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Models and Polyborazine Precursors for Boron Nitride Ceramics

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Elimination–condensation reactions between $Me(Cl_2)B_3N_3Me_3$ and $(Me_3Si)_2NMe$ and between $(ClBNMe)_3$ and $(Me_3Si)_2NH$ form oligomeric borazinylamines, and a metathesis reaction between Li_2S and $(ClBNH)_3$ produces an oligomeric borazinyl sulfide. The pyrolysis chemistry of these oligomers has been examined, and conditions have been defined that produce hexagonal h-BN. Reactions that model the first stage of oligomer formation also have been studied, and the molecular species $[Me_3N_3B_3(Me_2)]_2NH$, $[Me_3N_3B_3(Me_2)]_2NMe$, $[Me_3N_3B_3(Me_2)]_2S$, and $[Me_3N_3B_3(Me_2)]_2O$ have been isolated and characterized. Single-crystal X-ray diffraction analyses for these compounds have been completed, and crystal data are as follows: $[Me_3N_3B_3(Me_2)]_2NH$, triclinic, $P\bar{1}$, $Z = 2$, at 293 K, $a = 8.078$ (1) Å, $b = 9.121$ (1) Å, $c = 14.139$ (2) Å, $\alpha = 97.07$ (1)°, $\beta = 95.44$ (1)°, $\gamma = 115.32$ (1)°, and $V = 921.8$ (2) Å^3; $[Me_3N_3B_3(Me_2)]_2NMe$, triclinic, $P\bar{1}$, $Z = 2$, at 293 K, $a = 8.075$ (2) Å, $b = 9.210$ (2) Å, $c = 14.912$ (3) Å, $\alpha = 91.51$ (2)°, $\beta = 94.07$ (2)°, $\gamma = 113.27$ (2)°, and $V = 1007.0$ (5) Å^3; $[Me_3N_3B_3(Me_2)]_2O$, orthorhombic, $Pbcn$, $Z = 4$, at 293 K, $a = 14.166$ (7) Å, $b = 11.378$ (6) Å, $c = 11.983$ (6) Å, and $V = 1931$ (2) Å^3; $[Me_3N_3B_3(Me_2)]_2S$, monoclinic $P2/n$, $Z = 2$, at 293 K, $a = 6.339$ (1) Å, $b = 6.351$ (1) Å, $c = 23.677$ (4) Å, $\beta = 97.42$ (1)°, and $V = 945.3$ (2) Å^3. The molecular structure of each compound features a central atom, N(H), N(Me), O, or S, bonded to two pentamethylborazinyl rings.

Introduction

Boron nitride is a well-known, technologically important ceramic that is obtained in a graphitic structural modification (h-BN) or a hard, diamond modification (c-BN).[1] The h-BN form is typically prepared as a powder by high-temperature reactions of simple boron and nitrogen reagents, e.g., $B(OH)_3$ and $(NH_2)_2CO$ or $B(OH)_3$, C, and N_2. Alternatively, powders and thin films of h-BN are produced by vapor deposition techniques.[2] Although these syntheses are relatively routine, they suffer from several shortcomings. In particular, these routes do not produce high-quality fibers, defect-free coatings, or low-density materials. As a result, several groups have sought to prepare boron nitride by pyrolysis of monomeric and polymeric precursors that are soluble or fusible, and a review of this chemistry is available.[3]

Among the potential molecular boron–nitrogen compounds that might serve as useful preceramics are the large family of borazine compounds studied extensively in the 1960s.[4-8] For example, Paciorek and co-workers[9] and Rice and co-workers[10] have reported pyrolysis chemistry of several substituted borazines; however, for a variety of reasons, most of these reagents were found to be impractical ceramic precursors, or they produced impure products. Nevertheless, this chemistry suggested that borazine ring opening and subsequent elimination and condensation processes were facilitated by the presence of NH_2 or N(H)R groups on the boron atoms,[11,12] and further developments with these compounds might be successful. It was further noted that a low-melting polymer formed from gentle thermolysis of $[(H_2N)BN(SiR_3)]_3$ and an organic-solvent-soluble oligomer resulted from $([(R_3Si)(H)N]BNH)_3$.[13-15] These materials were found to be useful for forming melt drawn fibers and solution-deposited fiber coatings. Taniguchi and co-workers[16] reported the formation of a meltable polymer from $[(H_2N)BN(C_6H_5)]_3$; however, difficulty was encountered in reproducing this work.[12]

Several other borazine high polymers have been reported by Lappert[5,17] and Wagner,[18] but little attention has been given to these materials as ceramic precursors. Recently, Sneddon and co-workers[19] reported a novel approach involving polymerization of vinylborazine, and the resulting polymer was efficiently converted to h-BN. They have also described details of the thermal polymerization of the parent borazine $(HBNH)_3$ and the conversion of that polymer to h-BN.[20]

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In our own group, we have explored oligomerization reactions of trichloroborazines and dichloroborazines with disilazanes in an effort to obtain useful preceramic polymers, and preliminary reports on that work have appeared.[21-23] Aspects of some of this condensation chemistry were first examined by Lappert[5,17] and Meller;[24-27] however, utilization of the oligomers as ceramic precursors was not explored. In this report, we describe additional borazine oligomerization chemistry as well as the preparation and structural characterization of model compounds for the oligomerization process.

Experimental Section

General Information. Standard inert-atmosphere techniques were used in the synthesis and manipulations of all compounds. Solvents were dried with appropriate drying agents and distilled under dry nitrogen. Hexamethyldisilazane and heptamethyldisilazane (Aldrich) were freshly distilled before use. 1,3,5-Trimethyl-2,4,6-trichloroborazine,[3,28] 1,2,3,4,5-pentamethyl-6-chloroborazine,[29,30] and 1,2,3,5-tetramethyl-4,6-dichloroborazine[30] were prepared by literature methods. Lithium triethylborohydride solution (Aldrich) was used as received. Infrared spectra were obtained on a Nicolet 6000 FT-IR spectrometer, and data for model compounds 2–5 are summarized in the supplementary material (see the paragraph at the end of the paper). NMR spectra were obtained from Varian FT-80A and JEOL GSX-400 spectrometers. Spectral standards were $(CH_3)_4Si$ (^1H, ^{13}C) and $F_3B{\cdot}Et_2O$ (^{11}B). Thermogravimetric analyses were performed on a Du Pont Model 1090 TGA. X-ray powder diffraction analyses were obtained from a Scintag Model PAD-V diffractometer. Transmission electron microscopy was accomplished on a JEOL JEM-2000 FX microscope operating at 200 keV. Mass spectra were obtained with a solids probe on a Finnigan Model 4500 spectrometer, and only parent ions containing the ^{11}B isotope are reported. Elemental analyses were obtained from Galbraith Laboratories (Knoxville, TN) or from the UNM microanalytical services facility (Perkin-Elmer Model 2400 CHN analyzer). It has proven very difficult to obtain reliable and reproducible analyses for the preceramic polymer materials. This is, in part, due to the presence of small, variable amounts of chloride and silylamide end-blocking groups in the green polymer and variable polymer structures that change with specific reaction conditions. In addition, small amounts of solvent remain trapped in nanometer-sized pores of the green polymers. As a result, analytical data for the polymers in our experience are not particularly reliable. Analyses for the model compounds and the final ceramic products are more reliable. Analyses for the polymers reported here are for green polymer samples that were pumped on at 25 °C overnight with an oil pump vacuum.

