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Note

1,2-Azaboretidine formation in the reactions of (boryl)(silyl)iminomethanes via possible generation of (amino)(boryl)carbene species

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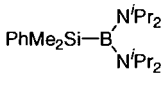
This paper is dedicated to Professor François Mathey on the occasion of his 60th birthday in recognition of his outstanding contribution to organometallic chemistry

Abstract

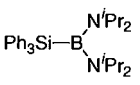
[Bis(diisopropylamino)boryl](organosilyl)(*N*-arylimino)methanes, which was formed in the reaction of aryl isocyanides with (organosilyl)bis(diisopropylamino)borane at room temperature, underwent new skeletal rearrangement reaction to provide aryl(1,2-azaboretidin-3-yl)(organosilyl)amines at 110 °C. Reaction of 1,2-diisocyanobenzene with the silylborane afforded 2-(organosilyl)-3-(1,2-azaboretidin-3-yl)-4,5-benzoimidazole, which was isolated as the corresponding borane complexes. The reactions may proceed through (amino)(boryl)carbene intermediates, which is formed via aza-Brook-type 1,2-silyl migration, giving the 1,2-azaboretidines by intramolecular insertion into the C–H bonds α to the nitrogen atoms. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Silyl migration; Azaboretidine; Isocyanide; (Amino)(boryl)carbene; Quinoxaline; Silylborane

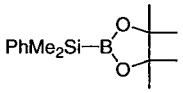
Iminomethanes carrying boryl groups at the imino carbon have hardly been isolated in monomeric forms [1], although there have been known many reactions involving the boryliminomethanes as reactive intermediates [2]. Recently, we reported a ready synthetic access to monomeric (boryl)(silyl)(*N*-arylimino)methanes via insertion of isonitriles into the silicon–boron bond of silylboranes **1** [3]. The reaction proceeded under mild reaction conditions below 50 °C in the absence of catalysts such as transition–metal complexes [4].



1a



1b



1c

In the course of our further investigation on the reactivity of the new (boryl)(silyl)iminomethanes, we found that the imines underwent the new thermal rearrangement reaction. Herein, we disclose the skeletal rearrangement of (boryl)(silyl)iminomethanes, which presumably proceeds through generation of (boryl)(amino)carbene species by 1,2-shift of the silyl group from carbon to nitrogen. Furthermore, related reactions of (boryl)(silyl)[*N*-(2-isocyanophenyl)imino]-methanes, which are derived from 1,2-diisocyanobenzenes via similar generation of carbene intermediates are also described.

3,5-Dimethylphenyl isocyanide (**2a**) was reacted with silylborane **1a** bearing diisopropylamino groups on the boron atom (Scheme 1). As reported previously, the reaction afforded (boryl)(silyl)(*N*-3,5-xylylimino)-methane (**3a**) in high yield at room temperature in toluene. To our surprise, however, an attempted reaction of **1a** with **2a** under toluene reflux (110 °C) resulted in clean formation of an unexpected product **4a** which might be derived via a skeletal rearrangement of **3a**. The product **4a** isolated by silica gel column chromatography (pretreated with Et_3N; eluent: hexane) ex-

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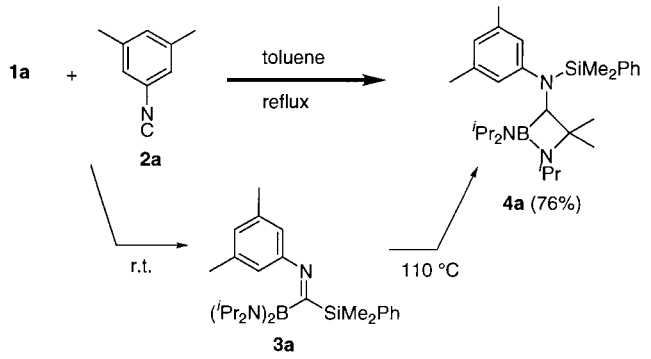
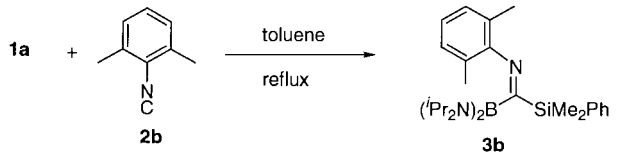
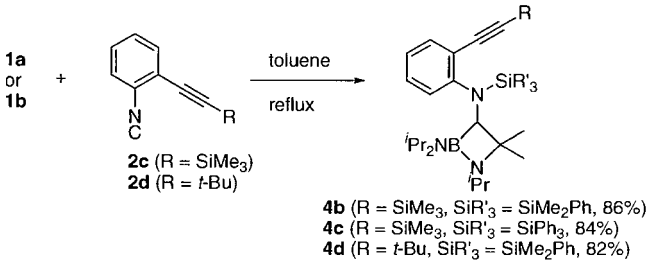


Scheme 1.



