Synthesis of Silylborazines and Their Utilization as Precursors to Silicon-Containing Boron Nitride☆

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Received February 12, 1998

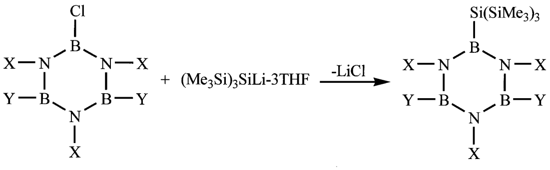
Keywords: Borazines / Silyl borazines / Oligomers / Pyrolysis / Ceramics

The reactions of $LiSi(SiMe_3)_3$ with $Cl(Me)_2B_3N_3(Me)_3$, $Cl_2(Me)B_3N_3(Me)_3$, $(ClBNMe)_3$, and $(ClBNH)_3$ result in the formation of molecular species $(Me_3Si)_3Si(Me)_2B_3N_3(Me)_3$, $[(Me_3Si)_3Si]_2(Me)B_3N_3(Me)_3$, $[(Me_3Si)_3SiBNMe]_3$, and $[(Me_3Si)_3SiBNH]_3$. The new compounds have been characterized by spectroscopic techniques, and a single-crystal X-ray diffraction analysis for $[(Me_3Si)_3SiBNMe]_3$ has been completed. The monomer $(Me_3Si)_3Si(Cl)_2B_3N_3H_3$ was also prepared and combined with $(Me_3Si)_2NH$ in hexane to form an organic solvent soluble oligomer. Pyrolysis of this oligomer provides composites containing BN and an $Si_XN_YC_Z$ phase that suppresses the crystallization of BN.

After about a decade of intense study, it has been demonstrated that inorganic and organometallic polymers may be used to produce a number of ceramic powders including SiC, Si_3N_4, BN, B_4C, and AlN[1][2][3], albeit at greater expense than traditional metallurgical routes. Despite the economic drawback, many polymer precursors offer the advantage that they can be processed into useful physical forms (e.g., fibers, coatings, binders, and porous bodies) that cannot be achieved by classical powder-processing approaches. One additional area where polymer precursors are showing potentially useful benefits and applications is in the fabrication of composite materials[2][3][4][5]. Polymer-derived syntheses of ceramic-ceramic composites have most often been accomplished by three chemical approaches: blending and pyrolysis of a liquid or soluble polymeric precursor with an elemental filler, blending and pyrolysis of two or more processible polymeric precursors, and pyrolysis of a "single-source" preceramic polymer[4][5]. Successes have been demonstrated with each approach. However, until very recently the least attention and fewest successes have been realized with the "single-source" approach, primarily due to the lack of appropriate monomers and polymers. This situation has begun to change. In particular, several groups have noted that addition of boron to silicon-based ceramics can produce enhanced stability in the resulting composite, as well as improve property performances[6]. These observations, in turn, have resulted in new efforts to obtain processible single-source preceramic polymers that convert readily to so-called SiNCB ceramic composites[7][8][9][10][11][12][139[14][15][16][17][18][19][20][21]. In this report, the syntheses of model molecular silyl-substituted borazines and a silylborazine oligomer are described along with our initial efforts to define the pyrolysis chemistry of the polymer that results in formation of SiNCB composites.

Results and Discussion

Relatively few compounds with boron−silicon bonds have been prepared, and the interesting development of this chemistry has been briefly summarized by Berry and coworkers[22]. Pertinent to our work, two reports of the formation of *B*-silylborazines, $(Ph_3SiBNMe)_3$ and $(Ph_3SiBNPh)_3$, formed from salt-elimination reactions, have appeared[23][24]. Similarly, salt-elimination reactions involving the *B*-chloroborazines, $Cl(Me)_2B_3N_3(Me)_3$, $Cl_2(Me)B_3N_3(Me)_3$, $(ClBNMe)_3$, and $(ClBNH)_3$ with $LiSi(SiMe_3)_3$ produce *B*-silylborazines $[(Me_3Si)_3Si](Me)_2B_3N_3(Me)_3$ (**2**), $[(Me_3Si)_3Si](Me)B_3N_3(Me)_3$ (**3**), $[(Me_3Si)_3SiBNMe]_3$ (**4**), and $[(Me_3Si)_3SiBNH]_3$ (**5**) in high yields as summarized in Eq. 1. Compound **2** is obtained as a white solid, which when recrystallized from benzene gives blocky, colorless crystals. The remaining compounds are isolated as waxy or gummy solids. Each compound is soluble in Et_2O, THF, benzene, and pentane and is moisture-sensitive in both the solid state and in solutions.