Syntheses of Model Compounds. (a) $[Me_3N_3B_3(Me_2)]_2NH$ (2). Hexamethyldisilazane (0.87 g, 5.4 mmol) was added in one portion to a stirred, cooled (−78 °C) solution of 1,2,3,4,5-pentamethyl-6-chloroborazine (2.0 g, 10.8 mmol) in CH_2Cl_2 (25 mL). The mixture was slowly warmed to 25 °C over 12 h, and the volatiles were subsequently removed by vacuum evaporation. The remaining solid was sublimed (90 °C/0.02 Torr), and colorless crystals were collected; yield 1.3 g, 73%; mp 142–145 °C. Anal. Calcd for $C_{10}H_{31}B_6N_7$: C, 38.22; H, 9.94; N, 31.20. Found: C, 37.57; H, 9.73; N, 29.97. Mass spectrum (30 eV) [*m/e* (rel intensity)] M^+ 315(3). NMR ($CDCl_3$) $^{11}B\{^1H\}$ δ 37.2, 30.0; ^1H δ 2.87, 2.78, 0.5.

(b) $[Me_3N_3B_3(Me_2)]_2NMe$ (3). Heptamethyldisilazane (0.38 g, 2.17 mmol) was added in one portion to a stirred, cooled (−78 °C) solution of 1,2,3,4,5-pentamethyl-6-chloroborazine (0.81 g, 4.37 mmol) in CH_2Cl_2 (25 mL). The mixture was slowly warmed to 25 °C over 12 h, and the volatiles were removed by vacuum evaporation. A viscous oil was obtained that slowly produced colorless crystals at 25 °C; yield 0.70 g, 98%; mp 124–126 °C. Anal. Calcd for $C_{11}H_{33}B_6N_7$: C, 40.24; H, 10.13; N, 29.87. Found: C, 41.71; H, 10.19; N, 28.58. Mass spectrum (30 eV) [*m/e* (rel intensity)] M^+ 329 (25). NMR ($CDCl_3$) $^{11}B\{^1H\}$ δ 38.0, 29.0; ^1H δ 2.90, 2.85, 2.78, 0.51.

(c) $[Me_3N_3B_3(Me_2)]_2S$ (4). Sulfur (0.0868 g, 2.7 mmol) and 5.4 mL of 1 M $Li(Et_3BH)$ in THF were combined in a Schlenk flask, and the resulting honey-colored solution containing Li_2S was stirred for 30 min.[31] 1,2,3,4,5-Pentamethyl-6-chloroborazine in 40 mL of THF was added in portions to the Li_2S/THF solution over 5 min. A cloudy precipitate initially formed but redissolved with continued stirring (12 h). The volatiles were removed by vacuum evaporation. Hexane (25 mL) was added to the residue, and the resulting mixture was filtered to remove the majority of the insoluble LiCl. Recrystallization (twice) of the pale yellow solid in hexane gave a white crystalline solid; yield 0.50 g (56%); mp 168–169 °C. Anal. Calcd for $C_{10}H_{30}B_6N_6S$: C, 36.25; H, 9.13; N, 25.37. Found: C, 36.40; H, 9.30; N, 25.34. Mass spectrum (70 eV) [*m/e* (rel intensity)] M^+ 332(38). NMR (C_6D_6) ^{11}B δ 36 ($h/2 \sim 360$ Hz); ^1H δ 3.11, 2.69, 0.43.

(d) $[Me_3N_3B_3(Me_2)]_2O$ (5). A sample of $[Me_3N_3B_3(Me_2)]_2S$ (0.44 g, 1.33 mmol) was dissolved in THF (40 mL), and water (23.9 μL, 1.33 mmol) was introduced to the stirred solution. The mixture was stirred for 1 h, and the solvent was removed by vacuum evaporation. A pale yellow solid was recovered and recrystallized in a minimum of fresh THF, leaving colorless needles; yield 0.23 g (54%); mp 132–135 °C. Anal. Calcd for $C_{10}H_{30}B_6N_6O$: C, 38.11; H, 9.59; N, 26.66. Found: C, 37.92; H, 9.92; N, 26.68. Mass spectrum (50 eV) [*m/e* (rel intensity)] M^+ 316 (87). NMR (C_6D_6) ^{11}B δ 37 ($h/2 \sim 320$ Hz), 24 ($h/2 \sim 190$ Hz); ^1H δ 2.79, 2.77, 0.49; $^{13}C\{^1H\}$ δ 34.45, 31.55, −0.25.

Syntheses of Polyborazines. (a) $[Me_3N_3B_3(Me)(NMe)_2]_n$ (6). Heptamethyldisilazane (6.83 g, 38.9 mmol) was added to a stirred solution of 1,2,3,5-tetramethyl-4,6-dichloroborazine in chlorobenzene (100 mL). The mixture was refluxed for 12 h, and the majority of volatile reagents were then removed by vacuum evaporation. A white solid was obtained; yield 6.3 g (97%). Anal. Found: C, 38.9; H, 10.2; N, 30.1. NMR ($CDCl_3$) ^{11}B δ 35 ($h/2 \sim 500$ Hz); ^1H δ 2.81, 2.73, 2.5, 0.46.

(b) $[Me_3N_3B_3(NH)_2]_n$ (7). Hexamethyldisilazane (39.6 g, 245.3 mmol) was added to a stirred solution of 1,3,5-trimethyl-2,4,6-trichloroborazine (36.9 g, 163.3 mmol) in diethyl ether (400 mL). After the addition was complete (5 min), stirring was stopped, and the mixture was allowed to stand overnight at room temperature. A white gel was obtained that included all of the solvent. Vacuum evaporation of the volatiles left a white granular solid; yield 29.0 g. Anal. Found: C, 29.04; H, 7.37; N, 29.72; B, 17.87; Cl, 5.64.

(c) $[H_3N_3B_3S_2]_n$ (8). Sulfur (0.785 g, 2.45 mmol) was added to 50 mL of 1 M $LiBEt_3H$ (49 mmol) in THF. After gas evolution ceased, the resulting solution was stirred for 30 min and cooled to −78 °C, and 2,4,6-trichloroborazine (3.0 g, 16.3 mmol) in 40 mL of THF was added dropwise. The resulting solution was allowed to warm over 3 h to 25 °C, and the volatiles were then removed in vacuo. The resulting product containing LiCl, residual THF, Et_3B, and the polyborazinyl sulfide was heated to 90 °C for 14 h in vacuo to remove some of the trapped volatiles, and a faintly yellow solid (4.47 g) was isolated. Analytical data for this polymer were particularly variable. The solid was then heated to 350 °C for 15 h, and the resulting material extracted in three stages with THF in a Soxhlet extractor. Typically, 95–97% of the LiCl produced in the reaction and occluded in the polymer was removed and analyzed gravimetrically by AgCl precipitation.

