Table II. Fractional Coordinates[a] and Isotropic Thermal Parameters[b] for $[Sn(N(SiMe_3)_2)(\mu\text{-}O^tBu)]_2$

	x	y	z	$10B_{iso}$, Å^2
Sn(1)	4108.3 (4)	4187.3 (3)	9040.4 (3)	13
N(2)	3319 (4)	4946 (3)	7483 (4)	14
Si(3)	2355 (2)	4177 (1)	6539 (1)	16
C(4)	3227 (7)	3034 (5)	6412 (7)	24
C(5)	781 (8)	3922 (6)	7148 (7)	30
C(6)	1931 (8)	4577 (6)	4960 (6)	26
Si(7)	3367 (2)	6128 (1)	7121 (1)	15
C(8)	4224 (7)	6881 (5)	8332 (6)	21
C(9)	4255 (7)	6322 (5)	5804 (6)	22
C(10)	1678 (7)	6635 (6)	6778 (7)	26
O(11)	6021 (4)	4826 (3)	9517 (3)	14
C(12)	7186 (6)	4692 (4)	8936 (5)	17
C(13)	6808 (7)	4062 (7)	7854 (7)	34
C(14)	8214 (8)	4219 (7)	9810 (7)	36
C(15)	7647 (8)	5634 (6)	8536 (8)	36
H(1)	340 (7)	263 (5)	715 (7)	43 (7)
H(2)	265 (9)	260 (7)	587 (7)	62 (7)
H(3)	396 (8)	310 (5)	606 (7)	39 (7)
H(4)	46 (9)	445 (7)	733 (8)	55 (6)
H(5)	44 (10)	353 (8)	664 (9)	75 (6)
H(6)	109 (9)	357 (7)	791 (9)	68 (6)
H(7)	151 (8)	514 (7)	489 (7)	54 (6)
H(8)	276 (8)	464 (5)	461 (6)	34 (7)
H(9)	145 (9)	420 (6)	453 (7)	50 (6)
H(10)	510 (10)	673 (7)	849 (8)	67 (6)
H(11)	407 (8)	749 (7)	810 (7)	48 (7)
H(12)	385 (5)	690 (4)	902 (5)	15 (7)
H(13)	504 (10)	615 (7)	594 (8)	58 (7)
H(14)	374 (10)	615 (7)	511 (9)	70 (7)
H(15)	432 (7)	703 (6)	568 (6)	46 (7)
H(16)	177 (12)	721 (9)	661 (10)	99 (6)
H(17)	103 (11)	635 (9)	609 (10)	94 (6)
H(18)	111 (10)	658 (7)	724 (9)	70 (6)
H(19)	602 (10)	428 (7)	727 (8)	65 (6)
H(20)	760 (9)	403 (5)	757 (7)	48 (7)
H(21)	630 (10)	350 (7)	799 (8)	66 (6)
H(22)	801 (7)	354 (5)	998 (6)	32 (7)
H(23)	849 (10)	463 (7)	1046 (9)	75 (6)
H(24)	891 (8)	424 (5)	951 (7)	42 (6)
H(25)	842 (7)	556 (4)	812 (6)	26 (7)
H(26)	788 (13)	606 (9)	920 (11)	109 (5)
H(27)	702 (12)	588 (8)	811 (10)	87 (5)

[a] Fractional coordinates are ×10^4 for non-hydrogen atoms and ×10^3 for hydrogen atoms. B_{iso} values are ×10. [b] Isotropic values for those atoms refined anisotropically are calculated with use of the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

Table III. Selected Bond Distances (Å) and Angles (deg) for $[Sn(N(SiMe_3)_2)(\mu\text{-}O^tBu)]_2$

