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Cyclic (alkyl)(boryl)germylene derived from cyclic (alkyl)(amino)germylene

Bin Rao^[a] and Rei Kinjo^{*[a]}

Abstract: Cyclic (alkyl)(amino)germylene **1** undergoes a ring expansion reaction with dibromomesitylborane (MesBBr₂) to afford a six-membered dibromogermane derivative **2**. In the presence of Lewis bases (PMe₃ or Me₂NHC), reduction of **2** with two equivalents of potassium graphite (KC₈) gives rise to cyclic (alkyl)(boryl)germylene-base adducts **3** and **4**, respectively. Upon heating, compound **3** reacts with H₂ to yield the germane **6**, probably through a base-free germylene **V** featuring the small HOMO-LUMO gap.

Harris and Lappert's report on the synthesis of dicoordinate germylene in the 1970's,^[1] represents a landmark in the chemistry of the group 14 heavier tetrelenes.^[2] Since then, a variety of isolable germynes featuring various steric and electronic impacts around the germylene center have come forward, and their utilities in application have been widely explored.^[2,3] While diverse germynes are synthetically accessible nowadays, only a few examples of the boryl-substituted germynes have been described thus far (Fig. 1). In 2012, the team of Jones, Kaltsoyannis, Mountford and Aldridge first reported (amino)(boryl)germylene **I**.^[4] The same group subsequently reported another example **II**^[5] in 2015, and also developed N-heterocyclic carbene (NHC) adduct of (boryl)(chloro)germylene **III**^[6] as well as (aryl)(boryl)germylene **IV**^[7] in 2016. For the installation of the boryl group onto the germylene centre by the conventional method, the use of boryllithium^[8] (CHDippN)₂BLi(thf)₂ is prerequisite. Accordingly, all of the reported derivatives **I-IV** bear the same boryl group (CHDippN)₂B and therefore they are based on acyclic system. Considering the reported unique reactivity of boryl-substituted germynes towards small molecules such as SiH₄, BH₃NMe₃ and acetylene,^[5,7] development of an alternative synthetic strategy is highly desirable. Of particular interest is the cyclic system as it has been demonstrated that the cyclic tetrelenes differ from acyclic counterparts in its electronic structure, stability, reactivity, and coordination ability to metals.^[9] To the best of our knowledge, however, cyclic germylene with boryl group has never been described to date.

In this contribution, we show that the synthesis of cyclic (alkyl)(boryl)germylene **V** in its Lewis base adduct form is feasible (Fig. 1). We also discuss the thermal stability of **V**, as well as, the reactivity toward H₂.

Figure 1. Reported examples of boryl-substituted germynes **I-IV** (Dipp = 2,6-ⁱPr₂C₆H₃, Mes = 2,4,6-Me₃C₆H₂) and a proposed species **V**, which is stabilized by a Lewis base in this work (Ad = adamantyl).

A toluene solution of cyclic (alkyl)(amino)germylene (cAAGe) **1**^[10] was reacted with one equivalent of dibromomesitylborane at room temperature for 24 hours (Scheme 1). After workup, a dibromogermane derivative **2** was obtained in 80% isolated yield, and fully characterized by standard spectroscopic and analytical means. In the ¹¹B NMR spectrum of **2**, a singlet appears at 46.6 ppm, in a typical range for tricoordinate boron. Colorless single crystals of **2** were obtained from a saturated hexane solution at room temperature, and the solid-state structure determined by X-ray diffractometry revealed the formation of a GeBNC₃ six-membered ring (Fig. 2, left). While the detail of the reaction mechanism is unclear at present, to the best of our knowledge, the formation of **2** represents the first example for a ring expansion reaction of a cyclic germylene accompanied by oxidation of Ge(II) to Ge(IV) via insertion of a boron atom into the Ge–N bond.^[11]

Scheme 1. Synthesis of **2**.

With dibromogermanium derivative **2** in hand, cyclic (alkyl)(boryl)germylene **V** was targeted. In an initial attempt to access the germylene, compound **2** was treated with two equivalents of KC₈ in THF. However, this led to a complex mixture, and no evidence for the generation of **V** was detected. Repeating the reaction in the presence of excess trimethyl phosphine (PMe₃) resulted in the formation of germylene-PMe₃.