(1)

	1a	**1b**	**1c**	**1d**
X	Me	Me	Me	H
Y	Me	Me, Cl	Cl	Cl

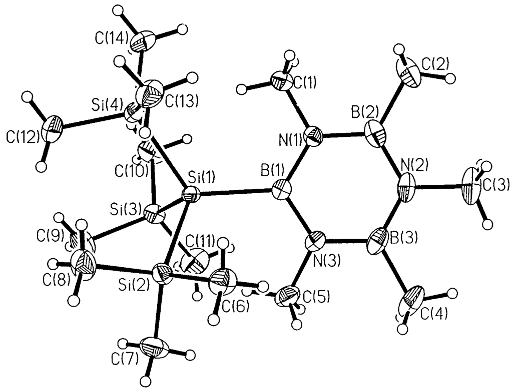
	2	**3**	**4**	**5**
X	Me	Me	Me	H
Y	Me	Me, $Si(SiMe_3)_3$	$Si(SiMe_3)_3$	$Si(SiMe_3)_3$

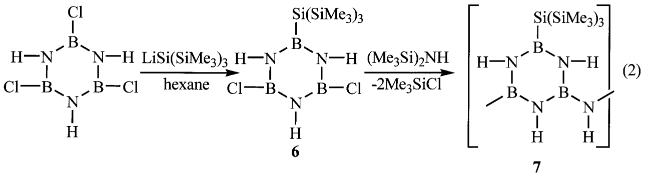
Compounds **2**−**4** give satisfactory CHN analyses; however, **5** retains small amounts of reactants and adequate analyses are not obtained. All of the compounds display a moderately intense parent ion peak in the EI-mass spectrum that provides confirmation of the molecular composition. The $^{11}B\{^1H\}$-NMR spectra for **2** and **3** show two resonances; one resonance, in the range $\delta = 36.3-37.1$, is assigned to the BMe group[25] and the second resonance, in the range $\delta = 42.2-42.8$, is assigned to the $BSi(SiMe_3)_3$ group. Compounds **4** and **5** produce a single resonance at $\delta = 42.2$ and 38, respectively which are assigned to the $BSi(SiMe_3)_3$ group. The ^1H- and $^{13}C\{^1H\}$-NMR spectra are also consistent with the proposed structures showing resonances assigned to BMe, $BSi(SiMe_3)$, and NMe groups.

The molecular structure of compound **2** was determined by single-crystal X-ray diffraction analysis. A view of the molecule is shown in Figure 1 and selected bond lengths and angles are given in Table 1. As expected, the B_3N_3 ring is planar and the $(Me_3Si)_3Si$ group occupies an *exo* position bonded to B(1). The average B−N distance, 1.434 Å [range 1.453(6)−1.407(8) Å] is identical to the average values in several borazine compounds: $(HNBH)_3$[26], 1.436 Å; $(Me_2NBNH)_3$[27], 1.433 Å; and $(Me_3N_3Me_2B_3)_2NH$[28], 1.438 Å. Four of the B−N distances are within one standard deviation of the average value, while the two distances associated with B(3) vary from the average by slightly more than 3σ. Such a variation is not typical for borazine rings although a similar behavior was found in $[Me_3N_3Me_2B_3]_2NMe$[28] [B−N distance range 1.463(6) Å−1.414(7) Å]. The average $B-CH_3$ and $N-CH_3$ distances, 1.593 and 1.475 Å, are comparable with the values in $(Me_3N_3Me_2B_3)_2NH$, 1.580 and 1.476 Å, and in $(Me_3N_3Me_2B_3)_2NMe$, 1.586 and 1.479 Å[28]. The terminal B−Si bond length, 2.097(4) Å, is somewhat unique. We are unaware of structural data for closely comparable compounds containing an *exo*, two-center, two-electron B−Si bond with the boron atom having formal sp^2 hybridization. The observed distance is longer than the sum of covalent radii: 0.88 Å (B) + 1.17 Å (Si) = 2.05 Å[29], and not surprisingly it is significantly longer than the distance in $tBuN{\equiv}B-Si(SiMe_3)_3$, 1.976(4) Å[30], which contains a formally sp-hybridized B atom (N≡B−Si, 176.6°). On the other hand, the B−Si distances in $Cy_3P \cdot B(H)_2SiMe_3$, 2.007(4) Å[31] and in $Cp_2Ta[\eta^2\text{-}BH_3\{Si(tBu)_2H\}]$, 2.02(1) Å[22], which contain sp^3-hybridized boron atoms, are also significantly shorter than the distance in **2**. The long distance in **2** may result from steric interactions between the bulky Me_3Si groups on the Si atom and the Me groups on the *ortho* N atoms in the borazine ring. The molecular structure of the *B,B′,B′′*-trisilyl derivative **4** was also determined[32], but disorder in several silylmethyl carbon atoms led to a large *R* value. Nonetheless, the composition and anticipated structure of **4** is confirmed. It is also noteworthy that the B−Si bond lengths are long: 2.11(2) Å (average).