Sn(1)–Sn(1)′	3.5102 (9)	Si(7)–N(2)	1.736 (5)
Sn(1)–O(11)	2.168 (4)	Si(7)–C(8)	1.862 (7)
Sn(1)–O(11)′	2.173 (4)	Si(7)–C(9)	1.877 (7)
Sn(1)–N(2)	2.128 (5)	Si(7)–C(10)	1.874 (7)
Si(3)–N(2)	1.740 (5)	O(11)–C(12)	1.462 (7)
Si(3)–C(4)	1.876 (7)	C(12)–C(13)	1.523 (10)
Si(3)–C(5)	1.886 (7)	C(12)–C(14)	1.502 (10)
Si(3)–C(6)	1.868 (7)	C(12)–C(15)	1.515 (10)
O(11)–Sn(1)–O(11)′	72.10 (15)	C(9)–Si(7)–C(10)	108.8 (4)
O(11)–Sn(1)N(2)	102.67 (17)	Sn(1)–O(11)–Sn(1)′	107.90 (15)
O(11)′–Sn(1)–N(2)	103.69 (17)	Sn(1)–O(11)–C(12)	127.6 (3)
N(2)–Si(3)–C(4)	110.8 (3)	Sn(1)′–O(11)–C(12)	124.4 (3)
N(2)–Si(3)–C(5)	110.1 (3)	Sn(1)–N(2)–Si(3)	107.82 (25)
N(2)–Si(3)–C(6)	115.5 (3)	Sn(1)–N(2)–Si(7)	131.91 (26)
C(4)–Si(3)–C(5)	107.9 (4)	Si(3)–N(2)–Si(7)	119.95 (27)
C(4)–Si(3)–C(6)	103.9 (4)	O(11)–C(12)–C(13)	107.8 (5)
C(5)–Si(3)–C(6)	108.2 (4)	O(11)–C(12)–C(14)	108.1 (5)
N(2)–Si(7)–C(8)	114.33 (28)	O(11)–C(12)–C(15)	109.4 (5)
N(2)–Si(7)–C(9)	111.3 (3)	C(13)–C(12)–C(14)	109.9 (6)
N(2)–Si(7)–C(10)	111.5 (3)	C(13)–C(12)–C(15)	109.7 (6)
C(8)–Si(7)–C(9)	105.4 (3)	C(14)–C(12)–C(15)	111.8 (7)
C(8)–Si(7)–C(10)	105.0 (4)		

of the Sn atom. The results of the structure determination are given in Tables II and III and Figures 1 and 2. Refined C–H distances range from 0.82 (11) to 1.03 (12) Å.

Acknowledgment. This work was supported by the Department of Energy. We thank Scott Horn for skilled technical assistance.

Supplementary Material Available: Full crystallographic details (Table S1) and anisotropic thermal parameters (Table S2) (2 pages); observed and calculated structure factors (Table S3) (5 pages). Ordering information is given on any current masthead page.

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Synthesis of Boron Nitride Ceramics from 2,4,6-Triaminoborazine

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The hexagonal crystalline modification of boron nitride is often prepared by pyrolysis of simple starting materials, such as boric acid and urea, or by plasma and chemical vapor deposition techniques from mixtures of ammonia and diborane(6) or boron trihalides.[1] Even though these syntheses are useful, Wynne and Rice[2] have pointed out that increasingly sophisticated applications for boron nitride demand the development of new approaches for forming and processing this ceramic. In response, several groups have sought molecular- and polymer-based syntheses that may offer advantages for forming BN fibers, films, and composites.[3] For example, Rice and co-workers[4] and Paciorek and co-workers[5] have described the pyrolysis chemistry of several substituted borazenes, $[RNBR']_3$. At modest temperatures, several borazenes were found to oligomerize, and at higher pyrolysis temperatures, ceramic products were produced. Sneddon and co-workers[6] have observed that, in the presence of ammonia, conversion of commercial $Me_2S{\cdot}B(H)Br_2$, *B*-alkenylpentaborane, and *B*-alkenylborazene to polymeric ceramic precursors occurs. Pyrolysis of these precursors provide h-BN. Further, Rees and Seyferth[7] have found that oligomeric $[B_{10}H_{12}(\text{diamine})]_n$ reagents produce h-BN when pyrolyzed in NH_3. Indeed, several of these precursors may be used to produce fibers and films.[5-7]

In our group, we have previously described cross-linking reactions of *B*-chloroborazenes with hexamethyldisilazane.[8] Subsequent pyrolyses of the oligomers produce pure h-BN or carbon-contaminated boron nitride, depending upon the monomer employed and the pyrolysis conditions. We report here alternative deamination chemistry of a readily available borazene, $[HNB(NMe_2)]_3$, and conversion of the resulting solid polymers to h-BN.