Scheme 2.



Scheme 3.

hibited ^{1}H-NMR spectrum indicating the presence of only three of the four expected isopropyl groups on the nitrogen atoms [5]. The NMR data as well as single crystal X-ray studies for the related compounds (see below) convinced us that the product has 1,2-azaboretidine structure, a four-membered ring containing a B–N bond [6]. It was proven that the azaboretidine **4a** was formed via (boryl)(silyl)iminomethane (**3a**) on the basis of an experiment in which a solution of **1a** and **2a** was stirred at room temperature to the complete consumption of both the reactants followed by raising the reaction temperature to 110 °C. Initially formed **3a** was completely converted into **4a** at 110 °C. In sharp contrast to the reactivity of the 3,5-xylyl isocyanide (**2a**), 2,6-xylyl isocyanide (**2b**) only afforded the corresponding imine **3b** even at 110 °C (Scheme 2). The imine **3b** hardly underwent the further rearrangement, probably due to the increased steric hindrance.

The formation of the azaboretidine ring was also found in the reactions of *o*-alkynylisocyanobenzene [7] with **1a** under the reaction conditions identical to those for **2a** (Scheme 3). Thus, isocyanide **2c** afforded the

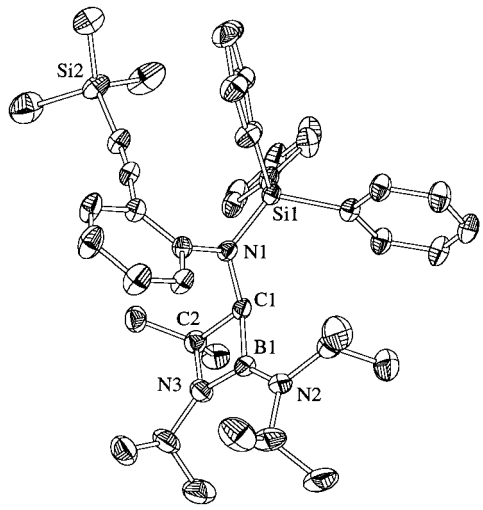


Fig. 1. Crystal structure of **4c**. The thermal ellipsoids are plotted at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond distance (Å) and angles (°) are as follows: Si1–N1 = 1.738(2), N1–C1 = 1.494(3), C1–B1 = 1.617(4), B1–N3 = 1.423(4), N3–C2 = 1.490(4), C2–C1 = 1.593(4), B1–N2 = 1.408(4); C2–C1–B1 = 84.5(2), C1–B1–N3 = 90.6(2), B1–N3–C2 = 95.6(2), N3–C2–C1 = 89.2(2).

azaboretidine **4b** in 86% yield, in which the alkynyl moiety was left intact. Similarly, (triphenylsilyl)bis(diisopropylamino)borane **1b** provided the corresponding azaboretidine **4c** in good yield [8]. *tert*-Butyl-substituted alkynylisocyanide (**2d**) also afforded **4d** in good yield in the reaction with **1a**. We also examined the reaction of **2c** with silylborane **1c**, which carried a pinacol ligand on the boron instead of the diisopropylamino groups. Although the corresponding imine was formed in high yield, no further reaction took place at 110 °C at all. The triphenyl derivative **4c** isolated as single crystals was subjected to X-ray crystallographic analysis, establishing the formation of the azaboretidine ring, in which the four angular atoms were in one plane without puckering, as evidenced by the sum of the four interior angles (360.0°) (Fig. 1) [9].

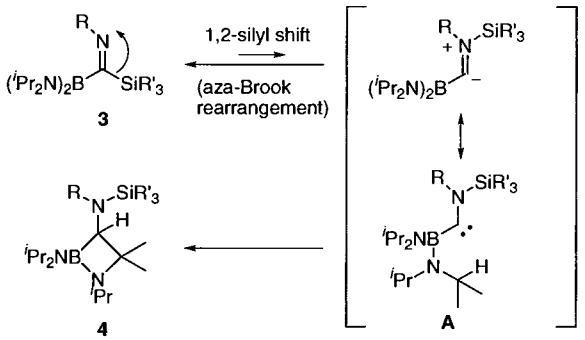
Although there is no further information for the mechanistic elucidation of the azaboretidine formation, we may propose the following mechanism which involves 1,2-carbon-to-nitrogen silyl migration as the key step, resulting in the reversible generation of (amino)(boryl)carbene species **A** (Scheme 4). The carbene may undergo insertion into the C–H bond of the isopropylamino group, thus forming the azaboretidine ring.