In previous reports[28][33] we have described the syntheses of polyborazinylamine oligomers by reaction of chloroborazine with hexamethyldisilazane and heptamethyldisilazane. Extending this approach, the borazine monomer $H_3N_3B_3(Cl)_2Si(SiMe_3)_3$ was prepared from the 1:1 reaction of $(HNBCl)_3$ and $LiSi(SiMe_3)_3$ in hexane. The reaction mixture was filtered to remove LiCl and the monomer solution containing **6** was combined with $(Me_3Si)_2NH$ at 23 °C. This produces a glassy, colorless solid (**7**), following solvent evaporation, that is soluble in pentane, hexane, benzene, and Et_2O. The oligomer formation is summarized in Eq. 2. Elemental analysis (CHN) of the oligomer is in close agreement with the calculated values for **7** although a small amount of residue is typically found according to the combustion analysis. The ^1H-NMR spectrum displays a sharp resonance at $\delta = 0.25$ that is assigned to the $Si(SiMe_3)_3$ groups in the oligomer and a broad peak at $\delta = 0.35$ is assigned to N−H groups. The ^{11}B-NMR spectrum displays two broad resonances centered at $\delta = 18$ and 38. No further attempts were made to characterize the structure of the oligomer.

Figure 1. Molecular structure and atom-labeling scheme for $[(Me_3Si)_3Si](Me)_2B_3N_3(Me)_3$ (**2**)





The pyrolysis behavior of **7** was initially surveyed by TGA from 50−1400 °C under argon. There are two primary weight loss ranges. From 100−300 °C about 35% of the mass is lost and from 350−500 °C another 18% of the mass is lost. No significant further change occurs above 600 °C. The overall ceramic yield is ca. 47%. Bulk samples of the polymer were initially pyrolyzed at 1200 °C for 12 h under a slow stream of pure nitrogen. The product is a shiny black hard solid. The infrared spectrum of the material shows a strong, broad peak centered at ca. 1400 cm^{-1} and a medium-intensity band at ca. 800 cm^{-1}. These bands closely resemble those of a standard sample of turbostratic BN[33]. In addition, weaker bands appear at 1030, 840, and 470 that may be tentatively assigned to Si_3N_4. The XRD pattern (Figure 2) for this sample shows only a weak, broad peak centered at $2\theta = 42°$ ($d = 2.1$ Å). This is interesting since pyrolyzed samples of polyborazinylamine polymers typically show a strong reflection at $2\theta = 26°$ ($d = 3.3$ Å) and weaker, broad reflections centered at $2\theta = 34°$ and 42° following pyrolysis at temperatures as low as 900 °C. This leads to the tentative conclusion that the crystallization of the boron nitride formed in this study is depressed by the presence of the silicon present as amorphous Si_3N_4, SiC, and/or a ternary SiNC material.

