dimesitylgermylene (Chart 1).⁶ The isolation



of the heavy carbene analogue—germylene complexes and the successful use of N-heterocyclic carbenes (NHCs) in the stabilization of other main-group compounds^{7–11} prompted us to explore the use of the NHC **3**¹² for the base stabilization of transient germynes. Only two NHC– GeR_2 species have been structurally characterized: NHC–GeI_2 ¹³ and an NHC–N-heterocyclic germylene complex.¹⁴ In both cases, the uncoordinated, free germanium(II) compounds are intrinsically stable and have been characterized independent of coordination. We now report the synthesis and characterization of the NHC–dimesitylgermylene complex **4**, which is the first example of base stabilization of a transient $:\text{GeR}_2$ species by a carbene. The germanium center has three carbon single bonds, has a lone pair of electrons, and forms a stable adduct with BH_3 , an example of an “in-series” coordination complex.¹⁵ Finally, **4** reacts with MeLi , demonstrating that the carbene can be displaced from the germanium by a stronger base.

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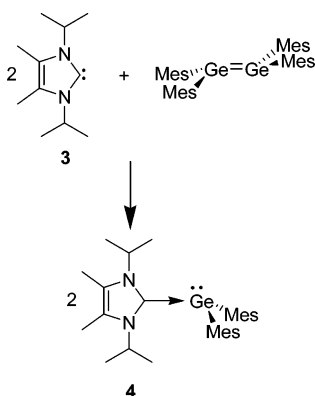
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Scheme 1



Two equivalents of carbene **3** was added to a yellow solution of tetramesityldigermene (Scheme 1).¹⁶ No visible change was observed. ¹H and ¹³C{¹H} NMR spectroscopic analysis of the yellow residue, obtained after removal of the solvent, indicated quantitative conversion of the starting materials to a single product.¹⁷ The ¹H NMR spectrum of the product revealed the carbene and dimesitylgermylene moieties to be in a 1:1 ratio, and the ¹³C signal attributable to the carbenic carbon shifted upfield from 206 to 176 ppm, which is indicative of carbene coordination. Crystals suitable for X-ray crystallographic analysis were grown from a concentrated toluene solution at −30 °C. The molecular structure of the product was unambiguously determined to be **4** by single-crystal X-ray diffraction analysis (Figure 1).¹⁸

The carbenic carbon–germanium bond length of 2.078(3) Å is consistent with a carbon–germanium single bond, and the germanium center is pyramidal, as expected, due to the presence of a stereochemically active lone pair of electrons. The same trends were observed in the related NHC–tin(II) and –lead(II) complexes.^{10,11}

Compound **4** can be considered as either a base-stabilized germylene or a zwitterionic germane. 2,3-Dimethylbutadiene (DMB), a well-known germylene trap, is often used to verify the presence of reactive germylenes; the diene undergoes rapid formal [2 + 4] cycloaddition with the germylene to give a germacyclopentene.^{19–21} Addition of DMB to a THF solution

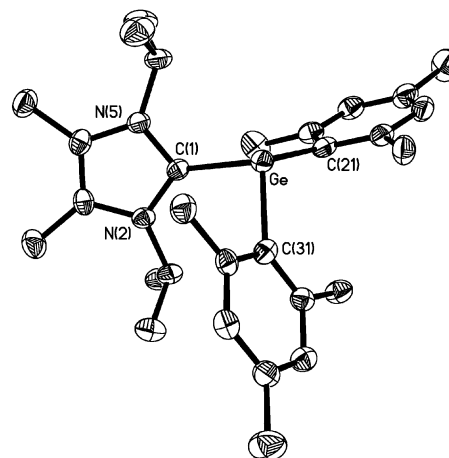
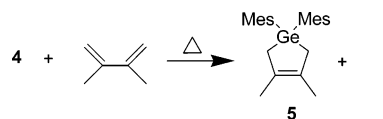
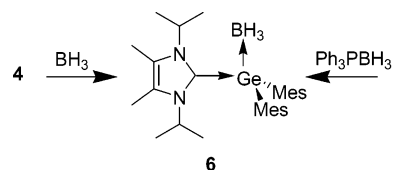


Figure 1. Thermal ellipsoid plot (50% probability surface) of **4**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ge–C1 = 2.078(3), Ge–C21 = 2.0649(18), Ge–C31 = 2.0713(16), C1–N2 = 1.359(4), C1–N5 = 1.357(4); C1–Ge–C21 = 109.18(11), C1–Ge–C31 = 95.93(12), C21–Ge–C31 = 112.61(19).

