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Synthesis of (Boryl)(silyl)iminomethanes by Insertion of Isonitriles into Silicon−Boron Bonds

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Summary: The insertion of alkyl and aryl isonitriles into the silicon−boron bond of silylboranes proceeded thermally to provide (boryl)(silyl)iminomethanes in moderate-to-good yields. The (boryl)(silyl)iminomethane reacted with borane (BH_3) to give the corresponding borane complex in good yield, whose crystal structure was determined by a single-crystal X-ray analysis.

It is commonly known that multistep reactions of isonitriles with organoboranes involve the coordination of the isonitrile to the boron followed by alkyl migration from the boron to the isocyano carbon, leading to the formation of boron- and nitrogen-containing heterocycles.[1] A simple 1:1 insertion product of isonitrile with organoborane has been scarcely known, to our best knowledge.[2,3]

Herein, we report a new insertion reaction of isonitriles into the silicon−boron bonds of silylboranes[4] to provide *N*-substituted (boryl)(silyl)iminomethanes in moderate-to-good yields. In contrast to our previous results involving silaborative reactions with carbon−carbon multiple bonds,[5−7] our present research indicates that no transition-metal catalyst is needed for the silaboration of isonitriles. It is interesting to note that reactions of the *N*-substituted (boryl)(silyl)iminomethanes with BH_3 afforded chromatographically stable borane−imine complexes. The structure of the borane−imine complex was determined by a single-crystal X-ray analysis.

The silylborane **1a** was subjected to a reaction with an equimolar amount of *tert*-butyl isonitrile (**2a**) at room temperature. The product **3aa** was isolated by bulb-to-

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[1] Casanova, J., Jr. In *Isonitrile Chemistry*; Ugi, I., Ed.; Academic Press: New York; 1971; p 109.

[2] Reactions of isonitriles with B−H bonds of borazines and the B−B bond of tetrakis(dimethylamino)diborane were reported to afford monomeric (iminomethyl)borazines and iminobis(boryl)methanes, respectively: Meller, A.; Batka, H. *Monatsh. Chem.* **1970**, *101*, 648.

[3] Monomeric imino(boryl)methanes were prepared by the reaction of (iminomethyl)lithium with chlorobis(dimethylamino)borane: Sicker, U. S.; Meller, A.; Maringgele, W. *J. Organomet. Chem.* **1982**, *231*, 191.

[4] Seyferth, D.; Kogler, H. P. *J. Inorg. Nucl. Chem.* **1960**, *15*, 99. Cowly, A. H.; Sisler, H. H.; Ryschkewitach, G. E. *J. Am. Chem. Soc.* **1960**, *82*, 501. Nöth, H.; Höllerer, G. *Angew. Chem.* **1962**, *74*, 718. Biffer, W.; Nöth, H.; Schwerthöffer, R. *Liebigs Ann. Chem.* **1981**, 2067. Buynak, J. D.; Geng, B. *Organometallics* **1995**, *14*, 3112 and references therein.

[5] Suginome, M.; Nakamura, H.; Ito, Y. *Chem. Commun.* **1996**, 2777. Suginome, M.; Nakamura, H.; Ito, Y. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2516. Suginome, M.; Matsuda, T.; Nakamura, H.; Ito, Y. *Tetrahedron* **1999**, *55*, 8787. Suginome, M.; Ohmori, Y.; Ito, Y. *Synlett* **1999**, 1567. Suginome, M.; Matsuda, T.; Yoshimoto, T.; Ito, Y. *Org. Lett.* **1999**, *1*, 1567. See also: Onozawa, S.-y.; Hatanaka, Y.; Tanaka, M. *Chem. Commun.* **1997**, 1229.

[6] Suginome, M.; Nakamura, H.; Matsuda, T.; Ito, Y. *J. Am. Chem. Soc.* **1998**, *120*, 4248.

[7] Suginome, M.; Matsuda, T.; Ito, Y. *Organometallics* **1998**, *17*, 5233.

[8] Experimental procedure for the synthesis of **3aa**: to *tert*-butyl isocyanide (**2a**; 32 mg, 0.39 mmol) was added (bis(diethylamino)-boranyl)dimethylphenylsilane (**1a**; 96 mg, 0.33 mmol) at room temperature. The reaction mixture was stirred at room temperature for 2 h. Evaporation of volatile material followed by bulb-to-bulb distillation (100 °C/0.1 mmHg) gave **3aa** (111 mg, 90%). **3aa**: ^{1}H NMR (C_6D_6) δ 0.55 (s, 6H), 0.83 (t, $J = 7.0$ Hz, 12H), 1.32 (s, 9H), 2.75 (q, $J = 7.0$ Hz, 8H), 7.12−7.26 (m, 3H), 7.85−7.88 (m, 2H); ^{13}C NMR (C_6D_6) δ 1.8, 14.7, 29.1, 42.2, 63.0, 127.6, 128.8, 134.8, 139.9; IR (neat) 2976, 1430, 1270, 1250 cm^{-1}; HRMS *m*/*z* calcd for $C_{20}H_{37}BN_3Si$ (M − CH_3) 358.2849, found 358.2864.