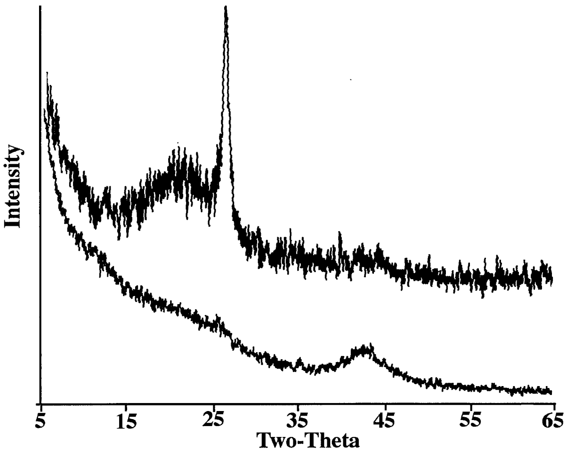
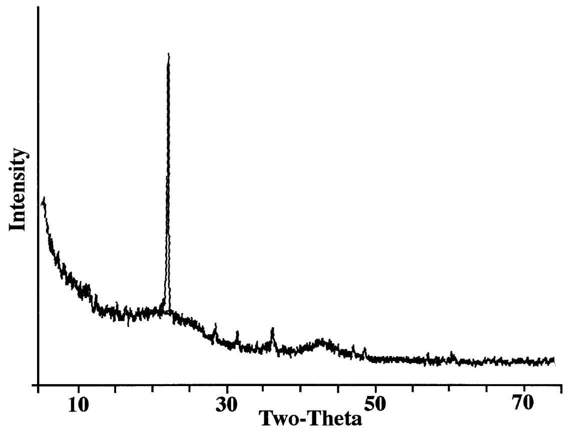


Figure 2. Powder XRD patterns from pyrolysis of polymer precursor **7**; lower trace: 1200°C, 12 h under N_2; upper trace: 1400°C, 12 h under N_2

Further heating of the black, glassy solid to 1400°C under nitrogen gave a gray solid. The sample analyzed as $B_{1.0}N_{1.28}Si_{0.29}C_{0.12}$. An infrared spectrum shows a strong, broad band at ca. 1400 cm^{-1} and a sharper band at ca. 800 cm^{-1} that are assigned to BN and additional bands at 1080, 930, 470, and 420 cm^{-1}. The XRD pattern (Figure 2) shows a broad reflection at $2\theta = 26°$ ($d = 3.37$ Å) and very weak peaks at $2\theta = 21°$ ($d = 4.0$ Å, broad), 39° ($d = 2.28$ Å), 44° ($d = 2.06$ Å), 50° ($d = 1.83$ Å) and 57° ($d = 1.60$ Å). Further heating of this material at 1600°C under Ar leads to gray solid that analysed as $B_{1.0}N_{1.26}Si_{0.25}C_{0.10}$. The XRD pattern (Figure 3) for this material now shows a sharp reflection at $2\theta = 22°$ ($d = 4.06$ Å) and very weak reflections at $2\theta = 28°$ ($d = 3.13$ Å), 32° ($d = 2.84$ Å), 36° ($d = 2.48$ Å), 47° ($d = 1.93$ Å), 48° ($d = 1.87$ Å), 60° ($d = 1.53$ Å). The reflection at $2\theta = 22°$ and weak reflections at $2\theta = 32°$ and 48° may be tentatively ascribed to α-Si_3N_4 that has begun to form in this sample. Other weak reflections may correspond to Si and β-SiC.

Figure 3. Powder XRD pattern from pyrolysis of polymer **7** at 1600°C, 12 h under N_2



A sample of the glassy polymer **7** was also heated at 350°C for 12 h under a flowing stream of NH_3 and then for 6 h under N_2. The resulting residue was heated at 1200°C for 12 h under N_2. The remaining solid was cream-colored, displayed no crystallinity, and analyzed as $B_{1.0}N_{1.42}Si_{0.27}$.

