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Borane-Catalyzed Cross-Metathesis Strategy for Facile Transformation of Cyclic (Alkyl)(Amino)Germylenes

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

Abstract: A borane $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed metathesis reaction between the Si-C bond in cyclic (alkyl)(amino)germylene (CAAGe) **1** and the Si-H bond in silanes (R_3SiH) **2** is reported. Mechanistic studies propose that the initial step of the reaction involves Si-H bond activation to furnish an ionic species $[\text{1-SiR}_3]^+[\text{HB}(\text{C}_6\text{F}_5)_3]^-$, from which $[\text{Me}_3\text{Si}]^+[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ and an azagermole intermediate are generated. The former yields Me_3SiH concomitant with the regeneration of $\text{B}(\text{C}_6\text{F}_5)_3$ whereas the latter undergoes isomerization to afford CAAGes bearing various silyl groups on the carbon next to the Ge center. This strategy has allowed for the straightforward synthesis of eight new CAAGes starting from **1**.

Germylenes ($\text{R}_2\text{Ge:}$), a member of the group 14 heavier tetrylene family, have been attracting considerable attention on account of its diverse utilities in various applications.^[1] Thus far, a variety of cyclic and acyclic dicoordinate germylene derivatives have been reported.^[2] Despite a relatively long history of dicoordinate germylenes since the first isolation of stable germylene by Harris and Lappert in the 1970s,^[3] its synthetic route is still limited: the most widely employed methods for the preparation of isolable dicoordinate germylenes **I** are (i) the substitution reaction between: GeCl_2 -dioxane complex and nucleophiles (R-M), (ii) the reductive dehalogenation reaction of the corresponding dihalide precursors with metals, and (iii) transmetalation/ deprotonation with diaminogermylene ($:\text{Ge}(\text{N}(\text{SiMe}_3)_2)_2$) (Figure 1A). Other reported specific approaches include the reaction of a germole dianion with hafnocene,^[4] as well as, the conversion of base-stabilized tricoordinate germylenes,^[5] while the generation of transient dicoordinate germylenes by thermolysis and photolysis reaction^[2a,6] or dissociation from digermenes^[2g,7] has been described. To date, only one example for the synthesis of a dicoordinate cyclic germylene from a dicoordinate cyclic germylene has been reported by Weidenbruch et al., who demonstrated that an N-heterocyclic germylene **II** undergoes the cross-coupling reaction with an N-heterocyclic silylene to afford a cyclic (silyl)(amino)germylene **III** via a skeletal isomerisation of a germasilene intermediate (Figure 1B).^[8] All above-mentioned protocols are on the basis of direct and stoichiometric reactions, and to the best of our knowledge, the formation of dicoordinate germylenes by catalysis has never been achieved. Recently, we have reported the first isolation of a cyclic

(alkyl)(amino)germylene **1**,^[9] a heavier congener of cyclic (alkyl)(amino)carbenes (CAACs).^[10,11] Here we show a metal-free catalytic strategy to lead the diverse cyclic (alkyl)(amino)germylenes (CAAGes) from **1** promoted by $\text{B}(\text{C}_6\text{F}_5)_3$ (Figure 1C).

Figure 1. (A) General synthetic routes to dicoordinate germylenes **I**. (B) Transformation of dicoordinate cyclic germylene **II** to dicoordinate cyclic germylene **III** via a germasilene intermediate. (C) Present work.