Pyrolysis of Polyborazines. The pyrolyses of 6–8 were examined under a variety of conditions, and some specific details

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Table I. Crystallographic Data for Compounds 2–5

	2	**3**	**4**	**5**
formula	$C_{10}H_{31}B_6N_7$	$C_{11}H_{33}B_6N_7$	$C_{10}H_{30}B_6N_6S$	$C_{10}H_{30}B_6N_6O$
fw	314.3	328.3	331.3	315.3
T, °C	20 (2)	20 (2)	20 (2)	20 (2)
cryst syst	triclinic	triclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P\bar{1}$	$P2/n$	$Pbcn$
a, Å	8.078 (1)	8.075 (2)	6.339 (1)	14.166 (7)
b, Å	9.121 (1)	9.210 (2)	6.351 (1)	11.378 (6)
c, Å	14.139 (2)	14.912 (3)	23.677 (4)	11.983 (6)
α, deg	97.07 (1)	91.51 (2)		$\alpha = \beta = \gamma = 90°$
β, deg	95.44 (1)	94.07 (2)	97.42 (1)	
γ, deg	115.32 (1)	113.27 (2)		
V, Å^3	921.8 (2)	1007.0 (5)	945.3 (2)	1931 (2)
Z	2	2	2	4
D_{calcd}, g cm^{-3}	1.132	1.082	1.164	1.084
μ, cm^{-1}	0.63	0.60	1.66	0.63
$F(000)$	340	356	356	680
no. of rflctns				
in octants	$\pm h,k,\pm l$	$\pm h,\pm k,\pm l$	$\pm h,\pm k,\pm l$	$+h,+k,+l$; $-h,-k,-l$
measd	3438	7322	6701	4051
independ	3253	3572	1682	1712
obsd ($F \geq 3\sigma(F)$)	2229	2295	1493	890
R_F, %	7.65	9.61	6.61	11.54
R_{wF}, %	7.90	9.69	7.66	10.98

are summarized here. A sample of 6 (10.4 g) was placed in a boron nitride crucible and pyrolyzed at 1200 °C under ammonia for 12 h and then under nitrogen for 12 h. Methylamine, methylamine hydrochloride, and small amounts of chlorobenzene solvent were identified in the volatile products. A gray–black solid (2.59 g) was obtained that gave an infrared spectrum similar to that of h-BN. Powder X-ray diffraction analysis showed lines at $d = 3.42$ (002) and 2.14. To remove some carbon impurity, a sample (1.4 g) was heated at 700 °C in air for 2 h, leaving a gray-white solid (1.3 g). Anal. Calcd for BN: B, 43.56; N, 56.44. Found: B, 40.9; N, 52.6; H, 0.6; C, 5.5.

A sample of 7 (8 g) was pyrolyzed in a boron nitride crucible under NH_3 for 12 h at 1200 °C and then under N_2 for 12 h at 1200 °C, and 3.1 g of white solid was isolated. Methylamine, ammonia, hydrochloride salts, and a small amount of diethyl ether were identified in the volatile products. Pyrolysis of 1.5 g of this material at 700 °C for 12 h in air left 1.45 g of a white residue that displayed an X-ray powder pattern and infrared spectrum identical with those of turbostratic h-BN. Anal. Calcd for BN: B, 43.56; N, 56.44. Found: B, 42.9; N, 55.8; H, 0.8.

The pyrolysis of 8 is complicated by the presence of residual LiCl in the polymer.[32] A sample of 8 (4.47 g) was placed in a boron nitride crucible, and the crucible was enclosed in a hollow graphite tube. This combination was set inside a quartz tube in a tube furnace. The contents were heated over 6 h to 1000 °C under vacuum and held at 1000 °C for 4 h. A black solid (10 g) was recovered, and this was heated at 700 °C in air for 1 h to remove residual carbon. The remaining cream-colored solid (0.82 g) displayed an X-ray powder pattern and infrared spectrum identical with those of turbostratic h-BN.

Alternatively, 3.65 g of 8 was heated under an NH_3/N_2 gas mixture at 1000 °C for 1 h. The resulting light gray solid was washed with water to remove residual LiCl and then dried. The resulting solid (1.0 g) showed good crystallinity, an infrared spectrum typical of h-BN, and no chloride impurity.[32]

Crystallographic Measurements and Structure Solutions. Suitable crystals of 2–5 were mounted in glass capillary tubes and centered on a Syntex P3/F automated diffractometer. Determinations of crystal class, orientation matrix, and unit cell dimensions were performed in a standard fashion. Data were collected with use of Mo Kα radiation ($\bar{\lambda} = 0.710\,69$ Å;, a highly oriented graphite crystal monochromator, a scintillation counter, and pulse height analyzer. Data collection parameters are summarized in Table I, and additional details are provided in the supplementary material. Space group assignments were made by inspection of the data,[33] and small empirical corrections for absorption were made on the basis of upon ψ scans.[34] Redundant and equivalent data were averaged and converted to unscaled $|F_o|$ values following corrections for Lorentz and polarization effects.

Table II. Fractional Coordinates (×10^4) and Their Esd's for $[Me_3N_3B_3(Me_2)]_2NH$, 2

atom	x	y	z
N(1)	2287 (5)	4724 (4)	2988 (2)
B(2)	2434 (6)	4234 (5)	1999 (3)
N(3)	2572 (4)	2728 (3)	1672 (2)
B(4)	2550 (6)	2179 (5)	674 (3)
N(5)	2511 (4)	3229 (4)	2 (2)
B(6)	2553 (5)	4811 (5)	295 (3)
N(7)	2525 (4)	5284 (3)	1303 (2)
B(8)	1312 (6)	3878 (5)	3708 (3)
N(9)	−413 (4)	2397 (3)	3460 (2)
B(10)	−1241 (6)	1456 (5)	4168 (3)
N(11)	−364 (4)	2091 (4)	5162 (2)
B(12)	1226 (6)	3669 (6)	5466 (3)
N(13)	2037 (4)	4538 (3)	4719 (2)
C(1)	2792 (6)	1742 (5)	2385 (3)
C(2)	2573 (6)	465 (5)	342 (3)
C(3)	2435 (6)	2659 (5)	−1031 (3)
C(4)	2576 (6)	5973 (5)	−447 (3)
C(5)	2476 (7)	6859 (5)	1631 (3)
C(6)	−1410 (6)	1868 (5)	2452 (3)
C(7)	−3088 (6)	−212 (5)	3871 (3)
C(8)	−1202 (6)	1109 (6)	5903 (3)
C(9)	2099 (6)	4384 (6)	6565 (3)
C(10)	3688 (6)	6139 (5)	4977 (3)

All calculations for 3 and 5 were performed with the R3/SHELXTL structure determination package.[35] Least-squares refinements in the package use a blocked-cascade algorithm with full-matrix blocks of 103 parameters.[36] Calculations involving 2 and 4 used

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(32) Lithium chloride is a product of the preparative metathesis reaction. Chloride was analyzed in the final ceramic products by standard silver chloride test and by EDS analysis.