The silyl-substituted monomer molecules **2**−**5** have been prepared and characterized by spectroscopic techniques, and the molecular structure determination for **2** confirms substitution of the very bulky $(Me_3Si)_3Si$ group on the borazine ring at a boron atom. The monomer **6** has also been produced but not isolated. It has been combined with hexamethyldisilazane to provide an organic solvent soluble $(Me_3Si)_3Si$-derivatized polyborazinylamine oligomer **7**. Pyrolysis of this oligomer in nitrogen produces a ceramic product rich in boron and nitrogen containing small amounts of silicon and carbon. The Si appears to suppress the crystallization of BN at 1200°C. At approximately 1400°C the Si present begins to form crystalline phases that at 1600°C show some evidence for formation of α-Si_3N_4. These results are similar to findings reported by Sneddon and coworkers on the pyrolysis of borazine/silazane backbone copolymers. The results suggest that related silyl-substituted borazine monomers should be explored as potential SiNCB precursors.

This work was supported by the *UNM/NSF Center for Microengineered Materials* and its industrial partners.

Experimental Section

Standard vacuum-line and inert-atmosphere techniques were used for the manipulation of reactants and products. − Infrared spectra were obtained with a Nicolet 6000 FT-IR spectrometer and NMR spectra were recorded with Bruker AC-250 and JEOL GSX-400 spectrometers. − NMR spectra were recorded from C_6D_6 solutions and referenced with Me_4Si (^1H, ^{13}C) and $BF_3 \cdot OEt_2$ (^{11}B). − Mass spectra were obtained with a Finnegan mass spectrometer through a solids probe. − Reagents $(Me_3Si)_3SiLi \cdot 3THF$[34], $(ClBNMe)_3$ (**1c**)[35], $(ClBNH)_3$ (**1d**)[36], $Cl_2(Me)B_3N_3(Me)_3$ (**1b**)[37], and $Cl(Me)_2B_3N_3(Me)_3$ (**1a**)[38] were prepared as described in the literature. Solvents were dried by standard procedures and vacuum-transferred from storage vessels into reaction flasks immediately before use.

Synthesis of Molecular Model Compounds [(Me$_3$*Si)*$_3$*Si]-(Me)*$_2$*B*$_3$*N*$_3$*(Me)*$_3$ (**2**): A sample of $LiSi(SiMe_3)_3 \cdot 3$ THF (1.0 g, 2.1 mmol) was added over 10 min to a stirred solution (−78°C) of 2-chloro-1,3,4,5,6-pentamethylborazine, ($Cl(Me)_2B_3N_3(Me)_3$; 0.4 g, 2.1 mmol) in 40 ml of hexane. The reaction mixture was warmed to 25°C and stirred overnight. Volatile materials were removed in vacuo. The white residue was combined with hexane (50 ml) and filtered. Solvent removal from the filtrate afforded a solid **2** that was recrystallized from a minimum of hexane. Yield: 0.75 g (90%); mp 85°C; soluble in Et_2O, pentane, THF, benzene. − IR (KBr): $\tilde{\nu} = 2953$ cm^{-1} (m), 2899 (m), 1477 (s,sh), 1447 (s), 1400 (s), 1388 (s), 1244 (m), 1105 (m), 1075 (m), 997 (m), 863 (s,sh), 836 (s), 682 (m), 625 (m), 515 (w), 430 (w). − MS (50 eV); *m/z* (%): 397 (28) $[M^+]$, 382 (24) $[M - CH_3^+]$, 324 (32) $[M - SiMe_3^+]$, 250 (17) $[M - 2\ SiMe_3^+]$, 150 (11) $[M - (Me_3Si)_3Si^+]$, 73 (100) $[Me_3Si^+]$. − ^1H NMR: $\delta = 0.36$ (CH_3−Si, 27 H), 0.43 (CH_3−B, 6 H), 2.68 (CH_3−N, 3 H), 3.09 (CH_3−N, 6 H). − $^{13}C\{^1H\}$ NMR: $\delta = 1.92$ (CH_3−B), 4.22 (CH_3−Si), 34.2 (CH_3−N), 41.8 (CH_3−N). −

$^{11}B\{^1H\}$ NMR: δ = 36.3 (B−CH_3, 2 B), 42.2 [B−Si($SiMe_3$)$_3$, 1 B]. − $C_{14}H_{42}B_3N_3Si_4$ (397.28): calcd. C 42.32, H 10.60, N 10.60; found C 42.28, H 10.77, N 10.67.