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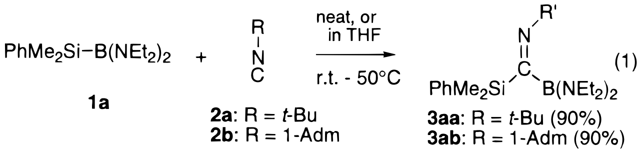
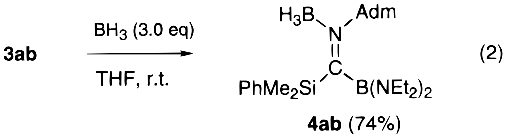
bulb distillation in high yield.[8] Reaction of **1a** with 1-adamantyl isonitrile (**2b**) also afforded the corresponding imine **3ab** in high yield at 50 °C in THF (eq 1). The presence of a catalytic amount of a palladium



complex, which was effective for the insertion reactions of isonitriles into Si−Si[9] and Si−Sn[10] bonds, resulted in the formation of a complex mixture.

The imines **3aa** and **3ab** did not tolerate silica gel chromatography, due to their sensitivity to moisture. However, treatment of the imine **3ab** with borane−THF gave the corresponding borane−imine complex **4ab** in high yield, which could be isolated by silica gel column chromatography (eq 2).



It has been reported that the imino carbons of the bis(silyl)iminomethanes and (silyl)(stannyl)iminomethanes exhibit their ^{13}C NMR signals in the range of 200−220 ppm.[9,10] The comparison of the chemical shift of the newly synthesized (boryl)(silyl)iminomethane **3** with the those of the related bis(metal)iminomethanes was difficult, due to the low intensity of the signal corresponding to the boryl-substituted imino carbon. Thus, (boryl)(silyl)iminomethane **3bb***, whose imino carbon was labeled by ^{13}C, was synthesized from silylborane **1b** and ^{13}C-labeled 1-adamantyl isonitrile **2b***. The ^{13}C NMR spectra of the insertion product **3bb*** and the corresponding borane complex **4bb*** showed broad signals corresponding to the imino carbons at 206.2 and 215.0 ppm, respectively, unambiguously indicating the presence of C=N bonds (eq 3).

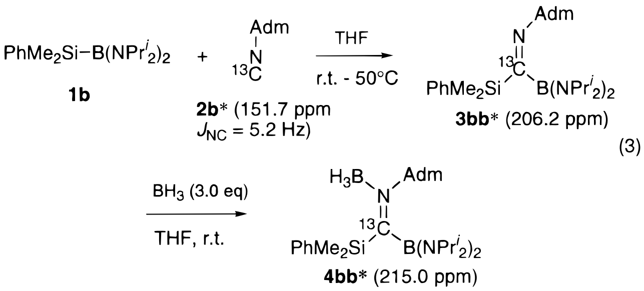
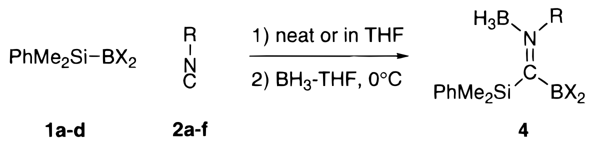
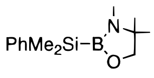
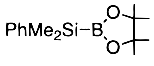


Table 1. One-Pot Synthesis of the Borane−Imine Complexes 4[a]



entry	silylborane **1**	isonitrile **2**	*T*/°C	product	yield/%[b]
1	**1a**	1-AdmNC (**2b**)	80	**4ab**	76
2	**1b**	*t*-BuNC (**2a**)	room temp	**4ba**	89
3	**1b**	**2b**	80	**4bb**	76
4	**1b**	*n*-HexNC (**2c**)	80	**4bc**	73
5	**1b**	*c*-HexNC (**2d**)	80	**4bd**	75
6	**1b**	2,6-XyNC (**2e**)	80	**4be**	82
7	**1b**	MeO_2CCH_2NC (**2f**)	room temp	**4bf**	60
8	 **1c**	**2a**	80	**4ca**	75
9	 **1d**	**2b**	80	**4db**	80

[a] After the reaction of **1** with **2** (1.1 equiv) in THF, borane-THF (3 equiv) was added to the resultant reaction mixture at 0 °C. [b] Isolated yield based on **1**.