(33) Space group notations as given in: *International Tables for X-ray Crystallography*; Reidel: Dordrecht, Holland, 1983; Vol. I, pp 73–346. A referee raised concern regarding the monoclinic space group selection for 4. After transformation to C-orthorhombic, we find that many reflections that should be equivalent are not ($R_{int} = 36.7\%$ compared to $R_{int} = 1.75\%$ for $P2/n$) in the orthorhombic setting, and no evidence for *mmm* or tetragonal symmetry is displayed. The monoclinic cell is therefore considered to be correctly identified. The reflections collected are those listed in Table I, plus their Friedel related reflections.

(34) The empirical absorption correction uses an ellipsoidal model fitted to azimuthal scan data, which is then applied to the intensity data: SHELXTL Manual, Revision 4; Nicolet XRD Corp.: Madison, WI, 1983.

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Table III. Atomic Coordinates (×10^4) and Their Esd's for $[Me_3N_3B_3(Me_2)]_2NMe$, 3

atom	*x*	*y*	*z*
B(1)	5697 (6)	3595 (5)	8225 (3)
N(2)	6308 (4)	3129 (3)	9028 (2)
B(3)	7207 (6)	4218 (6)	9829 (3)
N(4)	7593 (4)	5874 (4)	9783 (2)
B(5)	7166 (7)	6429 (5)	8978 (4)
N(6)	6279 (4)	5273 (4)	8198 (2)
N(7)	4487 (4)	2418 (4)	7485 (2)
B(8)	4616 (6)	968 (5)	7068 (3)
N(9)	6202 (4)	978 (4)	6705 (2)
B(10)	6188 (7)	−337 (6)	6099 (3)
N(11)	4517 (6)	−1743 (4)	5922 (2)
B(12)	2961 (8)	−1899 (6)	6377 (4)
N(13)	3066 (4)	−545 (4)	6952 (2)
C(1)	2959 (6)	2731 (5)	7064 (3)
C(2)	5817 (7)	1422 (5)	9074 (3)
C(3)	7722 (7)	3663 (7)	1 0745 (3)
C(4)	8517 (8)	7058 (6)	1 0604 (4)
C(5)	7659 (7)	8279 (5)	8948 (4)
C(6)	6153 (7)	5873 (6)	7322 (3)
C(7)	7882 (6)	2455 (5)	6893 (3)
C(8)	7906 (7)	−234 (6)	5632 (3)
C(9)	4449 (9)	−3074 (6)	5258 (3)
C(10)	1187 (8)	−3520 (6)	6233 (4)
C(11)	1563 (6)	−737 (5)	7504 (3)

Table IV. Atomic Coordinates (×10^4) and Their Esd's for $[Me_3N_3B_3(Me_2)]_2S$, 4

atom	*x*	*y*	*z*
S	2500	2271 (2)	2500
B(1)	3535 (5)	3923 (5)	3119 (1)
N(2)	5449 (3)	3240 (3)	3452 (1)
B(3)	6335 (5)	4356 (5)	3954 (1)
N(4)	5233 (3)	6195 (3)	4112 (1)
B(5)	3278 (5)	6898 (5)	3797 (1)
N(6)	2435 (3)	5712 (3)	3298 (1)
C(1)	6598 (5)	1370 (5)	3281 (1)
C(2)	8467 (5)	3583 (6)	4318 (2)
C(3)	6129 (6)	7379 (5)	4621 (1)
C(4)	2077 (5)	8920 (5)	3982 (2)
C(5)	370 (4)	6372 (6)	2982 (1)

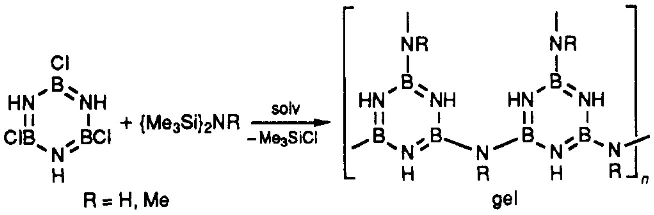
SHELXTL-PLUS with full-matrix least-squares refinements capable of handling 800 parameters in each full matrix block. The structures were solved by direct methods, and refinements proceeded in a normal fashion. Specific notes on the structure refinements, anisotropic thermal parameters, hydrogen atom positional parameters, and structure factor tables are provided in the supplementary material. Non-hydrogen atom positional parameters are listed in Tables II–V.

Results and Discussion

Table V. Atomic Coordinates (×10^4) and Their Esd's for $[Me_3N_3B_3(Me_2)]_2O$, 5

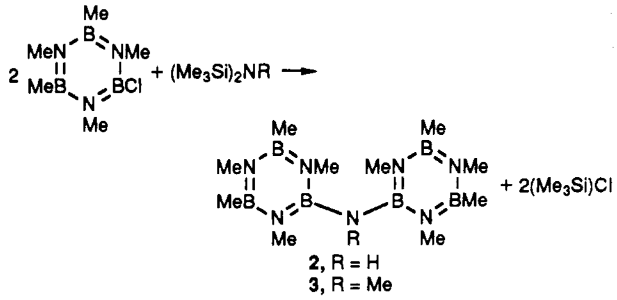
atom	*x*	*y*	*z*
O	5000	683 (6)	2500
B(6)	4075 (5)	976 (7)	2325 (6)
N(1)	3381 (4)	324 (4)	2867 (4)
C(1)	3693 (6)	−566 (6)	3674 (6)
B(2)	2407 (5)	500 (7)	2672 (7)
C(2)	1634 (5)	−272 (7)	3277 (6)
N(3)	2162 (3)	1381 (5)	1884 (4)
C(3)	1138 (5)	1542 (8)	1624 (8)
B(4)	2838 (7)	2101 (6)	1327 (6)
C(4)	2508 (6)	3108 (6)	500 (6)
N(5)	3806 (3)	1871 (4)	1537 (4)
C(5)	4555 (5)	2506 (6)	967 (6)

Scheme I



The reactions of silylamines and haloboranes have been studied extensively,[37] and they provide convenient routes to a large number of aminoboranes, such as $R_2NBR'_2$, and bisboranylamines, $(R_2B)_2NR'$. In preliminary reports,[21-23] we have described applications of this chemistry to the preparation of soluble or fusible preceramic polymers for boron nitride production. A general outline of chemistry for dichloro- and trichloroborazines is illustrated in Scheme I. Unfortunately, many of the polymers produced by this route are insoluble in common organic solvents. Consequently, it has not been possible to accurately characterize the polymer properties (e.g., connectivity, average molecular weight, molecular weight distribution). Nonetheless, several poly(borazinylamine) polymers are easily converted via pyrolysis to powder samples of h-BN, while other polymers are useful as melt coating reagents,[38] or they are soluble in liquid ammonia.[39] Given these facts, we have attempted to model at least the early stage of the oligomerization chemistry between chloroborazines and disilylamines by examining the reactions of monochloroborazines and silylamines.