Scheme 2



Scheme 3



of **4** at room temperature resulted in no reaction, indicating that the carbene–germanium bond is stable at room temperature. Heating the THF solution to 70 °C in a sealed tube resulted in the quantitative formation of DMB-trapped germylene **5**, along with a stoichiometric equivalent of the free NHC **3** (Scheme 2).²² We can conclude that **4** dissociates to the free carbene and the free germylene under these conditions. Thus, **4** is best represented as a base-stabilized germanium(II) species.

The germanium center in **4** has three bonds to carbon and a lone pair and, thus, is an isovalent analogue of phosphine (R₃Ge: cf. R₃P:). To evaluate the potential of **4** to act as a Lewis base, 1 equiv of BH₃·THF was added to a THF solution of **4** (Scheme 3), resulting in the formation of a clear and colorless solution.²³ Removal of the solvent in vacuo gave a white, air-stable powder. The ¹H NMR spectrum of the powder indicated that the carbene and dimesitylgermylene moieties remained in a 1:1 ratio. In addition, a broad signal, which was integrated for three hydrogens, was observed at 1.9 ppm. The FT-IR spectrum of the powder showed a series of signals centered at 2300 cm^{−1}, which is in the expected range for boron–hydrogen bond vibrations. High-resolution mass spectrometric analysis of the sample revealed an M⁺ ion consistent with a BH₃ adduct of **4**. A single crystal suitable for X-ray diffraction was grown by slow evaporation of a benzene solution of the reaction product and was confirmed to be **6**.

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(17) Synthesis of **4**: to a yellow solution of Mes₄Ge₂ (0.161 mmol, from the photolysis of 100 mg of Mes₄Ge₃)¹⁶ dissolved in THF (5 mL) was added the NHC **3** (0.32 mmol, 0.06 g) dissolved in THF (5 mL). The reaction mixture was stirred for 5 min. The solvent was removed under vacuum, giving a yellow powder of essentially pure **4** in 96% yield (0.15 g, 0.31 mmol). Crystals suitable for X-ray analysis were grown from a concentrated toluene solution stored at −30 °C. Mp: 144–146 °C. ¹H NMR: δ 0.96 (d, ³J_{HH} = 7 Hz, 12 H), 1.50 (s, 6 H), 2.29 (s, 6 H), 2.59 (s, 12 H), 5.73 (sept, ³J_{HH} = 7 Hz, 2 H), 6.93 (s, 4 H). ¹³C{¹H} NMR: δ 9.99, 20.79, 21.20, 25.54, 51.91, 125.88, 128.51, 134.37, 143.97, 152.31, 176.06. EI-MS: *m/z* 311 [Mes₂Ge, 6%], 180 [C{[N(*i*-Pr)C(CH₃)₂]}], 34%], 138 [C{[N(*i*-Pr)C(CH₃)₂]}] – *i*-Pr, 40%]. Although **4** was clean by ¹H NMR analysis (see the Supporting Information), the elemental analysis of **4** was unsatisfactory, most likely due to the air and moisture sensitivity of the compound. Selected crystal data for **4**: [C_{32.5}H₃₆GeN₂], *M_r* = 537.30, triclinic, space group *P*1̄, *a* = 8.8091(9) Å, *b* = 13.7282(17) Å, *c* = 14.061(2) Å, α = 63.736(5)°, β = 80.017(7)°, γ = 81.165(8)°, *V* = 1496(3) Å³, *Z* = 2, *T* = 150(2) K, μ = 1.046 mm^{−1}, 12 668 reflections collected, 4990 independent (*R*_{int} = 0.053), *R*₁ = 0.0678, *wR*₂ = 0.1347 (all data).