Cyclic (alkyl)(amino)germylene **1** was synthesized by following the reported procedure (Scheme S1).^[9] First, we confirmed that **1** does not react with diphenylsilane **2a** in C_6D_6 even at 120°C (Figure S1). By contrast, the addition of a catalytic amount (15 mol%) of tris(pentafluorophenyl)borane $\text{B}(\text{C}_6\text{F}_5)_3$ to the mixture of **1** and **2a** at room temperature led to the full consumption of **2a** after 24 h. Concomitantly, the formation of two new products in addition to trimethylsilane^[12] was observed. Optimization of the reaction condition has allowed for the selective formation of the product (Scheme 1). Thus, when 3.0 equivalents of **2a** were utilized, only one product **4** was formed after heating at 60°C for 12 h. Meanwhile, the same reaction with 0.7 equivalent of Ph_2SiH_2 **2a** at room temperature for 24 h led to the formation of **3** as the major product. Both **3** and **4** are germylenes as confirmed by the standard spectroscopic means, as well as, a single-crystal X-ray diffraction analysis (Figure S8). **4** bears two diphenylsilyl groups at the quaternary sp^3 carbon in the five-membered ring whereas **3** possesses one trimethylsilyl group

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and one diphenylsilyl group. These results indicate that $B(C_6F_5)_3$ promotes cross-metathesis of C–Si and Si–H bonds to furnish new silyl-functionalized germynes. [13]

Scheme 1. Synthesis of **3** and **4**.

To examine the scope of silane substrates, the C–Si/Si–H cross-metathesis reaction with various hydrosilane **2** was briefly investigated (Scheme 2). Treatment of **1** with three equivalents of dimethyl(phenyl)silane **2b** at 90 °C afforded **5** bearing two dimethyl(phenyl)silyl groups in 82% yield. The reaction with triphenylsilane **2c** led to only one silyl group-exchange and **6** with one trimethylsilyl group and one diphenylsilyl group was obtained in 60% yield. It can be envisaged that the steric hindrance of the bulky triphenylsilyl group confined the subsequent second silyl group-exchange. Interestingly, when a stoichiometric amount of 1,2-bis(dimethylsilyl)benzene **2d** was employed, **7** featuring a spiro-structure was exclusively formed (85% yield). We also confirmed that the reaction could be conducted on a large scale (2 mmol), from which 0.723 g of **7** was isolated (80% yield). The reaction with four equivalents of triethylsilane **2e** afforded a mixture of **8** bearing one trimethylsilyl group and one triethylsilyl group and **9** having two triethylsilyl groups in 26 % and 53% yields, respectively (Figure S2). We further confirmed that treatment of **9** with a half equivalent of **2a** yielded **10** possessing one triethylsilyl group and one diphenylsilyl group. The solid-state structures of products **5**, **6**, **7** and **10** were unambiguously verified by the single-crystal X-ray diffractometry (Figure S8).

To investigate the reversible nature of the metathesis reaction, we have carried out the reactions between **4** and **2e** in various ratios (**4**:**2e** = 1:1, 1:3, 1:6, 1:9) using 15 mol% of $B(C_6F_5)_3$ at ambient condition. Scheme 3 summarizes the ratios of **4**/**10** (5.2:1, 2.5:1, 1.7:1 and 1.3:1 respectively) in the respective equilibrium state, from which the nearly identical equilibrium constant of 0.036 was obtained (Figure S3). The metathesis reactions of **1** with **2** (Schemes 1 and 2) may release gaseous trimethylsilane (b.p. 6.7 °C), which could be a driving force for the smooth formation of the corresponding products.

Scheme 2. Synthesis of **5**, **6**, **7**, **8**, **9** and **10**. *toluene was used as a solvent.

Scheme 3. The reactions between **4** and **2e** in various ratios.

To gain insight into the reaction mechanism, we performed several control experiments (Scheme 4). A stoichiometric reaction of germene **1** with $B(C_6F_5)_3$ indicated a weak interaction between them while no obvious formation of the Lewis adduct^[14] was observed (Scheme 4A and Figure S4). During the catalytic reaction of **1** with Ph_2SiH_2 **2a** (Scheme 1), a peak corresponding to the borate $[HB(C_6F_5)_3]^-$ was detected at –

