NEW SYNTHETIC ACCESS TO 1,3-DIAZA-5-SILA-2-BORACYCLOHEXANE FRAMEWORKS BY THE REACTION OF BORANE WITH BIS[(*N*-ARYLIMINO)ORGANOSILYL-METHYL]SILANES[1]

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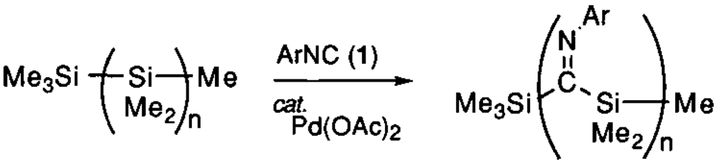
Abstract – *trans*-4,6-Bis(organosilyl)-1,3-diaryl-1,3-diaza-5-sila-2-boracyclohexane derivatives were synthesized by the reaction of borane with bis[(*N*-arylimino)(organosilyl)methyl]silanes which were prepared by palladium-catalyzed insertion of aryl isocyanides into the all Si–Si bonds of trisilane and tetrasilane.

Cyclic compounds with various metallic elements in the rings have attracted much attention as the potential precursors for synthesis of new organometallic polymers and ceramics, which might reveal intriguing electronic and magnetic properties.[2]

We have developed new methods for the synthesis of organosilicon compounds by the palladium-mediated insertion of unsaturated organic molecules into the Si–Si bonds of oligosilanes.[3,4] In particular, selective insertion of aryl isocyanides (**1**) into the Si–Si linkages of oligosilanes (**2**) provided oligo[(*N*-aryl)silaketenimine]s (**3**), which were otherwise difficult to synthesize (eq 1).[4a] In a series of the reactions we developed, isonitrile–palladium(0) complexes worked as highly active catalysts for the activation of the Si–Si σ-bonds.



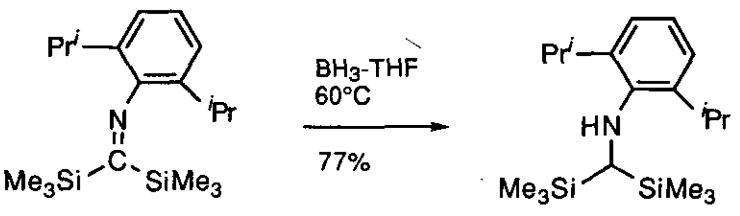
(1)

2 (n = 1–3)

3i (n = 1)
3ii (n = 2)
3iii (n = 3)

Herein we describe a new stereoselective synthesis of 1,3-diaza-5-sila-2-boracyclohexane derivatives (**5**) and (**6**), which contain four typical elements in the rings, by the reaction of borane with *N*-arylsilaketenimine dimer (**3ii**) and trimer (**3iii**), respectively.

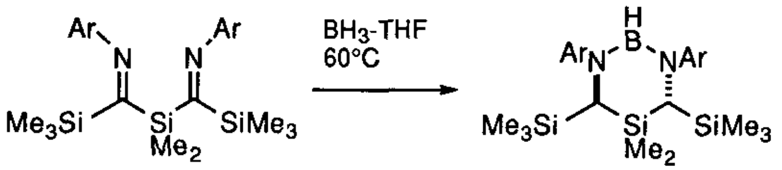
Bis(trimethylsilyl)[*N*-(diisopropylphenyl)imino]methane (**3i**), which was prepared by the reaction of hexamethyldisilane with 2,6-diisopropylphenyl isocyanide in the presence of $Pd(OAc)_2$, was reacted with an excess amount of borane-THF. The reaction was complete within 10 minutes at 60°C to give the corresponding amine (**4**) in good yield after basic hydrolysis followed by preparative tlc on silica gel (eq 2).[5] The yellow color characteristic of the bis(organsilyl)iminomethane moiety was completely disappeared.



3i **4**

(2)

The reactions of *N*-arylsilaketenimine dimer (**3ii**) with borane-THF similarly proceeded at 60°C. In contrast to the case with **3i**, the basic workup of the reaction mixture afforded 6-membered borane (**5**) as a single stereoisomer (**5a**, 52%; **5b**, 65%) (eq 3).[6] It is noted that the cyclic boranes **5a** and **5b** were stable on treatment with aqueous NaOH (1 mol dm^{-3}). at 60°C. The existence of the B–H bond was unambiguously confirmed by characteristic ir absorption at 2492–2504 cm^{-1}.