We then became interested in the reaction of 1,2-diisocyanobenzenes with silylboranes, since the two isocyano groups in close proximity may participate in the insertion reaction in a concerted or stepwise manner [10], thus leading to the formation of heterocyclic products functionalized by silyl and boryl groups. 1,2-Diisocyanobenzene (**5a**) was reacted with an equimolar amount of **1a** at room temperature (Scheme 5). ^{1}H-

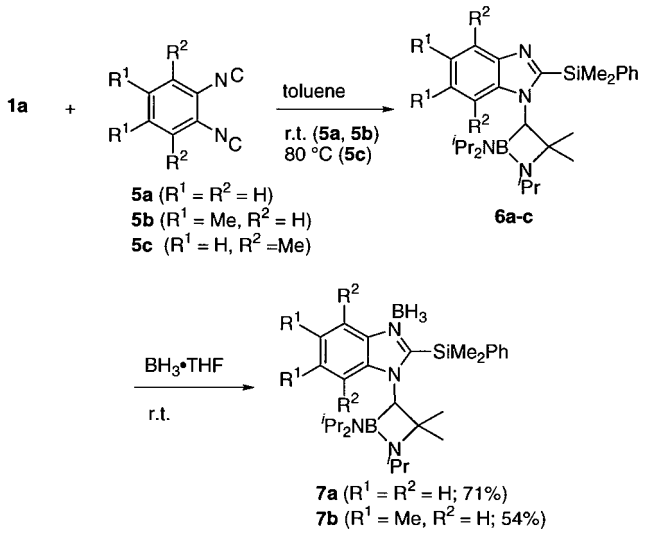
NMR monitoring of the reaction in C_6D_6 indicated an initial formation of an unidentifiable product, followed by clean conversion to a single final product **6a**, which showed NMR signals characteristic of azaboritidine derivatives. Although the product was distillable, further purification with silica gel column chromatography resulted in decomposition. Treatment of the reaction mixture with borane–THF at room temperature resulted in the formation of a chromatographically stable borane adduct **7a** [11]. When the reaction was carried out in a preparative scale in toluene, **7a** was isolated in 71% overall yield by silica gel column chromatography. 4,5-Dimethylphenyl-1,2-diisocyanobenzene (**5b**) similarly afforded the corresponding borane adduct **7b**.

A single crystal X-ray analysis of the borane adduct **7a** established the 4,5-benzoimidazole core bearing a silyl group and an 1,2-azaboritidin-3-yl group at 2- and 3-positions, respectively, with coordination to BH_3 at the 1-nitrogen [12] (Fig. 2).

We also carried out the reaction of 3,6-disubstituted 1,2-diisocyanobenzenes. Although 3,6-dimethyl-1,2-diisocyanobenzene (**5c**) gave the corresponding benzimidazole **6c** with the azaboretidine ring formation in high



Scheme 4.



Scheme 5.

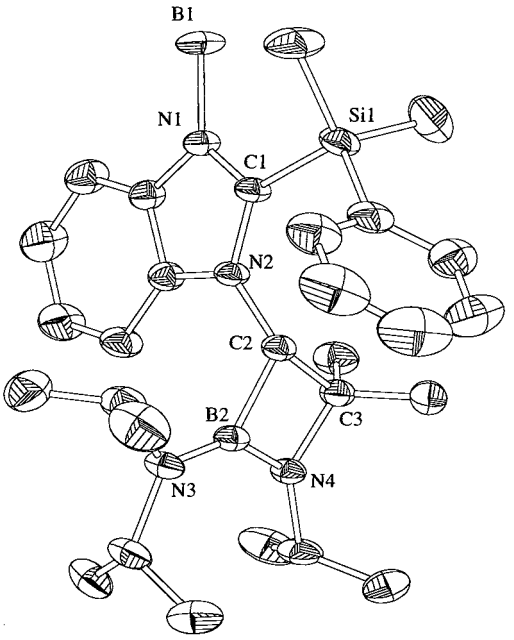
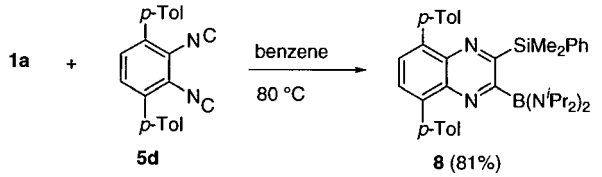


