Crystalline Boragermenes

Bin Rao[a] and Rei Kinjo*[a]

Abstract: Boragermene **3** featuring a double bond between the Ge and dicoordinate B atoms has been synthesized for the first time by the reaction of a cyclic (alkyl)(boryl)germylene-PMe_3 adduct **1** with $Cl_2BN(SiMe_3)_2$ followed by reductive dehalogenation with KC_8. Addition of a Lewis base (^{Me}NHC) to **3** leads to the formation of the corresponding adduct **4**, which shows a double bond character between the Ge and tricoordinate B atoms. Compound **3** undergoes hydrogenation with H_2 molecules concomitant with a complete scission of the Ge=B bond.

Multiply bonded species involving main group elements have been the subject of a number of landmark studies in the modern inorganic chemistry.[1] In particular, the chemistry of heteroatomic multiple bond between boron and other p-block elements has attracted significant attention, reflecting the unique electronic and structural nature, reactivity, and their associated potential utility as building blocks. Over the past few decades, myriad compounds involving a double bond between boron and other elements, such as Al,[2] pnictogen (N, P and As)[3] and chalcogen (O, S, Se and Te),[4] in addition to transition metals,[5] have been developed and extensively studied.[6] For the derivatives with group 14 elements, Nöth et al. reported the first structural characterization of methyleneborane (>C=B–) in 1985.[7] Since then, a number of methyleneboranes have been described to date.[1c,8,9] Meanwhile, its heavy analogue, borasilenes (>Si=B–), have still remained rare (Figure 1a), which is predominantly attributed to the strong Lewis acidity of the boron atom and the high polarization of the Si=B bond.[10] In 2006, Sekiguchi and co-workers synthesized the first stable borasilene **I** and its ionic derivative **II**.[11] Very recently, the group of Iwamoto[12] and that of Inoue[13] independently reported borasilene-chloride adduct **III** and borasilene **IV** supported by 1,3,4,5-tetramethyl-imidazolin-2-ylidene (^{Me}NHC), respectively.

Given the fact that the difference of the period between germanium (the fourth period) and boron (the second period) is much greater, thus, being less efficient overlap between 4p and 2p orbitals in forming a π-bond, construction of Ge-B multiple bond is extremely challenging. Indeed, related compounds involving a Ge-B multiple bond have been much less described in the literature (Figure 1b). In 2005, the group of Sekiguchi proposed the generation of a transient boragermene species **V**, but only the product reacted with tetrahydrofuran (THF) via ring-expansion was spectroscopically characterized.[10] Recently, the group of Müller and Albers et al. reported the synthesis of aminoborole complex of germanium (II) by the reaction of a germole dianion with aminoboron dichlorides, in which an intermediate **VI** bearing a Ge=B bond is proposed and computationally supported.[14] To the best of our knowledge, neither base-free boragermene nor its base adduct have been isolated thus far. In this respect, isolable Ge=B species have long been sought after. In this contribution, we report the synthesis, single crystal X-ray diffraction, and computational studies of boragermene **VII** (Figure 1c). We also show that boragermene-Lewis base adduct **VIII** can be readily prepared from **VII**.

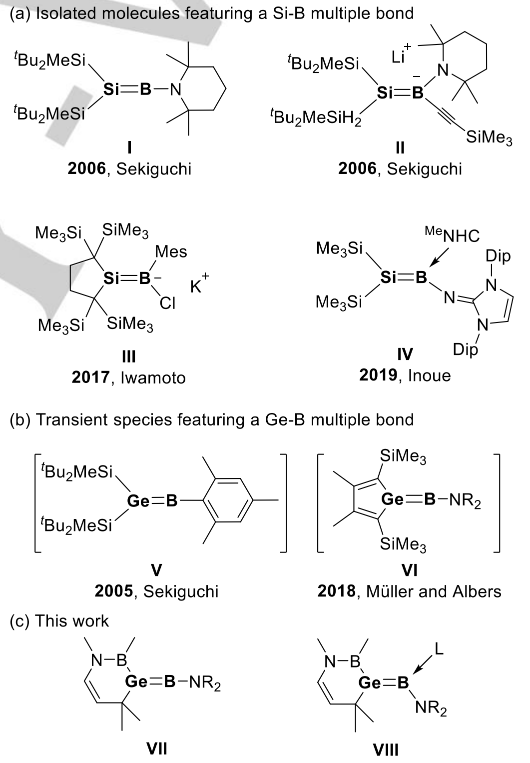

Figure 1. (a) Isolable Si=B double bond species (Mes = mesityl, ^{Me}NHC = 1,3,4,5-tetramethyl-imidazolin-2-ylidene, Ad = adamantyl); (b) proposed intermediates containing a Ge=B bond; (c) present work.