Reactions of 1,2,3,4,5-pentamethyl-6-chloroborazine (1) with hexamethyldisilazane, $(Me_3Si)_2NH$, and heptamethyldisilazane, $(Me_3Si)_2NMe$, produce the respective bisborazinylamines 2 and 3 in high yield, as shown in eq 1. Although samples of 3[40] and related bisborazinylamines have been reported previously,[7,17] neither 2 nor 3 have been fully characterized. The mass spectra of 2 and 3 display a parent ion consistent with the proposed molecular formulation. Infrared spectra obtained from KBr pellets show



(1)

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(36) A general description of the least-squares algebra is found in: *Crystallographic Computing*; Ahmed, F. R., Hall, S. R., Huber, C. P., Eds.; Munksgaard: Copenhagen, 1970; p 187. The least-squares refinements minimize $\sum w(|F_o| - |F_c|)^2$, where $w = 1/[\sigma(F)^2 + gF^2]$: **2**, $g = 0.0006$; **3**, $g = 0.00097$; **4**, $g = 0.0022$; **5**, $g = 0.00073$. $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ and $\mathrm{GOF} = [\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$, where NO = number of observations and NV = number of variables.

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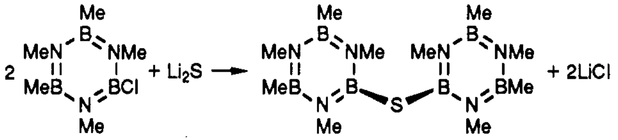
(40) Meller, A. *Monatsh. Chem.* **1968**, *99*, 1670.

bands in regions corresponding to N–CH_3, B–CH_3, and B–N ring stretches, and the spectra compare favorably with extensive reports on infrared analyses for substituted borazines.[41] Compound **2** also exhibits a single band at 3409 cm^{-1} that may be assigned to the bridging N–H amino groups. The ^{11}B NMR spectra reveal two broad resonances in an approximate 2:1 area ratio: **2**, δ 37.2 and 30.0; **3**, δ 38.0 and 29.0. The lower field resonances are attributed to the B–Me units, and the high-field resonances are ascribed to the B–N(R)–B bridge units.[7,42] The ^1H NMR spectrum for **2** shows resonances at δ 2.87, 2.78, and 0.5 in area ratios 1:2:2. These are assigned to borazine ring nitrogen methyl groups in position 3 and in positions 1 and 5 and to boron methyl groups in positions 2 and 4, respectively. The ^1H NMR spectrum for **3** displays resonances at δ 2.90, 2.85, 2.78, and 0.51 in area ratios 2:4:1:4. These are identified with borazine ring nitrogen methyl groups in position 3 and in positions 1 and 5, to the bridge N–CH_3 group, and to the boron methyl group in positions 2 and 4, respectively. These data may be compared with ^{11}B and ^1H NMR data for 1,2,3,4,5-pentamethyl-6-chloroborazine (^{11}B δ 37.0, 30.5 (area 2:1); ^1H, δ 2.92, 2.89, 0.5 (area 2:1:2)) and for 1,2,3,4,5-pentamethyl-6-aminoborazine (^{11}B δ 36.3, 26.2 (area 2:1); ^1H δ 2.77, 2.55, 1.93 (br), 0.47 (area (1.5:3:1:3)). As expected, the substitution of the chloro group by π-donating NH and NMe groups influences the proton shifts for the ortho-ring NMe groups.

Since boron–sulfur bonds are relatively reactive, we were interested in constructing polyborazinyl sulfides as potential ceramic precursors. To model these materials, the reaction of 1,2,3,4,5-pentamethyl-6-chloroborazine with Li_2S was examined as shown in eq 2. The model compound, bis(1,2,3,4,5-pentamethylborazinyl) sulfide, **4**, was obtained in good yield.[43] Compound **4** displays a parent ion in its mass spectrum, and its infrared spectrum shows N–CH_3, B–CH_3, and B–N ring bands expected for a pentamethylborazine derivative. The ^{11}B NMR spectrum shows a single broad resonance centered at δ 36. The resonance for the sulfur-bonded boron atoms, which might be expected to appear in the region δ 35–30, was not resolved. The ^1H NMR spectrum displays three resonances, δ 3.11, 2.69, and 0.43, in area ratios 2:1:2. The order of appearance of the NMe groups, position 1 and 5 at lower field than position 3, resembles the pattern displayed by 1,2,3,4,5-pentamethyl-6-chloroborazine rather than the order displayed by **2** and **3**.



(2)

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During the course of this study, it was noted that **3** and the respective polyborazinyl sulfide polymer (vide infra) were particularly moisture sensitive. Consequently, the stoichiometric hydrolysis of **4** in THF was examined. Indeed, the known compound,[44] bis(1,2,3,4,5-pentamethylborazinyl) oxide, **5**, was isolated as a colorless crystalline solid. The compound shows a parent ion in its mass spectrum, and the infrared spectrum is in good agreement with that reported earlier by Wagner and Bradford.[18] The ^{11}B NMR spectrum displays two resonances centered at δ 37 and 24; the higher field resonance may be assigned to the B–O–B boron atoms. The ^1H NMR spectrum gave resonances at δ 2.79, 2.77, and 0.49 in an area ratio 2:1:2.

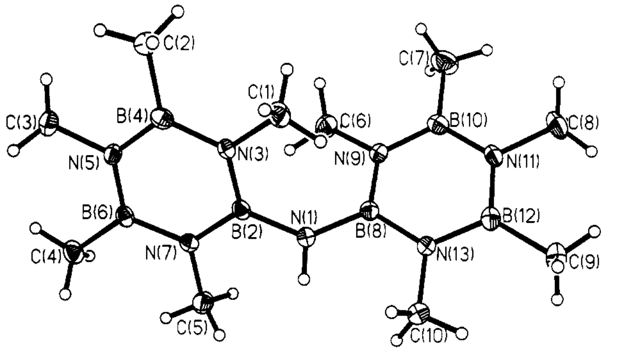

Figure 1. Molecular structure and atom-labeling scheme for $[Me_3N_3B_3(Me_2)]_2NH$ **2** (25% thermal ellipsoids).