(18) The exact mechanism for the formation of **4** is not known. We have shown that tetramesityldigermene is stable in solution at room temperature and have found no evidence for the spontaneous dissociation into 2 equiv of dimesitylgermylene.^{6,16}

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(22) The NHC **3** does not react with DMB under these conditions.

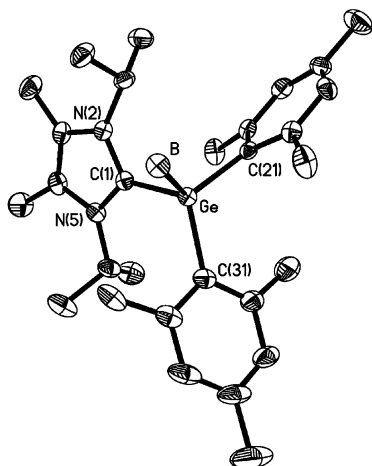


Figure 2. Thermal ellipsoid plot (50% probability surface) of **6**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): C1–Ge = 2.045(2), Ge–B = 2.094(3), Ge–C21 = 2.005(2), Ge–C31 = 2.001(2), C1–N2 = 1.361(3), C1–N5 = 1.353(3); C1–Ge–B = 104.6(1), C1–Ge–C21 = 102.67(9), C1–Ge–C31 = 109.47(9), C21–Ge–C31 = 112.98(19).

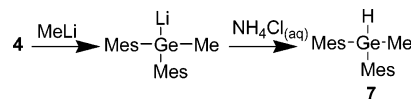
The molecular structure of **6** is shown in Figure 2. Complex **6** can be viewed as a carbene–germylene–borane “in-series” coordination complex, where the germanium is simultaneously an electron pair acceptor and an electron pair donor (Scheme 3). The metrics of **6** are similar to those of **4**; however, the NHC–Ge–Mes angles are slightly more obtuse²⁴ and the germanium–carbon bond lengths are somewhat shorter.²⁵ Both observations are consistent with the conversion of the lone pair

(23) Synthesis of **6**: to a yellow solution of **4** (0.15 g, 0.31 mmol) dissolved in THF (10 mL) was added a 1 M solution of $\text{BH}_3 \cdot \text{THF}$ in THF (0.31 mL, 0.31 mmol). The yellow solution faded to a clear and colorless solution after 15 min. The solvent was removed under vacuum, giving a white powder of pure **6** in quantitative yield. Crystals suitable for X-ray analysis were grown by the slow evaporation of a saturated C_6H_6 solution. Mp: 155–162 °C dec. ^1H NMR: δ 1.00 (d, $^3J_{\text{HH}} = 7$ Hz, 12 H), 1.51 (s, 6 H), 1.70–2.10 (broad, 3 H), 2.18 (s, 6 H), 2.52 (s, 12 H), 5.55 (broad, 2 H), 6.82 (s, 4 H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 10.12, 21.04, 21.39, 26.02, 51.41, 127.55, 129.42, 136.97, 143.01, 144.46, 164.60. ^{11}B NMR: δ –28.49 (broad). IR: 847 (m), 1035 (s), 1374 (s), 1457 (broad, s), 1600 (m), 2268 (s), 2298 (s), 2349 (s), 2375 (m), 2731 (w), 2867 (s), 2921 (s), 2874 (s) cm^{-1} . EI-MS: m/z 505 [M^+ , 5%], 492 [$\text{M}^+ - \text{BH}_3$, 100%], 373 [$\text{C}\{[\text{N}(i\text{-Pr})\text{C}(\text{CH}_3)]_2\}\text{GeMes}$, 10%], 311 [Mes_2Ge , 20%]. High resolution EI-MS: m/z calcd for $\text{C}_{29}\text{H}_{45}^{11}\text{B}^{74}\text{GeN}_2$ 505.2818, found 505.2820. Anal. Calcd for $\text{C}_{29}\text{H}_{45}\text{BGeN}_2$: C, 68.96; H, 8.98. Found: C, 68.62; H, 9.45. Selected crystal data for **6**: $[\text{C}_{32}\text{H}_{48}\text{BGeN}_2]$, $M_r = 544.12$, monoclinic, space group $P2_1/c$, $a = 22.0634(5)$ Å, $b = 8.6076(2)$ Å, $c = 16.2745(2)$ Å, $\beta = 93.0960(10)^\circ$, $V = 3086.23(14)$ Å³, $Z = 4$, $T = 150(2)$ K, $\mu = 1.014$ mm^{–1}, 28 738 reflections collected, 5429 independent ($R_{\text{int}} = 0.057$), $R1 = 0.0524$, $wR2 = 0.0924$ (all data).