24.1 ppm, $J_{\text{B-H}} = 81.8$ Hz) in the ^{11}B NMR spectrum (Figure S5),^[14,15] which indicates that $\text{B}(\text{C}_6\text{F}_5)_3$ activates the Si-H bond of silane during the reaction. Concomitantly generated silyl cation $[\text{R}_3\text{Si}]^+$ will be coordinated by the Lewis basic Ge center of **1** to furnish a germlyl cation $[\text{1-SiR}_3]^+$.^[16] Thus, we inferred that the ionic species $[\text{1-SiR}_3]^+[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ would be the key intermediate generated at the initial stage of the reaction, from which the exchange of silyl groups may proceed. To bear out this hypothesis, a stoichiometric reaction between **1** and a silyl cation was carried out (Scheme 4B and Figure S6). Germlylene **1** was treated with $[\text{Et}_3\text{Si}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ in $\text{C}_6\text{D}_5\text{Cl}$ at room temperature, and the reaction was monitored by NMR spectroscopy, which indicated the immediate formation of an ionic species, which is most likely $[\text{1-SiEt}_3]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ **A**. Within 1.5 hours, we observed a partial conversion of **A** to other three ionic species that are tentatively assigned to **B**, **C** and **D** (Figure S6). Indeed, the addition of a hydride source $\text{KHB}(\text{Bu})_3$ to the reaction mixture of **A-D** furnished germlylenes **1** and **8**, along with $\text{K}^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ and $\text{B}(\text{Bu})_3$ (Figure S6).

Scheme 4. Stoichiometric reactions between **1** and $\text{B}(\text{C}_6\text{F}_5)_3$ (A), and **1** and $[\text{Et}_3\text{Si}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (B). A proposed transformation process from **A** to **8** via **E** (C).

These results suggest that after the initial formation of **A**, one of the trimethylsilyl groups is spontaneously dissociated from **A** to release trimethylsilyl cation $[\text{Me}_3\text{Si}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ concomitant with the generation of an azagermole derivative **E** which would undergo isomerisation to afford **8** (Scheme 4C). Recombination of **8** with $[\text{Me}_3\text{Si}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ may lead to the formation of **D**. The same process could occur from **B-D**, resulting in the scrambling formation of **A-D**. When **1** was reacted with 0.8 equivalent of

$[\text{Et}_3\text{Si}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$, generation of **8** besides **A-D** was confirmed (Figure S7).

To examine the relative energy of the key intermediates, we carried out a theoretical study on the cationic part $[\text{1-SiMe}_3]^+$ of **B** using the DFT method (Figure 4). Generation of azagermole **E'** from $[\text{1-SiMe}_3]^+$ via dissociation of a trimethylsilyl group is endergonic with $\Delta G = 29.5$ kcal·mol⁻¹. Note that $[\text{Me}_3\text{Si-H-SiMe}_3]^+$ could also be considered as the plausible intermediate in the actual catalytic reaction due to its slightly higher stability in comparison to $[\text{Me}_3\text{Si}^+(\text{C}_6\text{H}_6)]^+$,^[17] which may lead to the smaller ΔG for the generation of **E'** from $[\text{1-SiMe}_3]^+$. Compared with **E'**, germlylene **1** is thermodynamically by 5.5 kcal·mol⁻¹ stable, which is in line with the proposed **E**→**8** isomerisation (Scheme 4c). It can be envisaged that germlylene featuring the divalent Ge center with the adjacent N atom is more stable than azagermole with the doubly bonded Ge atom. It is salient to mention that the azagermole→germlylene isomerisation process via 1,2-silyl migration is in stark contrast to the silylene→silene isomerisation observed by Kira and Iwamoto et.al.^[18]

Figure 4. Free energy differences (ΔG in kcal·mol⁻¹) among $[\text{1-SiMe}_3]^+$, **E'** and **1**, calculated at the B3LYP/6-311G* level of theory.

Scheme 5. Proposed catalytic cycle for the $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed Si-C/Si-H cross-metathesis reaction.