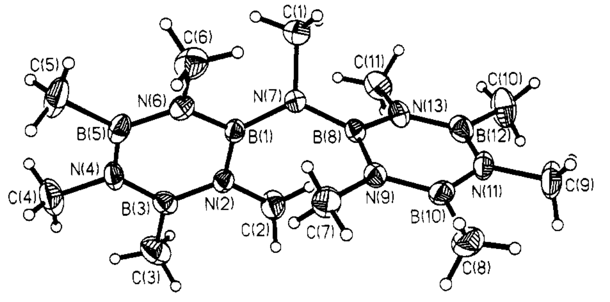

Figure 2. Molecular structure and atom-labeling scheme for $[Me_3N_3B_3(Me_2)]_2NMe$ **3** (25% thermal ellipsoids).

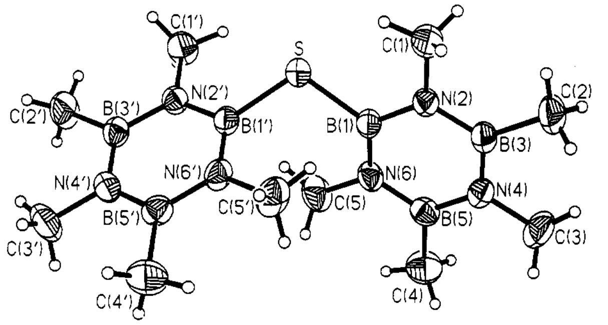

Figure 3. Molecular structure and atom-labeling scheme for $[Me_3N_3B_3(Me_2)]_2S$ **4** (50% thermal ellipsoids).

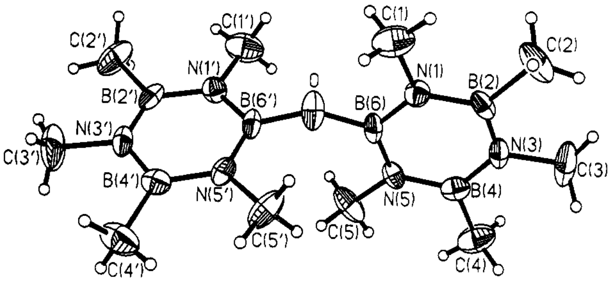

Figure 4. Molecular structure and atom-labeling scheme for $[Me_3N_3B_3(Me_2)]_2O$ **5** (25% thermal ellipsoids).

Molecular Structures of Metal Compounds. Since the structural features of **2**–**5** were of general interest and few molecular structure determinations on borazines have been reported, the structures of the compounds were analyzed by single-crystal X-ray diffraction techniques. Views of the molecules are provided in Figures 1–4, and selected bond distances and angles are summarized in

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[41] See ref 7 and references therein. Data for **2**–**5** are summarized in the supplementary material.

[42] (a) Nöth, H.; Wrackmeyer, B. Nuclear Magnetic Resonance Spectroscopy of Boron Compounds. In the series *NMR Basic Principles and Progress*; Springer-Verlag: Berlin, 1978; Vol. 14. (b) Nöth, H.; Rattay, W. *J. Organomet. Chem.* **1986**, *312*, 139.

[43] Syntheses that employed H_2S or $(Me_3Si)_2S$ as the sulfide source gave much lower yields of **4**.

[44] Wagner, R. I.; Bradford, J. L. *Inorg. Chem.* **1962**, *1*, 99.

Table VI. Selected Bond Distances (Å) and Angles (deg) for 2–5

	Compound 2		
N(1)–B(2)	1.447 (5)	N(9)–B(8)	1.439 (4)
N(1)–B(8)	1.442 (5)	N(9)–B(10)	1.425 (6)
N(3)–B(2)	1.448 (6)	N(11)–B(10)	1.440 (5)
N(3)–B(4)	1.435 (5)	N(11)–B(12)	1.438 (4)
N(5)–B(4)	1.437 (6)	N(13)–B(8)	1.441 (5)
N(5)–B(6)	1.436 (6)	N(13)–B(12)	1.437 (5)
N(7)–B(6)	1.442 (5)	B–CH_3 (av)	1.580
N(7)–B(2)	1.441 (6)	N–CH_3 (av)	1.476
B(2)–N(1)–B(8)	135.1 (3)		
	Compound 3		
N(7)–B(1)	1.459 (5)	N(9)–B(8)	1.423 (6)
N(7)–B(8)	1.463 (6)	N(9)–B(10)	1.435 (7)
N(2)–B(1)	1.430 (6)	N(11)–B(10)	1.439 (6)
N(2)–B(3)	1.425 (5)	N(11)–B(12)	1.435 (8)
N(4)–B(3)	1.441 (7)	N(13)–B(12)	1.414 (7)
N(4)–B(5)	1.421 (7)	N(13)–B(8)	1.443 (5)
N(6)–B(5)	1.428 (5)	N(7)–C(1)	1.485 (7)
N(6)–B(1)	1.433 (6)	B–CH_3 (av)	1.586
B(1)–N(7)–B(8)	128.2 (4)	N–CH_3 (av)	1.479
B(1)–N(7)–C(1)	117.3 (4)		
B(8)–N(7)–C(1)	114.5 (3)		
	Compound 4		
S–B(1)	1.852 (2)	N(6)–B(5)	1.445 (4)
N(2)–B(1)	1.427 (3)	N(6)–B(1)	1.426 (4)
N(2)–B(3)	1.435 (4)	B–CH_3 (av)	1.584
N(4)–B(3)	1.435 (1)	N–CH_3 (av)	1.476
N(4)–B(5)	1.433 (4)		
B(1)–S–B(1′)	110.9 (2)		
	Compound 5		
O–B(6)	1.369 (7)	N(5)–B(4)	1.418 (11)
N(1)–B(6)	1.392 (9)	N(5)–B(6)	1.439 (9)
N(1)–B(2)	1.414 (9)	B–CH_3 (av)	1.582
N(3)–B(2)	1.420 (9)	N–CH_3 (av)	1.473
N(3)–B(4)	1.426 (10)		
B(6)–O–B(6′)	151.8 (9)		

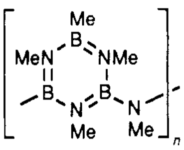
Table VI. The structures are related, with each displaying a pair of planar 1,2,3,4,5-pentamethylborazine rings linked through ring boron atoms to a central group, NH or NMe, or a sulfur or oxygen atom.