Recently, we have reported the isolation of a cyclic (alkyl)(boryl)germylene-PMe_3 adduct **1**, and demonstrated that compound **1** smoothly undergoes oxidative addition to H_2.[15] Accordingly, we postulated that the formation of Ge-B bond is feasible via a similar insertion of **1** into a B-X bond. Indeed, reaction of **1** with bis(trimethylsilyl)aminodichloroborane ($(Me_3Si)_2NBCl_2$), at room temperature in toluene proceeded cleanly over 14 hours, and an insertion product **2** was obtained as a white solid in 73% isolated yield (Scheme 1). Compound **2** was fully characterized by standard spectroscopic and crystallographic means (Figure 2, top). In the ^{11}B NMR spectrum of **2**, only a broad peak appears at 48.9 ppm, which could be the

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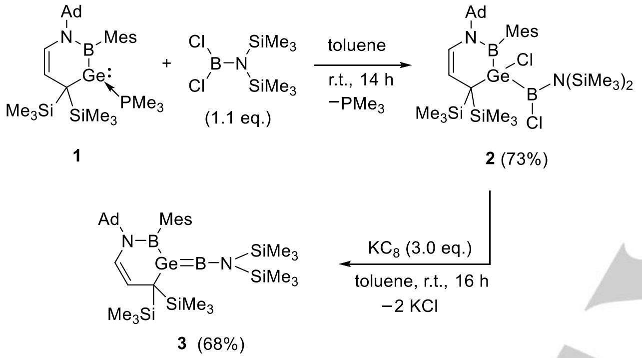
Supporting information for this article is given via a link at the end of the document.((Please delete this text if not appropriate)) overlapped signals of both tricoordinate boron atoms in **2**. Reduction of **2** with 3.0 equivalents of potassium graphite (KC_8) in toluene at room temperature for 16 hours, after workup, led to **3**, which was obtained as orange single crystals in 68% yield. **3** was characterized by standard crystallographic, spectroscopic and analytical methods. Particular diagnostic are the ^{11}B NMR signals at +94.5 ppm and +58.4 ppm, which are assigned to the dicoordinate boron atom at the Ge=B moiety and the tricoordinate boron atom in the C_3NBGe six-membered unit, respectively, based on the calculated results (+87.40 and +52.39 ppm) (Figure S11). The ^{11}B NMR signal (+94.5 ppm) for the Ge=B part is significantly shifted downfield with respect to that (48.9 ppm) of **2**, as well as, those of aminoboraalkenes (>C=B-N<, +59 ~ +71 ppm)[8] and **I** (>Si=B-N<, 87.7 ppm).[11a] In the ^1H NMR spectrum, only two sets of signals for four $SiMe_3$ groups are observed, suggesting the symmetric feature of **3** in the solution.



Scheme 1. Synthesis of **3**.

The solid-state structure of **3** determined by X-ray diffractometry (Figure 2, bottom) revealed the bent geometry with the Ge1-B2-N2 bond angle of 158.6(5)°, which is in stark contrast to the nearly linear fashion of its analogues >C=B-N< (174.8(3)°) reported by Bertrand and Stephan et al.[9a] and **I** >Si=B-N< (176.87(13)°) reported by Sekiguchi and coworkers.[11a] The Ge1 center in **3** exhibits a pyramidal geometry (Σ_{Ge1} = 340°) whereas the N2 atom is in a planar environment (Σ_{N2} = 359°). The B1-Ge1-C13 and Si3-N2-Si4 planes are nearly perpendicular to each other (79.74°). The Ge1-B2 (1.911(7) Å) bond distance is much shorter than that of **2** (2.122(7) Å), as well as, typical Ge-B single bond (2.045–2.165 Å),[16] indicative of a multiple bond character between the Ge1 and B2 atoms. The Ge1-B1 (2.029(7) Å) and N2-B2 (1.358(8) Å) bond distances of **3** are shorter than those of **2** (Ge1-B1 2.109(7), N2-B2 1.394(9) Å), suggesting enhanced interaction between those atoms.

To gain further insight into the electronic structure of **3**, DFT calculations were carried out at the M062X/Def2-TZVP level of theory (Figure 3a). The HOMO largely represents the π-type bonding interaction between the Ge1 and B2 atoms while the HOMO-6 corresponds to the Ge1-B2 σ-bond. A π-type bonding interaction between the B2 and N2 atoms is found in the HOMO-9 (Figure S4), suggesting a partial Ge=B=N hetero-allenic character. Natural bond orbital (NBO) analysis shows the Wiberg bond index (WBI) value of 1.67 for the Ge1-B2 moiety indicating a strong double bond character (Figure S6), which is in line with the short Ge1-B2 bond distance. While the WBI value of 0.94 for the B2-N2 moiety is slightly less than 1, natural resonance theory (NRT) analysis supports the Ge=B=N allenic character (Figure S12). The deformation density plots show that flow of electron densities occurs not only from the >***Ge:*** fragment to >N***B:*** fragment but also from the >N***B:*** to >***Ge:*** centers (Figure 3b), which can be putatively rationalized by the formal double donor-acceptor bonding model.[1,17] Natural population analysis (NPA) reveals that the charges on the Ge1-B2 moiety are +0.34 for the Ge1 atom and +0.59 for the B2 atom (Figure S5), respectively, which is in stark contrast to the high polar nature of the Si=B moiety of borasilene **I** (NPA charges: Si = –0.27, B = +0.36).[11]