The borane complexes of (boryl)(silyl)iminomethanes were also synthesized by a one-pot procedure, in which borane−THF was added at room temperature or below to the reaction mixture resulting from the 1,1-silaboration of isonitriles (Table 1). Indeed, **4ab** was obtained in 76% yield by the one-pot procedure (entry 1).[11] In addition to the tertiary alkyl isonitriles such as **2a** and **2b**, primary (**2c**) and secondary alkyl isonitriles (**2d**) reacted with silylborane **1b** to give the corresponding products **4bc** and **4bd**, respectively (entries 4 and 5). Furthermore, aryl isonitrile **2e** provided *N*-aryl imine **4be** in good yield (entry 6). Methyl isocyanoacetate (**2f**) also gave the corresponding *N*-(methoxycarbonyl)methyl derivative in moderate yield (entry 7). Silylboranes

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(9) (a) Ito, Y.; Nishimura, S.; Ishikawa, M. *Tetrahedron Lett.* **1987**, *28*, 1293. (b) Ito, Y.; Matsuura, T.; Murakami, M. *J. Am. Chem. Soc.* **1988**, *110*, 3692. (c) Ito, Y.; Suginome, M.; Matsuura, T.; Murakami, M. *J. Am. Chem. Soc.* **1991**, *113*, 8899.

(10) (a) Ito, Y.; Bando, T.; Matsuura, T.; Ishikawa, M. *J. Chem. Soc., Chem. Commun.* **1986**, 980. (b) Ito, Y.; Matsuura, T.; Murakami, M. *J. Am. Chem. Soc.* **1987**, *109*, 7888. (c) Murakami, M.; Matsuura, T.; Ito, Y. *Tetrahedron Lett.* **1988**, *29*, 355.

(11) Experimental procedure for the one-pot synthesis of **4ab**: to a solution of **2b** (62 mg, 0.38 mmol) in THF (0.2 mL) was added **1a** (100 mg, 0.34 mmol) at room temperature. The reaction mixture was stirred at 80 °C for 8 h and cooled to 0 °C. Borane−THF complex (1 M in THF, 1.1 mL, 1.1 mmol) was added, and the resulting mixture was stirred at 0 °C for 1 h. Evaporation of volatile materials resulted in deposition of a residue, which was subjected to column chromatography on silica gel (9:1 hexane−ether) to give **4ab** (122 mg, 76%). **4ab**: ^{1}H NMR (C_6D_6) δ 0.75 (s, 6H), 0.80 (t, $J = 6.9$ Hz, 12H), 1.51 (dd, $J = 12.3, 11.4$ Hz, 6H), 1.99 (br, 3H), 2.41 (d, $J = 2.7$ Hz, 6H), 2.70 (br, 8H), 7.14−7.27 (m, 3H), 7.82−7.85 (m, 2H); ^{13}C NMR (C_6D_6) δ 3.0, 14.0, 30.3, 36.3, 40.7, 41.0, 43.3, 70.3, 127.6, 128.7, 135.5, 139.9; IR (KBr) 2980, 2416, 2372, 1430 cm^{-1}. Anal. Calcd for $C_{27}H_{49}B_2N_3Si$: C, 69.68; H, 10.61; N, 9.03. Found: C, 69.43; H, 10.51; N, 8.94.

(12) The ^{13}C-labeling experiments were also carried out for the reactions of silylboranes having an N,O-ligand (**1c**) and a O,O-ligand (**1d**) with **2b***. The insertion products obtained from **1c** and **1d** exhibited their broad signals of the imino carbons at 197.2 and 194.0 ppm, respectively. The corresponding borane complexes showed signals at 206.1 (**4cb**) and 202.1 (**4db**) ppm, respectively. From these results, very weak signals between 200 and 220 ppm for nonlabeled derivatives **4** could be tentatively assigned as imino carbons.