On the basis of experimental and theoretical results, one of the plausible mechanisms for the $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed cross-metathesis reaction is proposed in scheme 5. The initial step is the activation of the Si-H bond of silane HSiR_3 by borane $\text{B}(\text{C}_6\text{F}_5)_3$ to afford an ionic intermediate $[\text{1-SiR}_3]^+[\text{HB}(\text{C}_6\text{F}_5)_3]^-$.^[19] Subsequent elimination of one of the trimethylsilyl groups leads to the generation of $[\text{Me}_3\text{Si}]^+[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ and an azagermole intermediate **E'**, which undergoes isomerization via a 1,2-shift of the silyl (R_3Si) group on the Ge center to afford germylene **11**. A hydride transfer from the B center to the Si center in $[\text{Me}_3\text{Si}]^+[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ yields gaseous trimethylsilane, and the concomitant reproduction of $\text{B}(\text{C}_6\text{F}_5)_3$ may complete the catalytic cycle.

In conclusion, we have demonstrated that a catalytic amount of $\text{B}(\text{C}_6\text{F}_5)_3$ promotes a Si-C/Si-H cross-metathesis reaction between cyclic (alkyl)(amino)germylenes and various hydrosilanes **2**, which has allowed straightforwardly accessing to new germylenes.

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Keywords: Germylene • Metathesis • $\text{B}(\text{C}_6\text{F}_5)_3$