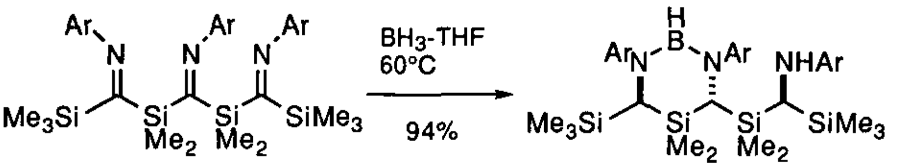


3iia (Ar = 2,6-dimethylphenyl)
3iib (Ar = 2,6-diisopropylphenyl)

5a 52%
5b 65%

(3)

The similar treatment of *N*-(2,6-dimethylphenyl)silaketenimine trimer (**3iii**) with an excess of borane-THF gave 6-membered borane (**6**) in 94%yield (eq 4). It is also noted that the addition reaction proceeded with extremely high diastereoselectivity to produce only a single stereoisomer. The selective formation of the monocyclic 6-membered borane (**6**) indicates that the B–N bond of the cyclic aminoborane is much more stable than that of acyclic one.



3iii (Ar = 2,6-dimethylphenyl)

6

(4)

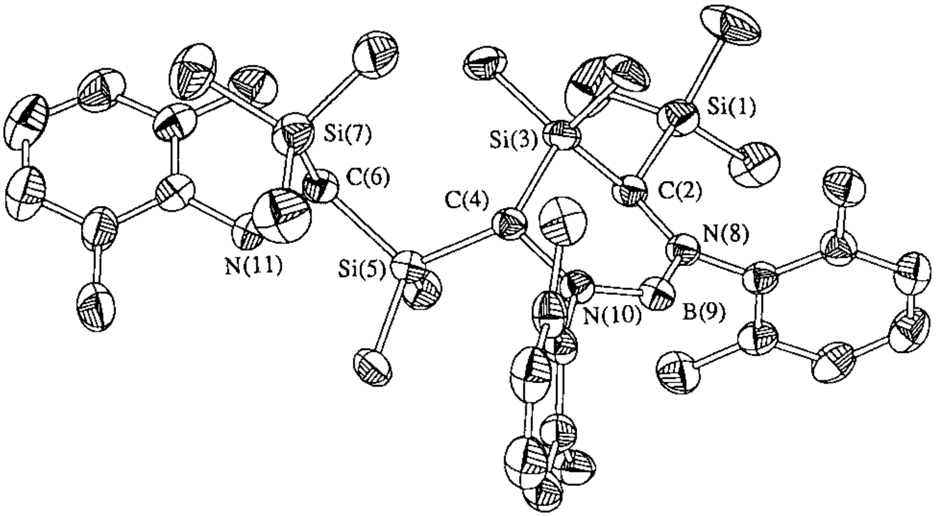


Figure 1. ORTEP view of **6** (30% probability). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Si(1)–C(2) = 1.916(4), C(2)–Si(3) = 1.895(4), Si(3)–C(4) = 1.899(4), C(4)–Si(5) = 1.893(4), Si(5)–C(6) = 1.898(4), C(6)–Si(7) = 1.901(4), C(2)–N(8) = 1.485(4), N(8)–B(9) = 1.408(5), B(9)–N(10) = 1.422(5), N(10)–C(4) = 1.497(5), C(6)–N(11) = 1.506(6); Si(3)–C(2)–N(8) = 105.3(2), C(2)–Si(3)–C(4) = 104.8(2), Si(3)–C(4)–N(10) = 106.8(2), C(2)–N(8)–B(9) = 124.4(3), N(8)–B(9)–N(10) = 127.4(4), C(4)–N(10)–B(9) = 125.8(3).

An X-ray diffraction study of **6** revealed that, in the 6-membered ring, the Si(3) atom deviates from the plane consisting of C(2)–N(8)–B(9)–N(10)–C(4) (Figure 1).[8]

*Procedure for the synthesis of **3iib***: A mixture of 2,6-diisopropylphenyl isocyanide (913 mg, 7.0 mmol), octamethyltrisilane (200 mg, 0.98 mmol), palladium(II) acetate (22 mg, 0.098 mmol) in toluene (2 ml) was heated under reflux for 40 h. The cooled mixture was passed through a column of Florisil pretreated with triethylamine (elution with dry hexane). The filtrate was condensed and **3iib** was obtained as yellow crystals by recrystallization from dry EtOH (64%).

