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Stabilization of a Transient Diorganogermylene by an N-Heterocyclic Carbene

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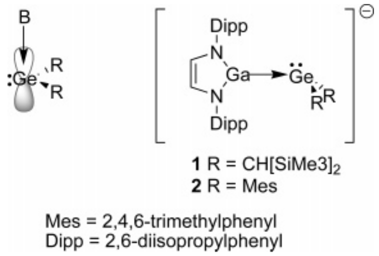
Summary: The synthesis of a carbene-stabilized transient germylene is presented; the resulting complex liberates free germylene upon heating, forms a stable adduct with BH_3, and reacts with MeLi to displace the carbene.

Germylenes, 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 germylenes 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 germylenes are known, and their reactivity has been well studied;[1e] however, far less is known about intermolecularly stabilized germylenes, particularly diorganogermylenes. Most intermolecularly base-stabilized $:GeR_2$ compounds are short-lived and are difficult to characterize.[1a,e,2] On the other hand, stable inorganic germanium(II) derivatives, such as $GeCl_2\cdot$(dioxane), have proven to be versatile reagents for the preparation of a variety of germanium compounds.[1] We believe that isolable, intermolecularly base-stabilized diorganogermylenes will have useful applications as ligands in coordination chemistry,[1f,3] as new thermal precursors for germylenes, 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 $Ge[CH(SiMe_3)_2]_2$[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 germylenes. 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 $:GeR_2$ 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.

Chart 1



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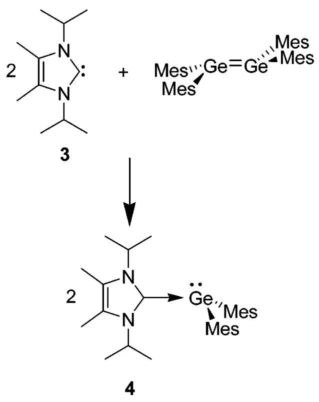
10.1021/om7006198 CCC: $37.00

Scheme 1



Two equivalents of carbene **3** was added to a yellow solution of tetramesityldigermene (Scheme 1).[16] No visible change was observed. ^{1}H and ^{13}C{^{1}H} 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 ^{1}H NMR spectrum of the product revealed the carbene and dimesitylgermylene moieties to be in a 1:1 ratio, and the ^{13}C 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 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.

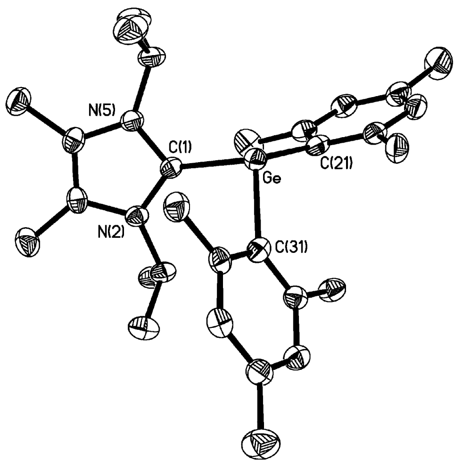
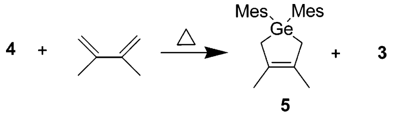
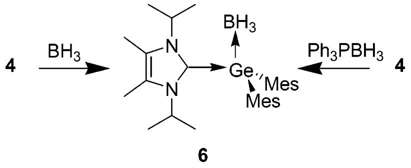


Figure 1. Thermal ellipsoid plot (50% probability surface) of **4**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ge−C1 = 2.078(3), Ge−C21 = 2.0649(18), Ge−C31 = 2.0713(16), C1−N2 = 1.359(4), C1−N5 = 1.357(4); C1−Ge−C21 = 109.18(11), C1−Ge−C31 = 95.93(12), C21−Ge−C31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