Experimental Section

General Information. Standard inert-atmosphere techniques were used for the preparation and manipulation of all reagents. Solvents were carefully dried with appropriate drying agents and distilled under dry nitrogen. Infrared spectra were recorded on a Nicolet FT-IR Model 6000 spectrometer, and NMR spectra were recorded on Varian FT-80A and JEOL GSX-400 spectrometers. Spectral standards were $(CH_3)_4Si$ (^1H) and $BF_3{\cdot}O(C_2H_5)_2$ (^{11}B). $[(CH_3)_2NBNH]_3$ was prepared as described in the literature.[9] Thermal gravimetric analyses were performed on a Du Pont Model 1090 TGA instrument. EDS analyses were performed by using a Tracor Northern Model 5500 system with a high take off detector. The sample tilt was 0° during X-ray analysis. The transmission electron microscope used was a JEOL JEM-2000 FX instrument operated at 200 kV. The point resolution was ~0.3 mm. The powder surface area and density were determined by the BET method and helium pycnometry, respectively.

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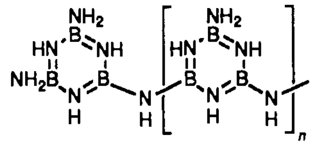
Synthesis of Boron Nitride. A sample (9.25 g, 43.5 mmol) of 2,4,6-tris(dimethylamino)borazene was dissolved in 50 mL of dry toluene, and the reaction mixture was cooled to −78 °C. Excess dry ammonia (~10 mL) was condensed into the cold solution, and the mixture was stirred for 5 h. The resulting mixture was slowly warmed to 25 °C, $(CH_3)_2NH$ and excess NH_3 were allowed to escape from the reaction vessel, and a white solid was retained with the toluene. Infrared spectrum (KBr, cm^{-1}): 3479 (m), 3408 (s), 1604 (s), 1485 (vs), 1429 (vs), 1365 (vs), 1189 (m), 1133 (m), 696 (s), 647 (m). The reaction mixture was then refluxed under dry nitrogen for 5 h. The mixture was cooled and filtered, and the white, insoluble residue was washed with 10 mL of toluene. Yield: 3.55 g. Infrared spectrum (KBr, cm^{-1}): 3436 (br, s), 1457 (br, s), 1104 (vs), 703 (vs), 618 (s).

A sample of the white residue (3.0 g) was pyrolyzed at 900 °C as the volatile byproducts were continuously vacuum-evaporated. The volatiles were collected at −196 °C and identified as NH_3 by infrared spectroscopy. The remaining white residue was transferred to a quartz pyrolysis tube lined with tungsten foil, and the tube was heated at 1200 °C for 12 h in Ar. The resulting white powder (1.25 g) was characterized. Infrared spectrum (KBr, cm^{-1}): 3429 (w), 1435 (b, vs), 801 (s). X-ray powder diffraction (*d*): 3.39, 2.33, 2.15, 1.77.

Results and Discussion

Gerrard and co-workers,[9] Toeniskoetter and Hall,[10] and Clément and Proux[11] have suggested that several *B*-amino-*N*-organoborazenes, $[(H_2N)BNR]_3$, undergo deamination at modest temperatures with the subsequent formation of borazinylamines, e.g., $[(RN)_3(H_2NB)_2B]_2NH$. Further, it has been noted that at least one aminoborazene, $[(H_2N)BN(C_6H_5)]_3$, when pyrolyzed at 300–400 °C, gave an insoluble solid product that, on the basis of elemental analysis, was suggested to contain boron nitride.[10,12] Attempts to duplicate the pyrolysis chemistry, however, showed formation of significant amounts of carbon in the ceramic product.[5] Alternatively, Paciorek noted that *B*-amino-*N*-silylborazenes, $[(H_2N)BN(SiR_3)]_3$, produced carbon-free boron nitride upon pyrolysis. In the context of these preliminary results, it is appropriate to examine deamination reactions of other *B*-aminoborazenes as potential sources of h-BN. *B,B′,B″*-Triaminoborazene, $[(H_2N)BNH]_3$, represents one ideal carbon-free precursor. This compound has been suggested to result from aminolysis of $[(Et_2N)BNH]_3$,[9] $[(Me_2N)BNH]_3$,[13] and $[(BuS)BNH]_3$;[14] however, it has never been isolated or characterized. Instead, the aminolysis product apparently readily decomposes, leaving an insoluble polymeric product of indefinite composition.[13]