General procedure for the synthesis of 4,5-bis(organosilyl)-1,3-diaza-5-sila-2-boracyclohexanes: To a solution of **3ii** or **3iii** (0.1 mmol) in THF (3 ml) was added borane-THF (0.6 mmol) at room temperature. The mixture was stirred at 60°C for 10 min under a nitrogen atmosphere and then cooled to room temperature. An excess amount of borane was quenched by addition of aqueous NaOH (1 mol dm^{-3}, 1 ml, CAUTION! vigorous hydrogen evolution) followed by stirring the mixture at 60°C for 20 min. Extractive workup followed by preparative tlc on silica gel (hexane / ether = 25 : 1) gave **5** or **6** in the yields shown in the equations.

REFERENCES AND NOTES

1. Dedicated to Emeritus Professor Shigeru Oae in celebration of his 77th birthday.
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3. M. Murakami, M. Suginome, and Y. Ito, *J. Syn. Org. Chem. Jpn.*, **1995**, *53*, 509.
4. (a) Y. Ito, M. Suginome, T. Matsuura, and M. Murakami, *J. Am. Chem. Soc.*, **1991**, *113*, 8899. (b) M. Murakami, M. Suginome, K. Fujimoto, H. Nakamura, P. G. Andersson, and Y. Ito, *J. Am. Chem. Soc.*, **1993**, *115*, 6487. (c) M. Suginome, H. Oike, and Y. Ito, *J. Am. Chem. Soc.*, **1995**, *117*, 1665.
5. Spectral data for **4**: ^{1}H Nmr ($CDCl_3$) δ 0.00 (s, 18 H), 1.24 (d, J = 7.0 Hz, 12 H), 2.51 (s, 1 H), 3.03 (s, 1 H), 3.05–3.40 (brs, 2 H), 6.82–7.04 (m, 3 H); ir (neat) 3436, 2968, 1450, 1252, 844 cm^{-1}; ms calcd for $C_{19}H_{37}NSi_2$ *m/z* 335.2465, found *m/z* 335.2487.
6. Spectral data for **5a**: ^{1}H Nmr ($CDCl_3$) δ 0.18 (s, 18 H), 0.45 (s, 6 H), 2.26 (s, 6 H), 2.38 (s, 6 H), 2.71 (s, 2 H), 6.90–7.02 (m, 6 H); ir (KBr) 2960, 2492, 1424, 1252, 842 cm^{-1}; ms (20 eV) *m/z* 480 (M^+). **5b**: ^{1}H Nmr ($CDCl_3$) δ 0.22 (s, 18 H), 0.43 (s, 6 H), 0.97 (d, J = 6.6 Hz, 6 H), 1.14 (d, J = 6.6 Hz, 6 H), 1.26 (d, J = 6.6 Hz, 6 H), 1.35 (d, J = 6.6 Hz, 6 H), 2.58 (s, 2 H), 3.36–3.55 (m, 4 H), 6.99–7.17 (m, 6 H); ir (KBr) 2968, 2504, 1416, 1254, 1046, 848 cm^{-1}; ms (20 eV) *m/z* 591 (M^+).
7. Spectral data for **6**: ^{1}H Nmr ($CDCl_3$) δ -0.37 (s, 3 H), -0.30 (s, 9 H), 0.01 (s, 9 H), 0.16 (s, 3 H), 0.42 (s, 3 H), 0.57 (s, 3 H), 2.13 (br s, 3 H), 2.19 (s, 3 H), 2.23 (s, 3 H), 2.28 (br s, 3 H), 2.31 (s, 3 H), 2.35 (s, 3 H), 2.76 (s, 1 H), 2.85 (s, 1 H), 2.86 (d, J = 10.5 Hz, 1 H, N*H*), 2.95 (d, J = 10.5 Hz, 1 H), 6.59–6.67 (m, 1 H), 6.85–7.02 (m, 8 H); ir (KBr) 3448, 2960, 2508, 1418, 1256, 842 cm^{-1}; ms (20 eV) *m/z* 670 (M^+).
8. Crystal data for **6**: crystal size 0.65 × 0.10 × 0.30 mm (recrystallized from EtOH); triclinic, space group $P\overline{1}$ (no. 2), $Z = 2$; $a = 8.455$, $b = 11.878$, $c = 22.098$ Å; $\alpha = 94.83°$, $\beta = 92.45°$, $\gamma = 108.90°$; $V = 1073$ Å^3, $\rho_{calcd} = 1.07$ g/cm^3; $\mu = 14.24$ cm^{-1}; max. $2\theta = 130°$ ($Cu_{K\alpha}$, $\lambda = 1.54178$ Å, graphite monochromator, $\omega/2\theta$-scan, $T = 293$ K); 7808 reflections measured, 7044 independent, 5989 included in the refinement, 572 parameters; $R = 0.080$, $R_w = 0.094$.

Received, 11th March, 1996