[(Me$_3$Si)$_3$Si]$_2$(Me)B$_3$N$_3$(Me)$_3$ (**3**): A sample of LiSi($SiMe_3$)$_3$ · 3 THF (1.4 g, 3.0 mmol) was added over 15 min to a stirred solution (−78°C) of 2,4-dichloro-1,3,5,6-tetramethylborazine ($Me_3N_3B_3(Me)Cl_2$; 0.32 g, 1.5 mmol) in hexane (40 ml). The mixture was subsequently warmed to 25°C and stirred for 12 h. The volatile components were evaporated leaving a white residue that was extracted with hexane (50 ml). The solution was filtered, the filtrate concentrated and a white waxy solid **3** was recovered. Yield: 0.80 g (85%); mp 103−106°C; soluble in Et_2O, pentane, benzene, and THF. − IR (KBr): $\tilde{\nu}$ = 2520 cm^{-1} (m), 2509 (m), 1484 (m), 1433 (m), 1381 (s,sh), 1357 (s), 1239 (s), 1107 (w), 1064 (m), 984 (m), 947 (w), 832 (s), 696 (w), 684 (m), 608 (m). − MS (50 eV); *m/z* (%): 629 (35) [M^+], 614 (20) [M − CH_3^+], 556 (40) [M − SiMe $_3^+$], 382 (18) [M − Si($SiMe_3$)$_3^+$], 73 (100) [Me_3Si^+]. − ^1H NMR: δ = 0.36 (C*H*$_3$−Si, 54 H), 0.44 (C*H*$_3$−B, 3 H), 3.07 (C*H*$_3$−N, 6 H), 3.56 (CH_3−N, 3 H). − $^{13}C\{^1H\}$ NMR: δ = 4.27 (*C*H$_3$−Si), (*C*H$_3$−N), 47.8 (*C*H$_3$−N). − $^{11}B\{^1H\}$ NMR: δ = 37.1 (B−CH_3, 1 B), 42.8 [B−Si($SiMe_3$)$_3$, 2 B]. − $C_{22}H_{66}N_3B_3Si_8$ (629.90): calcd. C 41.97, H 10.50, N 6.67; found C 40.92, H 10.99, N 6.91.

[(Me$_3$Si)$_3$Si]B$_3$N$_3$(Me)$_3$ (**4**): A sample of LiSi($SiMe_3$)$_3$ · 3 THF (1.95 g, 4.2 mmol) was added over 15 min to a stirred solution (−78°C) of 1,3,5-trimethyl-2,4,6-trichloroborazine ($Me_3N_3B_3Cl_3$; 0.32 g, 1.4 mmol) in hexane (40 ml). The reaction mixture was warmed to 25°C and stirred overnight. Removal of the volatiles from the reaction mixture afforded a white residue that was extracted with hexane (50 ml) and filtered. The solvent was removed from the filtrate under vacuum leaving a white waxy solid. Yield: 1.06 g (88%); soluble in Et_2O, pentane, benzene, and THF. − IR (KBr): $\tilde{\nu}$ = 2952 cm^{-1}(s), 2893 (s), 1924 (w), 1864 (w), 1472 (m), 1434 (w), 1348 (br., s) 1261 (m, sh), 1244 (s), 1074 (s), 967 (m), 838 (s, br.), 748 (m), 681 (m), 622 (m), 438 (w). − MS (50 eV); *m/z* (%): 862 (15) [M^+], 847 (15) [M − $SiMe_3^+$], 789 (35) [M − $SiMe_3^+$], 614 (52) [M − Si($SiMe_3$)$_3^+$]. − ^1H NMR: δ = 0.38 (C*H*$_3$−Si), 3.58 (C*H*$_3$−N). − 13{^1H} NMR: δ = 4.37 (*C*H$_3$−Si), 47.7 (*C*H$_3$−N). − $^{11}B\{^1H\}$ NMR: δ = 42.2. − $C_{30}H_{90}B_3N_3Si_{12}$ (862.52): calcd. C 41.80, H 10.50, N 4.88; found C 42.10, H 10.54, N 5.29.