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adduct **3**, which was isolated as a yellow solid in 57% yield (Scheme 2). In the ^{31}P NMR spectrum of **3**, a singlet for the PMe_3 moiety appears at $\delta = -34.9$ ppm. The ^{11}B NMR spectrum displays a broad singlet at $\delta = 60.9$ ppm, which is shifted downfield with respect to that of **2** ($\delta = 46.6$ ppm). An X-ray diffraction analysis reveals that the germanium centre of **3** coordinated by boron, carbon and phosphorus atoms exhibits a pyramidal geometry (the sum of bond angles = 308.87°) (Fig. 2, middle). The Ge–P bond length (2.4108(6) Å) is longer than those in the analogous PMe_3 -adducts of cyclic disilyl germylene (2.3484(6) Å),^[12] divinyl germylene (2.3900(7) Å)^[13] and (aryl)(germyl)germylene (2.4041(9) Å).^[14] The Ge–B bond distance is 2.121(2) Å, which is slightly longer than that (2.084(3) Å) in **2** and in range for the reported Ge–B single bond.^[4–7,15] When PEt_3 or PPh_3 were employed instead of PMe_3 , no corresponding germylene-phosphine adduct were formed.

Scheme 2. Reduction of **2** in the presence of bases ($\text{MeNHC} = 1,3,4,5$ -tetramethylimidazol-2-ylidene).

Likewise, reduction of **2** in the presence of one equivalent of 1,3,4,5-tetramethylimidazol-2-ylidene (MeNHC) afforded **4** as a

pale yellow solid in 62% yield (Scheme 2).^[16] The solid-state structure of **4** (Fig. 2b) confirmed the coordination of MeNHC to the Ge centre and the bond length between the Ge atom and the carbenic carbon (2.073(2) Å) is similar to those reported for germylene- MeNHC adducts (cf. 2.05 – 2.11 Å).^[17] We have also confirmed that treatment of **3** with one equivalent of MeNHC immediately led to **4** as well, accompanied with the release of free PMe_3 .

Formation of **3** and **4** indicates the pronounced Lewis acidic nature of the Ge center in **V**. Indeed, brief inspection of the frontier orbitals of **V** revealed that the LUMO (−2.368 eV) of **V** is lower in energy than that (−2.076 eV) of acyclic (aryl)(boryl)germylene, which can be rationalized on the basis of the interaction between the unoccupied p-orbitals of the Ge and B atoms (Fig. S4 and S5). Consequently, the HOMO-LUMO gap (2.667 eV) of **V** is smaller than that (2.894 eV) of acyclic system, suggesting the potential utility of **V** for small molecule activation.^[3] Accordingly, attention turned to the use of germylene-Lewis base adduct for the generation of **V**. While **4** is stable in the solution of THF and benzene under argon atmosphere at room temperature, **3** gradually decomposes under the similar condition. Therefore, we investigated the thermal stability of **3**. A THF-d_8 solution of **3** was heated at 40°C , and the reaction was monitored by NMR spectroscopy. Over 16 hours, the formation of a major product concomitant with the release of Me_3P was observed. After workup, compound **5** was isolated as a yellow solid in 78% yield (Scheme 3). **5** was characterized by standard spectroscopic techniques, and its atomic connectivity could be established definitively with the help of x-ray crystallography. Compound **5** can be described in terms of a spiro[3.6]molecule, and the GeBC_3N four-membered ring and the $\text{Ge}_2\text{BC}_3\text{N}$ ring are linked at the tetracoordinate Ge atom (Fig. 3, left). Interestingly, the $\text{Ge}_2\text{BC}_3\text{N}$ ring involves an (alkyl)(germyl)germylene moiety, in which the germylene centre Ge2 is coordinated by the C1-C2-C3 allylic moiety in an η^3 -fashion (Fig. S6 and S7).^[18] Significantly, when a THF-d_8