In the bisborazinylamines, **2** and **3**, the bridging nitrogen atoms N(1) and N(7), respectively, have a trigonal planar geometry, and the borazine rings are twisted with respect to each other: **2**, 58.0°; **3**, 87.5°. The greater twist in **3** mirrors greater steric interactions about the amino nitrogen atom between two pentamethylborazine substituents and a methyl group compared to a hydrogen atom. Further, the B(1)–N(7)–B(8) angle, 128.2 (4)°, in **3** is more compressed than the corresponding angle in **2**, B(2)–N(1)–B(8) 135.1 (3)°. The B–N bond distances involving the bridging nitrogen atoms, **2** 1.442 (5) and 1.447 (5) Å, **3** 1.459 (5) and 1.463 (6) Å, are identical within experimental error to the B–N distances in $B(NMe_2)_3$ (1.431 (12) Å)[45] and $(Me_2NBNH)_3$[46] (1.429 Å (exo B–NMe_2)) and considerably shorter than the B–N distance in $H_3N{\cdot}BH_3$ (1.56 ± 0.05 Å)[47] and the B–N(amino) distance in monoaminoborazine $[(HN)_3(HB)_2BNH_2]$ (1.498 (8) Å).[48] The bond distances and planar nitrogen geometries suggest that there is some degree of π interaction between the bridging exo nitrogen atom and the borazine ring boron atom in both **2** and **3**. The average B–N distances in the borazine rings in **2**, (1.438 Å) and in **3** (1.431 Å) are identical within experimental error, and they can be compared to average distances in $(HBNH)_3$[49] (1.436 (2) Å), $[(HN)_3(HB)_2BNH_2]$[48] (1.418 (4) Å), and $(Me_2NBNH)_3$[46] (1.433 Å). Although the B–N distances in each ring vary around the average distances in **2** and **3**, the variations are less than 3 times the individual standard deviations in bond distances. The average exo B–CH_3 and N–CH_3 distances in **2** (1.580 and 1.476 Å) and in **3** (1.586 and 1.479 Å) are identical.

The molecular structures of **4** and **5** are comparable, and the rings in each structure are related by a 2-fold rotation axis. The borazine rings are planar, and as expected, the B(6)–O–B(6′) angle, 151.8 (9)°, is considerably more open than the B(1)–S–B(1′) angle, 110.9°. In addition, the relative twist of the borazine ring planes in **5**, 96.2°, is much greater than in **4**, 69.7°. These observations are consistent with much larger steric interactions between adjacent ortho-methyl groups in the borazine rings of **5**. The O–B(6) bond distance in **5**, 1.369 (7) Å, is normal, and it falls in the middle of a broad range of B–O bond distances in three-coordinate boron–oxygen compounds.[50,51] The S–B(1) bond distance in **4**, 1.851 (2) Å, is also normal, and it can be compared with distances in $[(MeS)_2B]_3N$ (1.807 Å) and in $(tmpBS)_2$ (1.858 (2) Å).[52] It is interesting to note that the average ring B–N bond distance (1.433 Å) in **4** is identical with those in **2** and **3**, but the average distance in **5** (1.412 Å) is significantly shorter. The average B–CH_3 and N–CH_3 distances in **4** and **5** are comparable to those for **2** and **3**.

Preceramic Polymers: Synthesis. Since oligomerization of 2,4,6-trichloroborazine with hexamethyl- and heptamethyldisilazane[21–24] led to the formation of organic-solvent-insoluble polymers, it was reasoned that additional solubility might be gained by utilizing a borazine monomer that contained several organic substituents. In order not to severely reduce potential ceramic yields, two monomers with methyl substituent groups were selected for study: 1,2,3,5-tetramethyl-4,6-dichloroborazine and 1,3,5-trimethyl-2,4,6-trichloroborazine.

Combination of 1,2,3,5-tetramethyl-4,6-dichloroborazine and $(Me_3Si)_2NMe$ in chlorobenzene gave a soluble "two-point" oligomer, **6**, whose main repeating unit is schematically represented below. Vacuum evaporation of the solvent left a white solid that retained some solvent, as indicated by variable elemental analyses as well as by the presence of solvent in off gases removed from the solid during pyrolysis. The ^{11}B NMR spectrum of **6** dissolved in $CDCl_3$ showed a single broad resonance centered at δ 35; the expected two inequivalent boron environments were not resolved. The ^1H NMR spectrum showed four broadened resonances: δ 2.81 (N–Me ring), 2.73 (N–Me ring), 2.5 (N–Me bridge), and 0.46 (B–Me ring). This oligomer is closely related to a material reported previously by Meller and Füllgrabe[24] that was obtained from the combination of 1,2,3,5-tetramethyl-4,6-dichloroborazine



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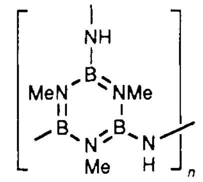

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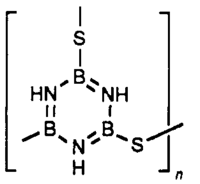
and hexamethyldisilazane. On the basis of mass spectrometric data, Meller proposed that their material contained four borazine rings cross-linked in a cyclic structure. Although the structure and oligomer number for **6** is not fully elucidated,[53] the oligomer represents a potential soluble, processable preceramic reagent if its pyrolysis chemistry provides clean samples of boron nitride.

Reaction of 1,3,5-trimethyl-2,4,6-trichloroborazine with hexamethyldisilazane in Et_2O over several hours results in a gel **7**, which occludes all of the solvent. Attempts to obtain spectroscopic data on the growing oligomer prior to gelation were uninformative.[53] Efforts to redissolve the gel in an organic solvent before or after vacuum evaporation of the reaction medium (Et_2O and Me_3SiCl) were unsuccessful, and this behavior severely limits this material in solution coating applications.

Anticipating that a weakly bonded bridging group might help organize borazine rings in a polymer yet be readily removed by appropriate chemical or thermal reactions, an effort was made to prepare an oligomer with a repeating unit, as represented in **8**.[54] Combination of Li_2S and 2,4,6-dichloroborazine in THF produces an initially soluble oligomer; however, after vacuum evaporation of the solvent, the solubility of the oligomer is greatly reduced. This suggests that oligomerization reactions proceed as the solution is concentrated. The solid oligomer tenaciously retains LiCl formed in the synthesis. The majority of this is washed out of the oligomer by repeated extractions with dry THF;[55] however, it has proved difficult to remove the last traces that are likely trapped in the nanopore structure of the dried gel.[56] The oligomer, **8**, is very moisture sensitive, and it must be protected by an inert atmosphere in all handling procedures.



8

Preceramic Polymers: Pyrolysis. The pyrolysis chemistry of the three preceramic materials, **6**–**8**, was studied first by TGA under argon and nitrogen and then by bulk pyrolysis in a tube furnace. The TGA curves for each material are similar. A steep weight loss (20–25%) occurs over the first 200 °C, and a more gradual weight loss (20–35%) occurs between 200 and 800 °C. The sulfur-bridged polymer shows no weight loss above ~550 °C. These results may be compared with the results of our earlier studies of the pyrolysis of carbon-free polymers (Scheme I) that showed that the majority of the gas-evolution chemistry was complete below 400 °C.[21–23,39]