[(Me$_3$Si)$_3$Si]$_3$B$_3$N$_3$H$_3$ (**5**): A sample of (Me_3Si)$_3$SiLi · 3 THF (1.55 g, 3.38 mmol) was added to a cooled (−78°C), stirred solution of $Cl_3B_3N_3H_3$ (0.208 g, 1.13 mmol) in hexane (40 ml). The solution was warmed slowly to 23°C and stirred overnight. The solvent was removed by vacuum evaporation leaving a white residue that was redissolved in fresh hexane (50 ml) and filtered to remove entrained LiCl. The filtrate was concentrated leaving a gummy solid **5** that was vacuum-dried. Yield: 0.81 g (88%); mp 78−83°C. Further attempts to purify this compound by sublimation and recrystallization were unsuccessful. − MS (50 eV); *m/z* (%): 819 (4) [M^+], 804 (1) [M − Me^+], 746 (1) [M − Me_3Si^+], 731 (1) [M − (Me_3Si)(Me)$^+$], 658 (4) [M − (Me_3Si)$_2$(Me)$^+$, 247 (4) [Si($SiMe_3$)$_3^+$]. − ^1H NMR: δ = 0.36 (C*H*$_3$Si). − $^{13}C\{^1H\}$ NMR: δ = 1.94 (*C*H$_3$Si). − $^{11}B\{^1H\}$ NMR: δ = 38.

Synthesis of Polymer **7**: In a typical reaction, LiSi($SiMe_3$)$_3$ · 3 THF (1.3 g, 2.9 mmol) was added with stirring over 15 min to ($ClBNH$)$_3$ (0.53 g, 2.9 mmol) in hexane (60 ml) cooled to −78°C. The mixture was warmed to 23°C and stirred overnight. The resulting mixture was filtered to remove LiCl, and the filtrate containing **6** was combined with (Me_3Si)$_2$NH (0.6 ml, 2.9 mmol). This mixture was stirred (23°C) for 24 h and the volatiles removed by vacuum evaporation. This left a glassy, colorless solid **7**. Yield: 0.9 g (90%); soluble in hexane, pentane, benzene, and Et_2O. − IR (KBr): 3446 cm^{-1} (s), 2956 (s), 2922 (s, sh), 2900 (s), 1456 (s), 1413 (s), 1251 (m), 1186 (w), 1111 (w), 1064 (m), 836 (s), 754 (m), 712 (w), 687 (m), 623 (w), 609 (w). − ^1H NMR: δ = 0.35−0.25 (br., m). − $^{13}C\{^1H\}$ NMR: δ = 3.9−1.9 (br.). − $C_9H_{31}B_3N_4Si_4$ (340.14): calcd. C 31.76, H 9.11, N 16.47; found C 32.29, H 8.52, N 14.43.

Polymer Pyrolysis: The TGA of the polymer was recorded under Ar (50−1400°C, 10°C/min). There is a significant weight loss (ca. 35%) between 100 and 350°C and a more gradual weight loss (ca. 18%) up to 500°C. Beyond this temperature, there is minimal weight loss. − Bulk pyrolyses were performed under a variety of conditions, and some representative results are summarized. Typically, a sample (0.35 g) of glassy polymer was placed in a Pt boat in a quartz pyrolysis tube, and the tube was evacuated and backfilled with dry N_2. The sample was then heated at 1200°C under a slow stream of N_2 purge gas. After 12 h, a black solid was collected and characterized. − IR (KBr): $\tilde{\nu}$ = 1410 cm^{-1} (vs), 1030 (vs), 830 (m), 800 (m), 470 (m). − XRD: *d* = 2.1 Å (br.). − The sample was further heated to 1400°C under N_2 for 12 h, and the resulting gray solid was characterized. − IR (KBr): $\tilde{\nu}$ = 1400 cm^{-1} (vs), 1130 (m), 1080 (s), 930 (m), 800 (s), 470 (m), 420 (w). − XRD: *d* = 4.0 Å, 3.38, 2.28, 2.06, 1.83, 1.60. − Found C 3.76, B 28.21, N 46.78, Si 21.25. − Continued heating of this sample at 1600°C for 12 h under N_2 results in a dark gray solid. − IR (KBr): $\tilde{\nu}$ = 1382 cm^{-1}, 1088, 894, 784, 476. − XRD: *d* = 4.06 Å, 3.13, 2.84, 2.48, 1.93, 1.87, 1.53. − Found C 3.27, B 29.47, N 48.11, Si, 19.14. − A sample (0.35 g) of glassy polymer was also heated at 350°C under