Figure 2. Solid-state structures of **2** (left), **3** (middle) and **4** (right) (all hydrogen atoms are omitted for clarity). Thermal ellipsoids are set at the 30% probability. Selected bond lengths [Å] and angles [$^\circ$]: **2** N1–B1 1.403(3), B1–Ge1 2.084(3), Ge1–C13 1.963(2), C13–C12 1.516(3), C12–C11 1.342(3), C11–N1 1.434(3), C11–N1–B1 121.92(19), N1–B1–Ge1 112.15(17), B1–Ge1–C13 109.90(10), Ge1–C13–C12 102.07(15), C13–C12–C11 132.4(2), C12–C11–N1 132.7(2); **3**, Ge1–P1 2.4108(6), N1–B1 1.426(3), B1–Ge1 2.121(2), Ge1–C13 2.061(2), C13–C12 1.504(3), C12–C11 1.336(3), C11–N1 1.429(3), C13–Ge1–B1 98.91(8), C13–Ge1–P1 112.10(6), B1–Ge1–P1 97.86(6); **4**, Ge1–C29 2.073(2), N1–B1 1.424(3), B1–Ge1 2.110(2), Ge1–C22 2.090(2), C22–C21 1.503(3), C21–C20 1.342(3), C20–N1 1.432(3), C22–Ge1–B1 99.37(9), C22–Ge1–C29 111.24(8), B1–Ge1–C29 89.25(9).

solution of **3** was heated in the presence of additional PMe_3 , no decomposition of **3** was observed even at 60 °C. This result implies that dissociation of Me_3P from the Ge centre in **3** may be involved as the initial step in the decomposition process (See also Scheme S2). While the reaction pathway for the formation of **5** is still unclear, we postulate that germylene **V** is generated from **3** concomitant with the release of Me_3P . To bear out our hypothesis, a C_6D_6 solution of **3** was heated at 50 °C under H_2 atmosphere. After heating for 12 hours, workup of the reaction mixture afforded a dihydrogermane derivative **6** in 74% yield, which was characterized by standard spectroscopic, analytical, and crystallographic methods (Fig. 3, right). The formation of **6** indicates that *in-situ* generated **V** readily cleaves the H–H bond.^[7,19] Note that **1** does not react with H_2 molecule even at 120 °C.

Scheme 3. Synthesis of **5** and **6**.

In conclusion, we have shown that five-membered cyclic (alkyl)(amino)germylene **1** can be converted into six-membered cyclic (alkyl)(boryl)germylene-Lewis base adducts **3**, **4** via a ring expansion reaction followed by reduction in the presence of Lewis base. Thermolysis of **3** leads to the formation of cyclic (alkyl)(germyl)germylene **5** featuring an η^3 -coordination system between the C1–C2–C3 allylic moiety and the germylene center. Upon heating, **3** reacts with H_2 to give the germane **6**, probably via the transient species **V**.

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Keywords: Germylene • Ring expansion • Boryl substituents

Figure 3. Solid-state structures of **5** (top) and **6** (bottom) (hydrogen atoms except for those on the Ge atom in **6** are omitted for clarity). Thermal ellipsoids are set at the 30% probability. Selected bond lengths [Å] and angles [°]: **5**, N1–B1 1.406(3), B1–Ge1 2.110(3), Ge1–Ge2 2.4664(3), Ge2–C23 2.191(2), Ge2–C22 2.214(2), Ge2–C21 2.193(2), C23–C22 1.436(3), C22–C21 1.416(3), C21–N1 1.457(3), Ge2–Ge1–B1 96.13(7), C23–Ge2–Ge1 107.68(6); **6**, N1–B1 1.416(3), B1–Ge1 2.076(3), Ge1–C3 1.998(3), C3–C2 1.535(3), C2–C1 1.348(3), C1–N1 1.455(3), C3–Ge1–B1 106.99(11).

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Ring expansion of a five-membered cyclic (alkyl)(amino)germylene with dihaloborane followed by reduction in the presence of Lewis base affords six-membered cyclic (alkyl)(boryl)germylene-Lewis base adducts. Upon heating, the latter does not only undergoes dimeric skeletal isomerization to give cyclic (alkyl)(germyl)germylene featuring an η^3 -coordination system, but also reacts with H_2 , most likely via a transient base-free cyclic (alkyl)(boryl)germylene species.

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