(13) Crystal data for **4ba** ($C_{25}H_{51}B_2N_3Si$): crystal size 0.50 × 0.50 × 0.15 mm (recrystallized from Et_2O); monoclinic, space group $P2_1/n$ (No. 14); $Z = 4$; $a = 13.655(3)$ Å, $b = 20.488(4)$ Å, $c = 10.363(3)$ Å; $\beta = 92.42(2)°$; $V = 2896(6)$ Å^3; $\rho_{calcd} = 1.016$ g/cm^3; $\mu = 7.953$ cm^{-1}; 2θ(max) = 125° (Cu Kα, $\lambda = 1.541\ 78$ Å, graphite monochromator, $\omega/2\theta$ scan, $T = 293$ K); 5349 reflections measured, 4284 independent reflections, 3176 reflections included in the refinement, Lorentzian polarization and empirical absorption correction based on azimuthal scans of several reflections; direct method, anisotropic refinement for non-hydrogen atoms by full-matrix least squares against $|F|^2$ with the program package CrystanG (MacScience), 331 parameters; $R = 0.083$, $R_w = 0.072$. Hydrogen atoms were included in the refinement at calculated positions (0.96 Å) with isotropic thermal parameters.

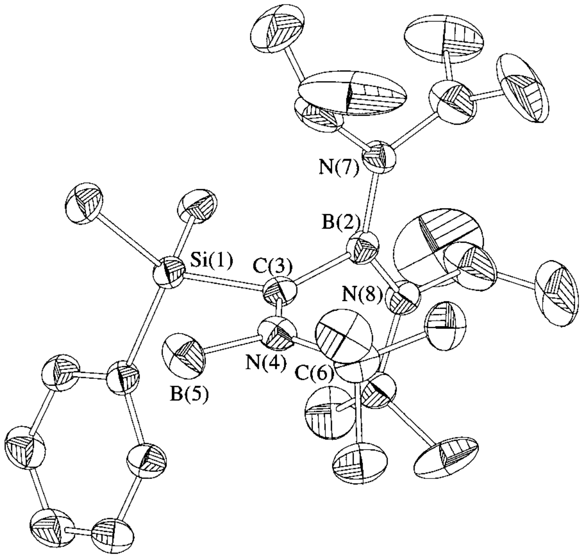
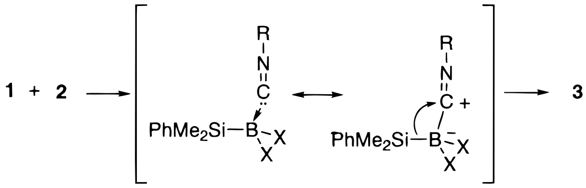


Figure 1. Crystal structure of **4ba**. Selected bond distances (Å) and angles (deg) are as follows: Si(1)−C(3) = 1.948(5), B(2)−C(3) = 1.613(8), C(3)−N(4) = 1.299(7), N(4)−B(5) = 1.608(10), N(4)−C(6) = 1.510(8); Si(1)−C(3)−B(2) = 112.4(4), Si(1)−C(3)−N(4) = 117.8(4), B(2)−C(3)−N(4) = 129.8(5), C(3)−N(4)−B(5) = 119.4(5), C(3)−N(4)−C(6) = 125.5(5), B(5)−N(4)−C(6) = 115.1(6).

bearing N,O as well as O,O ligands similarly gave borane complexes **4ca** and **4db** in good yields (entries 8 and 9).[12]

The crystal structure of the borane complex **4ba** was successfully determined by a single-crystal X-ray analysis (Figure 1).[13] The analysis revealed *E* geometry of the borane-coordinated imine moiety, in which the silyl group and the *tert*-butyl group are located trans to each other. It is interesting to note that the plane consisting of N(7)−B(2)−N(8) is perpendicular to the C=N bond of the imine, indicating there is no interaction between the π-orbital of the C=N bond and the vacant *p*-orbital of the boron. As observed for bis(organosilyl)iminomethane derivatives characterized so far by X-ray analyses, the bonding distance between Si(1) and C(3) (1.948(5) Å) is longer than the typical bond length of the silicon−carbon single bond (1.89 Å).

The reaction may proceed through the initial coordination of the isonitrile to the boron atom of the silylborane and subsequent migration of the silyl group from the boron to the isocyano carbon (eq 4). We observed



(4)

that the reactions of the isonitriles with the bis(dialkylamino)borane derivatives **1a** and **1b** proceeded much faster than that with the pinacol derivative **1d**. For instance, the reaction of *tert*-butyl isonitrile (**2a**) with **1a** was completed within 3 h at room temperature,as mentioned above, whereas the corresponding reaction of **2a** with **1d** required 50 °C for completion of the reaction (3 h). This result indicates that the migration of the silyl group rather than the coordination of the isonitrile may be involved as the rate-determining step, which is expected to be accelerated by the presence of a less negative element on the boron atom.

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Supporting Information Available: Text giving experimental procedures and characterization data for the new compounds and tables giving final atomic coordinates, thermal parameters, bond distances, and bond angles for compound **4ba**. This material is available free of charge via the Internet at http://pubs.acs.org.

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