Fig. 2. Crystal structure of **7a**. The thermal ellipsoids are plotted at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond distance (Å) and angles (°) are as follows: Si1–C1 = 1.920(5), N1–B1 = 1.613(9), N2–C2 = 1.468(7), C2–B2 = 1.618(8), B2–N4 = 1.418(8), N4–C3 = 1.492(7), C3–C2 = 1.566(8), B2–N3 = 1.379(9); B2–C2–C3 = 85.5(4), C2–B2–N4 = 89.5(5), B2–N4–C3 = 96.0(4), N4–C3–C2 = 89.0(4).

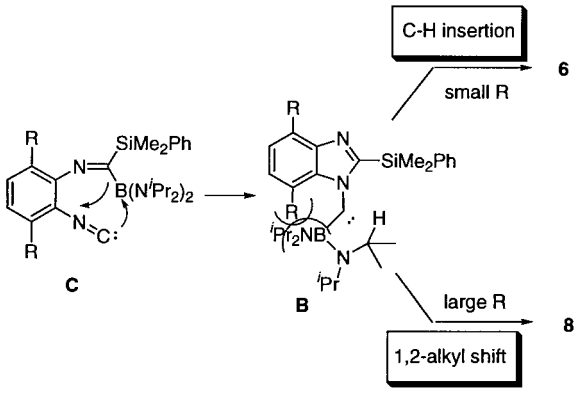


Scheme 6.

NMR yield, 3,6-di-*p*-tolyl-1,2-diisocyanobenzene (**5d**) afforded 2-silyl-3-borylquinoxaline derivative **8** in high yield without any appreciable formation of the corresponding imidazole product (Scheme 6) [13].

The formation of the azaboretidine **6** suggests that the reaction of **5a** with **1a** may proceed via the (imidazolyl)(boryl)carbene species **B**, which was derived from the primary adduct, *N*-(2-isocyanophenyl)imine **C**. On the other hand, the quinoxaline derivative **8** may be obtained through 1,2-shift of the silyl-substituted 2-carbon in **B** to the carbene. Presumably, steric repulsion between the bulky tolyl group and the bis(diisopropylamino)boryl group may make the C–H insertion process unfavorable (Scheme 7).

In summary, we reported some new skeletal rearrangement reactions of (boryl)(silyl)iminomethanes, in which the intermediary formation of (amino)(boryl)carbene species may be crucially involved. Our research program will be focused on the mechan-



Scheme 7.

istic clarification and synthetic application of the intriguing rearrangement reactions.

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[5] Spectral data for **4a**: ^{1}H-NMR ($CDCl_3$) δ 0.51 (s, 6H), 0.85–1.20 (brm, 6H), 1.00 (d, $J = 7.2$ Hz, 6H), 1.10 (s, 3H), 1.20 (s, 3H), 1.22 (d, $J = 6.8$ Hz, 3H), 1.24 (d, $J = 7.0$ Hz, 3H), 2.11 (s, 6H), 3.10 (s, 1H), 3.25–3.60 (m, 3H), 6.31 (s, 1H), 6.88 (s, 2H), 7.28–7.38 (m, 3H), 7.54–7.65 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ 0.19, 0.92, 21.46, 23.12, 23.62, 24.50, 30.75, 44.89, 45.80, 58.2 (br), 66.46, 119.00, 119.73, 127.76, 128.81, 133.85, 136.51, 140.71, 151.13.

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(c) M. Suginome, T. Fukuda, Y. Ito, Org. Lett. 1 (1999) 1977.

[8] Spectral data for **4d**: ^{1}H-NMR ($CDCl_3$) δ −0.13 (s, 9H), 0.60–1.00 (br, 6H), 1.07 (d, $J = 7.2$ Hz, 6H), 1.04–1.14 (m, 6H), 1.28 (s, 3H), 1.30 (s, 3H), 3.17–3.36 (brm, 2H), 3.35 (s, 1H), 3.45 (sept, $J = 7.2$ Hz, 1H), 6.79 (t, $J = 7.2$ Hz, 1H), 6.99 (d, $J = 6.3$ Hz, 1H), 7.18 (t, $J = 8.7$ Hz, 1H), 7.25 (t, $J = 6.6$ Hz, 6H), 7.28–7.38 (m, 3H), 7.56 (d, $J = 6.9$ Hz, 6H), 8.10 (d, $J = 8.7$ Hz, 1H); ^{13}C-NMR ($CDCl_3$) δ 0.58, 22.2 (br), 24.3, 24.5, 24.7, 24.9, 31.2, 45.2, 46.2 (br), 60.1 (br), 67.7, 98.7, 106.8, 121.5, 122.2, 126.9, 127.9, 128.1, 128.8, 135.1, 136.2, 137.6, 152.1.