(24) The sum of the bond angles around Ge in **6** is 325°, and the sum of the C–Ge–C bond angles around Ge in **4** is 318°.

(25) The sum of the C–Ge bond lengths in **6** is 6.063 Å, and the sum of the C–Ge bond lengths in compound **4** is 6.215 Å.

Scheme 4



of electrons on the germanium center into a bonding pair of electrons.²⁶ The Ge–B bond length is 2.094(3) Å. Heating **4** in the presence of $\text{Ph}_3\text{P} \cdot \text{BH}_3$ resulted in the formation of **6** and the recovery of free PPh_3 , demonstrating that **4** is a stronger donor than PPh_3 (Scheme 3).

Finally, in an effort to displace the carbene from the germanium, methyllithium was added to a solution of **4**. After an aqueous workup, compound **7**²⁷ was isolated.²⁸ The formation of **7** is consistent with nucleophilic attack of the methyllithium on the germanium center of **4** displacing carbene **3**, resulting in the formation of (dimesitylmethylgermyl)lithium, which is protonated upon aqueous workup (Scheme 4). Preliminary results show that when 0.5 equiv of methyllithium is added to **4**, $\text{Mes}_2(\text{Me})\text{GeGe}(\text{H})\text{Mes}_2$ is formed after workup, presumably by addition of $\text{Mes}_2\text{Ge}(\text{Me})\text{Li}$ to **4**.²⁹ Thus, we have established that **4** is a potential precursor for anionic germanium compounds.

To summarize, we have synthesized the first example of a carbene-stabilized transient diorganogermylene, **4**, from readily available starting materials. Complex **4** acts as a strong Lewis base toward BH_3 to give **6**, a rare example of an intermolecular group 14 “in-series” coordination compound. The carbene–germylene complex **4** is a thermal source of dimesitylgermylene and reacts with MeLi to displace the carbene. Currently, we are examining **4** as a germylene precursor for use in coordination chemistry^{8g} and as a precursor for anionic germanium compounds.

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Supporting Information Available: A CIF file giving crystallographic data and text giving detailed experimental procedures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(26) Similar bond angle shifts have been noted in a carbene–phosphinidene complex upon coordination to BH_3 . See: Arduengo, A. J., III; Carmalt, C. J.; Clyburne, J. A. C.; Cowley, A. H.; Pyati, R. *J. Chem. Soc., Chem. Commun.* **1997**, 981.

(27) **7** was previously synthesized by a different method. See: Castel, A.; Rivière, P.; Satgé, J.; Ko, Y. *J. Organomet. Chem.* **1988**, 342, C1.

(28) The carbene is presumably converted to the imidazolium chloride, which is removed in the aqueous phase.

(29) $\text{Mes}_2(\text{Me})\text{GeGe}(\text{H})\text{Mes}_2$ was previously synthesized by a different method. See the Supporting Information and: Dixon, C. E.; Netherton, M. R.; Baines, K. M. *J. Am. Chem. Soc.* **1998**, 120, 10365.