Scheme 2



Scheme 3



The germanium center in **4** has three bonds to carbon and a lone pair and, thus, is an isovalent analogue of phosphine ($R_3Ge:^-$ cf. $R_3P:$). To evaluate the potential of **4** to act as a Lewis base, 1 equiv of BH_3·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 ^{1}H 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 BH_3 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 Mes_4Ge_2 (0.161 mmol, from the photolysis of 100 mg of Mes_6Ge_3)[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. ^{1}H 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). ^{13}C{^{1}H} 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 [Mes_2Ge, 6%], 180 [C{[N(*i*-Pr)C(CH$_3$)]$_2$}, 34%], 138 [C{[N(*i*-Pr)C(CH$_3$)]$_2$} − *i*-Pr, 40%]. Although **4** was clean by ^{1}H 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**: [$C_{32.5}H_{36}GeN_2$], M_r = 537.30, triclinic, space group $P\bar{1}$, 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) Å^3, Z = 2, T = 150(2) K, μ = 1.046 mm^{-1}, 12 668 reflections collected, 4990 independent (R_{int} = 0.053), R1 = 0.0678, wR2 = 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.

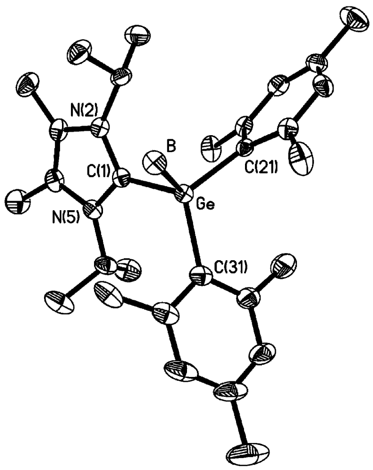
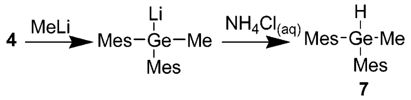


Figure 2. Thermal ellipsoid plot (50% probability surface) of **6**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): C1−Ge = 2.045(2), Ge−B = 2.094(3), Ge−C21 = 2.005(2), Ge−C31 = 2.001(2), C1−N2 = 1.361(3), C1−N5 = 1.353(3); C1−Ge−B = 104.6(1), C1−Ge−C21 = 102.67(9),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

Scheme 4



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 obtuse[24] and the germanium−carbon bond lengths are somewhat shorter.[25] Both observations are consistent with the conversion of the lone pair 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 $Ph_3P{\cdot}BH_3$ 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**, $Mes_2(Me)GeGe(H)Mes_2$ is formed after workup, presumably by addition of $Mes_2Ge(Me)Li$ 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.

Acknowledgment. We thank the NSERC (Canada) and the Ontario Photonics Consortium (OPC) for funding. We thank Doug Hairsine for acquiring mass spectrometric data. We also thank Teck Cominco Ltd. for a generous gift of $GeCl_4$.

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.

OM7006198

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(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 $BH_3{\cdot}THF$ 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, $^3J_{HH} = 7$ 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). $^{13}C\{^1H\}$ 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 [$M^+ - BH_3$, 100%], 373 [C{[N(*i*-Pr)C(CH_3)]$_2$}GeMes, 10%], 311 [Mes_2Ge, 20%]. High resolution EI-MS: *m/z* calcd for $C_{29}H_{45}{}^{11}B^{74}GeN_2$ 505.2818, found 505.2820. Anal. Calcd for $C_{29}H_{45}BGeN_2$: C, 68.96; H, 8.98. Found: C, 68.62; H, 9.45. Selected crystal data for **6**: [$C_{32}H_{48}BGeN_2$], $M_r = 544.12$, monoclinic, space group $P2_1/c$, $a = 22.0634(5)$ Å, $b = 8.6076(2)$ Å, $c = 16.2745(2)$ Å, $\beta = 93.0960(10)°$, $V = 3086.23(14)$ Å^3, $Z = 4$, $T = 150(2)$ K, $\mu = 1.014$ mm^{-1}, 28 738 reflections collected, 5429 independent ($R_{int} = 0.057$), 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.

(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) $Mes_2(Me)GeGe(H)Mes_2$ 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.