- [1] a) W. Petz, *Chem. Rev.* **1986**, *86*, 1019; b) P. P. Power, *Nature* **2010**, *463*, 171; c) P. P. Power, *Chem. Rev.* **2012**, *12*, 238; d) G. He, O. Shynkaruk, M. W. Lui, E. Rivard, *Chem. Rev.* **2014**, *114*, 7815; e) L. Álvarez-Rodríguez, J. A. Cabeza, P. García-Álvarez, D. Polo, *Coord. Chem. Rev.* **2015**, *300*, 1; f) S. Yadav, S. Saha, S. S. Sen, *ChemCatChem* **2015**, *8*, 486; g) T. Chu, G. I. Nikonov, *Chem. Rev.* **2018**, *118*, 3608. Catalytic examples: h) A. Brück, D. Gallego, W. Wang, E. Irran, M. Driess, J. F. Hartwig, *Angew. Chem. Int. Ed.* **2012**, *51*, 11478; *Angew. Chem.* **2012**, *124*, 11645; i) W. Wang, S. Inoue, S. Enthaler, M. Driess, *Angew. Chem. Int. Ed.* **2012**, *51*, 6167; *Angew. Chem.* **2012**, *124*, 6271; j) D. Gallego, A. Brück, E. Irran, F. Meier, M. Kaupp, M. Driess, J. F. Hartwig, *J. Am. Chem. Soc.* **2013**, *135*, 15617.
- [2] a) W. P. Neumann, *Chem. Rev.* **1991**, *91*, 311; b) N. Tokitoh, R. Okazaki, *Coord. Chem. Rev.* **2000**, *210*, 251; c) M. Kira, S. Ishida, T. Iwamoto, *Chem. Rev.* **2004**, *4*, 243; d) M. Lappert, A. Protchenko, P. Power, A. Seeber, in *Metal Amide Chemistry*, John Wiley & Sons, Ltd.: Chichester, UK, **2008**, pp. 263–326; e) S. Nagendran, H. W. Roesky, *Organometallics* **2008**, *27*, 457; f) A. V. Zabula, F. E. Hahn, *Eur. J. Inorg. Chem.* **2008**, *2008*, 5165; g) Y. Mizuhata, T. Sasamori, N. Tokitoh, *Chem. Rev.* **2009**, *109*, 3479; h) M. Asay, C. Jones, M. Driess, *Chem. Rev.* **2011**, *111*, 354.
- [3] a) D. H. Harris, M. F. Lappert, *J. Chem. Soc., Chem. Comm.* **1974**, 895; b) P. J. Davidson, D. H. Harris, M. F. Lappert, *J. Chem. Soc., Dalton Trans.* **1976**, 2268; c) M. J. S. Gynane, D. H. Harris, M. F. Lappert, P. P. Power, P. Rivière, M. Rivière-Baudet, *J. Chem. Soc., Dalton Trans.* **1977**, 2004.
- [4] a) Z. Dong, C. R. W. Reinhold, M. Schmidtman, T. Müller, *Angew. Chem. Int. Ed.* **2016**, *55*, 15899; *Angew. Chem.* **2016**, *128*, 16131; b) Z. Dong, K. Bedbur, M. Schmidtman, T. Müller, *J. Am. Chem. Soc.* **2018**, *140*, 3052.
- [5] a) M. Driess, S. Yao, M. Brym, C. v. Wüllen, *Angew. Chem. Int. Ed.* **2006**, *45*, 4349; b) A. Jana, I. Objartel, H. W. Roesky, D. Stalke, *Inorg. Chem.* **2009**, *48*, 798; c) W. Wang, S. Inoue, S. Yao, M. Driess, *Organometallics* **2011**, *30*, 6490; d) J. Berthe, J. M. Garcia, E. Ocampo, T. Kato, N. Saffon-Merceron, A. De Cózar, F. P. Cossio, A. Baceiredo, *J. Am. Chem. Soc.* **2011**, *133*, 15930; e) Y. Li, K. C. Mondal, P. Stollberg, H. Zhu, H. W. Roesky, R. Herbst-Irmer, D. Stalke, H. Fliegl, *Chem. Commun.* **2014**, *50*, 3356; f) T. Ochiai, T. Szilvási, D. Franz, E. Irran, S. Inoue, *Angew. Chem. Int. Ed.* **2016**, *55*, 11619; *Angew. Chem.* **2016**, *128*, 11791; g) N. Del Rio, A. Baceiredo, N. Saffon-Merceron, D. Hashizume, D. Lutters, T. Müller, T. Kato, *Angew. Chem. Int. Ed.* **2016**, *55*, 4753; *Angew. Chem.* **2016**, *128*, 4831.
- [6] a) W. P. Neumann, M. Schriewer, *Tetrahedron Lett.* **1980**, *21*, 3273; b) M. Schriewer, W. P. Neumann, *J. Am. Chem. Soc.* **1983**, *105*, 897; c) W. Ando, H. Ito, T. Tsumuraya, H. Yoshida, *Organometallics* **1988**, *7*, 1880; d) W. Ando, H. Itoh, T. Tsumuraya, *Organometallics* **1989**, *8*, 2759; e) M. Kira, K. Sakamoto, H. Sakurai, *J. Am. Chem. Soc.* **1983**, *105*, 7469.