[9] Crystal data for **4c** ($C_{42}H_{54}BN_3Si_2$): triclinic, space group $P\bar{1}$ (No. 2); $Z = 2$; $a = 10.886(1)$, $b = 11.555(1)$, $c = 17.226(2)$ Å; $\alpha = 103.322(4)$, $\beta = 104.661(3)$, $\gamma = 89.789(1)°$; $V = 2036.5(4)$ Å^3; $\rho_{calc} = 1.089$ g cm^{-3}; $\mu = 0.118$ cm^{-1}. Intensity data were measured on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo–K_α radiation ($\lambda = 0.7107$ Å, $T = 293$ K); 14 012 reflections measured, 8244 independent, 5997 included in the refinement, 433 parameters, $R = 0.068$, $R_w = 0.085$.

[10] For the chemistry of 1,2-diisocyanobenzenes, see: (a) Y. Ito, E. Ihara, M. Hirai, H. Ohsaki, A. Ohnishi, M. Murakami, J. Chem. Soc. Chem. Commun. (1990) 403;
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(d) Y. Ito, T. Miyake, S. Hatano, R. Shima, T. Ohara, M. Suginome, J. Am. Chem. Soc. 120 (1998) 11880;
(e) Y. Ito, T. Miyake, M. Suginome, Macromolecules 33 (2000) 4034 and references therein.

[11] Spectral data for **7a**: ^{1}H-NMR ($CDCl_3$) δ 0.52 (s, 3H), 0.70 (s, 3H), 0.6–1.0 (broad, 12H), 0.92 (d, $J = 6.9$ Hz, 3H), 0.99 (d, $J = 6.9$ Hz, 3H), 1.04 (s, 3H), 1.09 (s, 3H), 2.6–4.0 (br, 2H), 2.98 (sept, $J = 6.9$ Hz, 1H), 4.11 (s, 1H), 7.00–7.18 (m, 5H), 7.24–7.58 (m, 2H), 7.88–8.00 (m, 1H), 8.52–8.61 (m, 1H) (Three protons for the BH_3 group could not be detected.); ^{11}B-NMR (C_6D_6; standard: BF_3OEt_2) δ −19.3 (BH_3), 27.6 (ring B); ^{29}Si-NMR (C_6D_6) δ −11.6.

[12] Crystal data for **7a** ($C_{28}H_{46}B_2N_4Si$): triclinic, space group $P\bar{1}$ (No. 2); $Z = 2$; $a = 11.095(4)$, $b = 11.16(1)$, $c = 13.602(8)$ Å; $\alpha = 87.00(6)$, $\beta = 85.77(4)$, $\gamma = 66.34(5)°$; $V = 1538.410034(2)$ Å^3; $\rho_{calc} = 1.054$ g cm^{-3}; $\mu = 8.027$ cm^{-1}. Intensity data were measured on a Mac Science MXC^3 diffractometer with graphite monochromated Cu–K_α radiation ($\lambda = 1.54178$ Å, $T = 293$ K); 5431 reflections measured, 4799 independent, 4187 included in the refinement, 362 parameters, $R = 0.089$, $R_w = 0.103$.

[13] Spectral data for **8**: ^{1}H-NMR ($CDCl_3$) δ 0.81 (s, 6H), 0.83 (d, $J = 6.9$ Hz, 12H), 1.04 (d, $J = 6.9$ Hz, 12H), 2.198 (s, 3H), 2.203 (s, 3H), 3.47 (sept, $J = 6.9$ Hz, 4H), 7.08–7.21 (m, 7H), 7.56–7.66 (m, 4H), 7.73 (d, $J = 8.1$ Hz, 2H), 7.82 (d, $J = 8.1$ Hz, 2H); ^{13}C-NMR (C_6D_6) 1.2, 21.1, 24.2, 24.7, 48.3, 127.2, 128.7, 128.7, 128.9, 129.1, 129.8, 131.3, 131.5, 135.0, 136.6, 136.8, 136.9, 138.3, 138.7, 138.9, 140.6, 140.7, 166.0, 170.1 (br); IR (KBr) 3036, 2928, 1510, 1451, 1142, 1052, 812 cm^{-1}.