The pyrolysis chemistry of **8** is the most complicated, but it provides better quality h-BN than pyrolysis of **6** or **7**. The volatiles from bulk sample pyrolysis in vacuo were collected in several temperature ranges and identified by mass spectrometry and infrared spectroscopy. The compounds identified included THF, Et_3B, and H_2S (20–100 °C), H_2S, higher sulfanes, C_2H_4, and OCS (100–200 °C), and H_2S, C_2H_4, and higher sulfanes (200–400 °C). More than 80% of the total was H_2S. Bulk pyrolyses were performed with special care since the small amounts of residual LiCl in the polymer degrade quartz pyrolysis tubes at high temperature. The polymer **8** was most efficiently pyrolyzed at 1000 °C under a mixture of NH_3 and N_2. The remaining light gray solid typically retained small amounts of carbon and traces of LiCl identified by Auger or EDS analysis. Residual sulfur was not detected by these methods. The light gray solid was then washed with water to remove any traces of LiCl and then air dried. Longer heating periods at 1000 °C in NH_3/N_2 remove the discoloration caused by residual carbon. The ceramic product was recovered in 27% ceramic yield, corresponding to 98% chemical yield. The ceramic product formed displays infrared adsorptions (1385 and 783 cm^{-1}) and X-ray reflections (d = 3.38, 2,30, and 2.17) expected for h-BN.[3]

Due to the high carbon content in **6** and **7**, their pyrolysis chemistry was examined under a greater variety of conditions. The optimum scheme for pyrolysis of **6** and **7** employs NH_3 and then N_2 for 12 h at 1200 °C each. A gray–black and a white solid are formed, respectively. The product from **6** contains significant carbon impurity (~5% based on Auger and elemental analyses), while the product from **7** contains only trace impurities (based on Auger and EDS analyses). The bulk yields of these products are relatively low (**6** ~ 25%, **7** ~ 40%) compared to the yields obtained from other poly(borazinylamine) precursors that contain a minimum of organic residues.[21–23,38] The majority of the carbon is removed by brief pyrolysis of the ceramic products in air at 700 °C. X-ray powder diffraction patterns for the ceramic products before and after air treatment are identical, and they show lines at $d \cong 3.4$ (002), 2.2 (100, 101), and 1.7 (004). Infrared spectra are similar to spectra obtained from commercial samples of h-BN. Transmission electron micrographs from these powders clearly show the expected lattice fringes (d = 3.3 Å) on individual particles.

Conclusion

The objectives of this study were to model the early stages of the oligomerization reactions between disilazanes and trichloroborazine that have been shown to form useful preceramic polymers for h-BN[21–23,38,56] and to explore reactions that might produce more organic-solvent-soluble poly(borazinylamines). In the first case, we have isolated molecular model bisborazinylamine compounds, and these have been fully characterized. Further, this chemistry has suggested synthetic approaches to isolate higher molecular weight fragments of the oligomers. Work aimed at accomplishing this task is underway.

With regard to the second objective, we find that the sulfide preceramic oligomer **8**, as anticipated, provides relatively low overall ceramic yields due to the required loss of the heavy sulfide bridging atoms. Nonetheless, the pyrolytic conversions to h-BN are complete, no sulfur is

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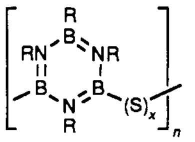
(53) Initial attempts to determine the average molecular weights for **6** and **7** by gel permeation chromatography indicate that ring condensation kinetics are initially relatively rapid and then slow, but the green polymer continues to grow with time. Insolubility (**7**) and polymerization kinetics (**6**) have hindered progress on the molecular weight measurements; however, further studies are planned.

(54) Toeniskoetter, R. H.; Didchenko, R. Canadian Patent 685,580 **1964**. Reactions of Na_2S, Na_2S_2 and Na_2S_4 with B-chloroborazines are reported to give low molecular weight polymers of the general type



(55) During the extraction, a low molecular weight fraction is dissolved and lost with the LiCl. Attempts to characterize the soluble oligomer fraction were unsuccessful. Elemental analysis of the insoluble fraction varied with the small amount of residual LiCl.

(56) Borazine oligomers that produce gels that include significant quantities of solvent may be dried, and the remaining solids typically have high surface areas and nanometer-sized pores. Characterization of some of these materials has appeared: Lindquist, D. A.; Borek, T. T.; Kramer, S. J.; Narula, C. K.; Johnston, G.; Schaeffer, R.; Smith, D. M.; Paine, R. T. *J. Am. Ceram. Soc.* **1990**, *73*, 1.

retained in the ceramic, the ceramic is nicely crystalline, and the formation of the crystalline phase occurs at a lower temperature than normally observed with other poly(borazinylamine) oligomers explored in our work. The crystallization behavior may result from the small LiCl impurity. Unfortunately, the organic solvent solubility of **8** is not well behaved; however, this material may find some special applications that utilize the lower processing temperature.

Oligomer **7**, with appropriate care, is converted to good quality h-BN with fair ceramic yield; however, the insoluble character of the oligomer limits its use for solution-based coating applications. Unfortunately, the one oligomer, **6**, with useful solubility properties is burdened by thermal chemistry that leaves carbon residues in the product. For applications that are not influenced by small amounts of carbon (5% or less), this material will be useful. Further chemical modifications of poly(borazinylamines) directed at achieving the design objectives for processible BN preceramics[3] are in progress.

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Registry No. **2**, 127232-88-6; **3**, 21348-06-1; **4**, 127232-89-7; **5**, 15270-88-9; **6** (homopolymer), 127232-90-0; **7** (homopolymer), 127232-91-1; **8** (homopolymer), 127232-92-2; boron nitride, 10043-11-5.

Supplementary Material Available: Table S-1, listing additional crystallographic data, Table S-2, listing anisotropic thermal parameters, Table S-3, listing hydrogen atom positional parameters for compounds **2**–**5**, Table S-4, listing bond distances and angles, and Table S-6 listing infrared spectra for compounds **2**-**6** (24 pages); Table S-5, listing structure factor tables for compounds **2**–**5** (37 pages). Ordering information is given on any current masthead page.

Synthesis of Boron Nitride Ceramics from Oligomeric Precursors Derived from 2-(Dimethylamino)-4,6-dichloroborazine

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2-(Dimethylamino)-4,6-dichloroborazine has been combined with hexamethyldisilazane and heptamethyldisilazane, and the chemical and thermal processing of the resulting oligomers has been examined. Pyrolysis of the oligomers under selected conditions results in formation of turbostratic BN that has been characterized by powder X-ray diffraction and transmission electron microscopy techniques. The oxidation stability of the boron nitride prepared in this fashion has also been examined.

Introduction

Most ceramic materials, such as boron nitride, have been commercially prepared for years by using classical high-temperature reaction techniques and simple, inexpensive reagents. Unfortunately, this preparative approach is rather inflexible, and it is difficult to obtain nonpowder forms (e.g., films and fibers) or systematically alter compositions and properties of ceramic products obtained in this fashion. It has been suggested that preceramic polymer reagents could offer useful alternatives for advanced ceramic syntheses and processing,[1] and in the past five years attempts have been made to develop preceramic polymers and to explore their conversion to solid-state materials.[1,2] In particular, several useful preceramic polymer routes have been devised for boron nitride.[3-7] With several of these chemical systems, it is now possible to produce amorphous and crystalline powders, fibers, and films of pure BN. Expanding upon our previous reports on poly(borazinylamine) precursors,[4] we report here the

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