- [7] a) S. Collins, S. Murakami, J. T. Snow, S. Masamune, *Tetrahedron Lett.* **1985**, *26*, 1281; b) T. Tsumuraya, S. Sato, W. Ando, *Organometallics* **1988**, *7*, 2015.
- [8] A. Schäfer, W. Saak, M. Weidenbruch, *Z. anorg. allg. Chem.* **1998**, *624*, 1405.
- [9] L. Wang, Y. S. Lim, Y. Li, R. Ganguly, R. Kinjo, *Molecules* **2016**, *21*, 990.
- [10] a) M. Melaimi, M. Soleilhavoup, G. Bertrand, *Angew. Chem. Int. Ed.* **2010**, *49*, 8810; *Angew. Chem.* **2010**, *122*, 8992; b) D. Martin, M. Soleilhavoup, G. Bertrand, *Chem. Sci.* **2011**, *2*, 389; c) D. Martin, M. Melaimi, M. Soleilhavoup, G. Bertrand, *Organometallics* **2011**, *30*, 5304; d) C. D. Martin, M. Soleilhavoup, G. Bertrand, *Chem. Sci.* **2013**, *4*, 3020; e) M. Soleilhavoup, G. Bertrand, *Acc. Chem. Res.* **2015**, *48*, 256; f) S. Roy, K. C. Mondal, H. W. Roesky, *Acc. Chem. Res.* **2016**, *49*, 357. g) M. Melaimi, R. Jazzar, M. Soleilhavoup, G. Bertrand, *Angew. Chem. Int. Ed.* **2017**, *56*, 10046; *Angew. Chem.* **2017**, *129*, 10180.
- [11] a) T. Kosai, S. Ishida, T. Iwamoto, *Angew. Chem. Int. Ed.* **2016**, *55*, 15554; *Angew. Chem.* **2016**, *128*, 15783; b) T. Kosai, T. Iwamoto, *J. Am. Chem. Soc.* **2017**, *139*, 18146.
- [12] S. Park, B. G. Kim, I. Göttker-Schnetmann, M. Brookhart, *ACS Catalysis* **2012**, *2*, 307.
- [13] a) A. Simonneau, M. Oestreich, *Nat. Chem.* **2015**, *7*, 816; b) Y. Ma, L. Zhang, Y. Luo, M. Nishiura, Z. Hou, *J. Am. Chem. Soc.* **2017**, *139*, 12434.
- [14] N. D. Rio, M. Lopez-Reyes, A. Baceiredo, N. Saffon-Merceron, D. Lutters, T. Müller, T. Kato, *Angew. Chem. Int. Ed.* **2017**, *56*, 1365; *Angew. Chem.* **2017**, *129*, 1385.
- [15] E. J. Lawrence, V. S. Oganessian, D. L. Hughes, A. E. Ashley, G. G. Wildgoose, *J. Am. Chem. Soc.* **2014**, *136*, 6031.
- [16] a) V. Y. Lee, A. Sekiguchi, *Organometallic Compounds of Low-Coordinate Si, Ge, Sn and Pb*; Wiley: Chichester, **2010**; b) V. S. V. S. N. Swamy, S. Pal, S. Khan, S. S. Sen, *Dalton Trans.* **2015**, *44*, 12903; c) H. Fang, Z. Wang, X. Fu, *Coord. Chem. Rev.* **2017**, *344*, 214.
- [17] M. F. Ibad, P. Langer, A. Schulz, A. Villinger, *J. Am. Chem. Soc.* **2011**, *133*, 21016.
- [18] S. Ishida, T. Iwamoto, M. Kira, *Organometallics* **2009**, *28*, 919.
- [19] Recent reviews on Si-H activation by borane $\text{B}(\text{C}_6\text{F}_5)_3$: a) W. E. Piers, A. J. V. Marwitz, L. G. Mercier, *Inorg. Chem.* **2011**, *50*, 12252; b) X. Feng, H. Du, *Tetrahedron Lett.* **2014**, *55*, 6959; c) D. W. Stephan, G. Erker, *Angew. Chem., Int. Ed.* **2015**, *54*, 6400; *Angew. Chem.* **2015**, *127*, 6498; d) D. W. Stephan, *Acc. Chem. Res.* **2015**, *48*, 306; e) M. Oestreich, J. Hermeke, J. Mohr, *Chem. Soc. Rev.* **2015**, *44*, 2202; f) D. W. Stephan, *J. Am. Chem. Soc.* **2015**, *137*, 10018; g) S. Park, S. Chang, *Angew. Chem. Int. Ed.* **2017**, *56*, 7720; *Angew. Chem.* **2017**, *129*, 7828.

COMMUNICATION

A simple and straightforward catalytic approach for transformation of cyclic (alkyl)(amino)germylenes (CAAGes) is reported. In the presence of a catalytic amount of B(C₆F₅)₃, CAAGe undergoes a Si-C/Si-H cross-metathesis reaction with hydrosilanes to afford new CAAGes bearing various silyl groups on the carbon next to the germylene center.

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