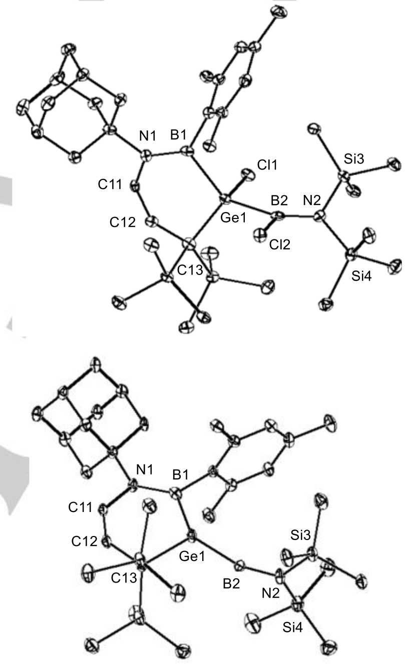


Figure 2. Solid-state structure of **2** (top) and **3** (bottom). Hydrogen atoms are omitted for clarify. Thermal ellipsoids are set at the 30% probability level.

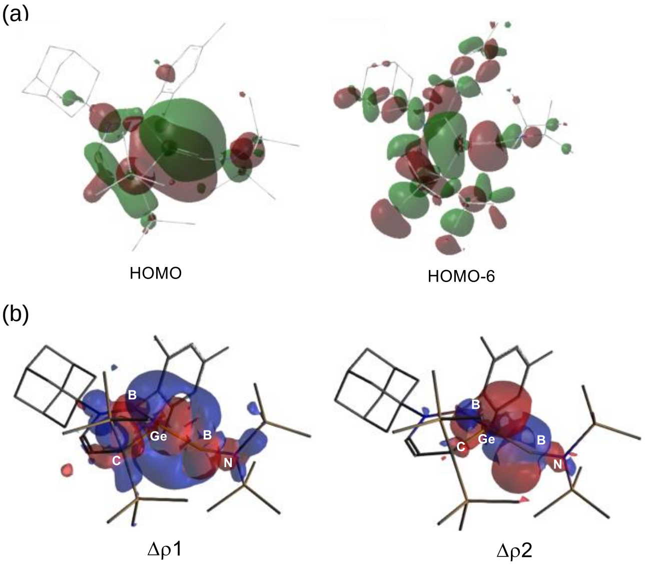
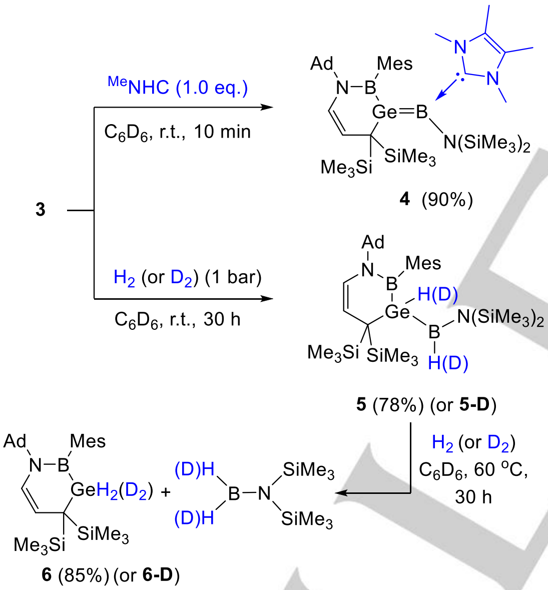


Figure 3. (a) Plots of the frontier molecular orbitals of **3** (Isovalue 0.02); (b) The first two density deformation plots of **3** (Charge flow: red → blue).