Table 1. Crystallographic data for [(Me_3Si)$_3$Si](Me)$_2$B$_3$N$_3$(Me)$_3$ (**2**)

empirical formula	$C_{14}H_{42}B_3N_3Si_4$
formula weight	397.3
T [°C]	22
crystal system	monoclinic
space group	$P2_1/c$
a [Å]	9.346(2)
b [Å]	11.677(2)
c [Å]	24.027(5)
α [°]	90.0
β [°]	98.82
γ [°]	90.0
V [Å^3]	2591.2(9)
Z	4
$D_{calcd.}$ [g cm^{-3}]	1.018
μ [cm^{-1}]	0.227
F(000)	872
reflections collected	$-h\ -k\ \pm l$
measured	5109
independent	4542
observed [$F > 3\sigma(F)$]	3023 [$F > 3\sigma(F)$]
R_F [%]	6.42
R_{wF} [%]	5.93

Table 2. Selected bond lengths and bond angles for [(Me_3Si)$_3$Si]-(Me)$_2$B$_3$N$_3$(Me)$_3$ (**2**)

Bond lengths [Å]			
B(1)−Si(1)	2.097(4)	Si(1)−Si(2)	2.382(2)
B(1)−N(1)	1.432(6)	Si(1)−Si(3)	2.362(2)
B(1)−N(3)	1.440(6)	Si(1)−Si(4)	2.385(2)
B(2)−N(1)	1.439(6)	N(1)−C(1)	1.470(6)
B(2)−N(2)	1.428(8)	N(2)−C(3)	1.488(6)
B(3)−N(2)	1.407(8)	N(3)−C(5)	1.470(6)
B(3)−N(3)	1.453(6)	B(2)−C(2)	1.585(8)
		B(3)−C(4)	1.601(9)
Bond angles [°]			
N(1)−B(1)−N(3)	115.6(3)	B(1)−N(1)−B(2)	123.4(4)
N(1)−B(2)−N(2)	117.8(4)	B(2)−N(2)−B(3)	122.0(4)
N(2)−B(3)−N(3)	118.2(5)	B(1)−N(3)−B(3)	122.5(4)

NH_3 for 12 h, then under N_2 at 350°C for 6 h, and 1200°C for an additional 12 h. The resulting solid was cream-colored. − IR (KBr): 1388 cm^{-1} (s), 1033 (s), 788 (m), 696 (w), 448 (w). − Found B 28.24, N 51.95, Si 19.81.

Crystallographic Measurements and Structure Solution: A suitable crystal of **2** was mounted in a glass capillary and centered on a Syntex P3/F automated diffractometer. Determinations of the crystal class, orientation matrix, and unit-cell dimensions were performed in a standard fashion. Data were collected with use of Mo-K_α radiation ($\lambda = 0.71069$ Å), a highly oriented graphite crystal monochromator, a scintillation counter, and pulse-height analyzer. Selected data-collection parameters are summarized in Table 2. The space-group assignment was made by inspection of a small data set[39], and no absorption correction was required. Redundant and equivalent data were averaged and converted to unscaled $|F_o|$ values following corrections for Lorentz and polarization effects. Standard intensities decayed by about 10% during data collection and intensities were scaled accordingly. All calculations were performed with the SHELXTL PLUS structure solution package[40]. The structure was solved by direct methods and refined with full-matrix least-squares techniques[41]. The heavy atoms were refined anisotropically, and the H atoms were initially refined (riding model) in idealized positions with fixed $U_{iso} = 1.2\ U_{equiv}$ of the parent atom. The hydrogen positions were then allowed to vary to achieve the final R value. Further information on the X-ray crystallographic structure determination for $(Me_3Si)_3SiBB_2Me_2N_3Me_3$ may be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, England, and may be ordered by quoting the depository number CCDC-101122.

☆ Dedicated to Professor *Heinrich Nöth* on the occasion of his 70th birthday.

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