To examine the electrophilic nature of the dicoordinate boron center in **3**, we have preliminary investigated the reactivity (Scheme 2). Treatment of **3** with ^{Me}NHC in C_6D_6 led to a dark blue solution immediately. After workup, the corresponding adduct **4** was isolated as a blue solid in 90% yield. Spectroscopically, the ^{11}B NMR spectrum of **4** displays a sharp peak at +35.5 ppm for the ^{Me}NHC-coordinated boron centre, which is significantly shifted upfield with respect to that of **3** (+94.5 ppm). Structurally (Figure 4), **4** features a slightly twisted geometry between the B1-Ge1-C3 and C4-B2-N2 planes with a dihedral angle of 22.82°, as well as, nearly planar Ge1 and B2 centers (Σ_{Ge1} = 359.26° and Σ_{B2} = 360°). The Ge1-B2 (1.967(4) Å) bond distance is slightly longer than that of **3** (1.911(7) Å) whereas the B2-N2 (1.500(5) Å) bond length is significantly longer than that of **3** (1.358(8) Å). Theoretically, π- and σ-type bonding interaction between Ge1 and B2 atoms are found in the HOMO and HOMO-1 of **4** (Figure 4 and Figure S8), indicating the multiple bond nature of the Ge1-B2 moiety. The introduction of ^{Me}NHC mainly decreases the interaction between the lone pair electrons on the N2 atom and the B2 center, leading to the decreased WBI value (0.77) for N2-B2 of **4** with respect to that (0.94) of **3**, whereas the WBI value (1.62) for Ge1-B2 in **4** is found to be comparable to that (1.67) in **3** (Figure S9).



Scheme 3. Reactivity of **3** with ^{Me}NHC and H_2

Interestingly, upon exposure of a benzene solution of **3** to hydrogen gas (1 bar) at room temperature for 30 hours, the clean formation of hydrogenation product **5** was observed (Scheme 2). In the ^{1}H NMR spectrum of **5**, a doublet appears at 4.00 ppm (Figure S1), which is assigned to the hydrogen atom on germanium. The ^{11}B NMR spectra shows a broad peak at 54.0 ppm, which could be the overlapped signals of the B atoms in the C_3NBGe ring and B-N(SiMe$_3$)$_3$ unit (Figure S1d). Continuous heating of a benzene solution of **5** under the hydrogen atmosphere (1 bar) at 60 °C resulted in the complete cleavage of the Ge-B bond, and the formation of dihydrogermane derivative **6**[15a] was observed (85% NMR yield), concomitant with the release of $H_2BN(SiMe_3)_2$ (Figure S1e). Employment of D_2 under the same reaction conditions gave rise to the corresponding D-labelled products (**5-D**, **6-D**, and $D_2BN(SiMe_3)_2$), respectively (Figure S2). The high electrophilicity of the B center in **3** must be responsible for the formation of **4** and **5** (Figure S13), which is reminiscent of the reactivity of carbene-borylene adducts (>C=BR).[5,9a,18,19]

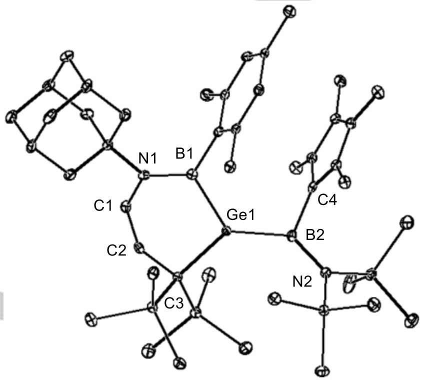


Figure 3. Solid-state structure of **4**. All hydrogen atoms are omitted for clarify. Thermal ellipsoids are set at the 30% probability level.

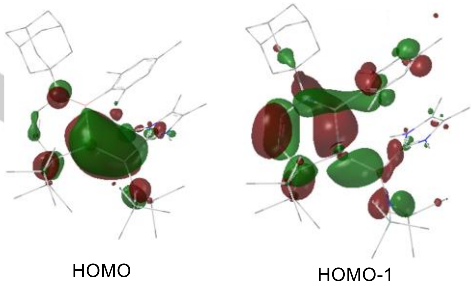


Figure 4. Plots of the frontier molecular orbitals of **4** (Isovalue 0.02).

Collectively, we have demonstrated that the synthesis of isolable boragermene **3** and its Lewis base-adduct **4** is feasible. An experimental and computational joint analysis indicates that both the former and the latter feature a multiple bond character between the Ge and B(*sp*) atoms and the B(*sp*^{2}) atom, respectively. Moreover, we have shown that double hydrogenation of the Ge=B moiety of **3** proceed stepwisely under the mild reaction condition.

Acknowledgments

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Keywords: Double bond • Germanium • Boron • H_2 activation

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COMMUNICATION

Boragermenes

Boragermene featuring a double bond between the germanium (Ge) and boron (B) atoms has been isolated for the first time from a cyclic (alkyl)(boryl)germylene-PMe_3 complex. This compound readily reacts with a Lewis base ^{Me}NHC to form corresponding adduct on the boron centre, and also undergoes hydrogenation with H_2 molecule over the Ge=B bond.

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