In the present study, addition of excess NH_3 to cold toluene solutions of $[(Me_2N)BNH]_3$ indeed produces a white solid (**1**) that is insoluble in common organic solvents. Infrared spectra of **1** show bands at 3479 and 3408 cm^{-1} that may be assigned to terminal N–H and NH_2 stretching modes, and vibrations corresponding to terminal dimethylamino groups are very weak.[15] Attempts to detect $[(H_2N)BNH]_3$ or other transient molecular (dimethylamino)aminoborazenes in solution by ^{11}B NMR spectroscopy were unsuccessful. The initial product may be a lightly cross-linked polyaminoborazene of the general type shown below; however, it is unlikely that **1** contains only this single simple structural unit.



Dimethylamine and excess NH_3 are vacuum-evaporated from the original reaction mixture, and the remaining slurry in toluene is heated at reflux under nitrogen. Additional NH_3 is evolved, and this is consistent with the appearance of further ring cross-linking reactions. A second white solid (**2**) is obtained that displays a single N–H vibration, 3436 cm^{-1}.[15]

The decomposition chemistry of **2** was initially examined by thermal gravimetric analysis (TGA). A gradual weight loss (~25%) is observed between 25 and 400 °C, and it is proposed that further deamination chemistry and borazene ring cross-linking occurs in this temperature region. In bulk pyrolyses, NH_3 is detected as the only volatile byproduct in this temperature region. In the temperature range 400–600 °C, an additional weight loss (~20%) occurs, and in the range 600–1100 °C, the weight loss is minimal (~5%). Since pyrolysis of another poly(borazinylamine) oligomer showed that only amorphous boron nitride is obtained at temperatures below 600 °C,[8] bulk samples of **2** were heated at 900 °C in vacuo. X-ray powder diffraction analysis of the resulting white solid (**3**) shows two broad lines, $d \sim 3.8$ and ~2.1, and the pattern resembles that reported previously for turbostratic BN prepared from boric acid and urea in a temperature range 500–950 °C.[16] Samples of **3** prepared at 900 °C and subsequently heated at 1200 °C show considerable sharpening of the powder X-ray diffraction lines. The *d* values[17] (Å), $d =$ 3.39 (002), 2.33 (100), 2.15 (101), and 1.77 (004), and relative intensities of the reflections agree closely with those reported in the literature for partially ordered, turbostratic BN.[16] Further sharpening of the diffraction pattern is achieved by heating samples in nitrogen at 1400 °C. The density of the material, estimated by helium pycnometry,[18] is 2.02 g cm^{-3}, and the surface area, estimated by the BET method,[18] is 3.27 m^2 g^{-1}.

The ceramic powder obtained at 1200 °C was also analyzed by transmission electron microscopy and energy-dispersive X-ray analysis. The latter shows no evidence for heavy atom ($Z > 10$) contamination except for small particles of tungsten that originate from the pyrolysis tube liner. The TEM analysis shows the formation of crystalline BN with well-defined, sharp lattice fringes.[19] The electron diffraction pattern is also consistent with

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the formation of crystalline BN.

Although, in its present form, the chemistry outlined here does not result in a fusible or soluble preceramic polymer, the results indicate that partially ordered hexagonal boron nitride powder can be readily obtained from the pyrolysis of a solid, insoluble poly(borazinylamine) precursor, **2**, that is easily formed from the well-known borazene monomer $[(Me_2N)BNH]_3$ and NH_3. The precise identity of the insoluble poly(borazinylamine) polymer was not elucidated in detail; however, observations made in TGA and bulk pyrolysis studies are consistent with the occurrence of a series of complex aminoborazine deamination cross-linking reactions, followed by borazene ring-opening, elimination–condensation processes of a type described earlier.[5,10] These observations suggest additional approaches for manipulating aminoborazene monomers, and extensions are being evaluated.

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Registry No. NH_3, 7664-41-7; BN, 10043-11-5; 2,4,6-tris(dimethylamino)borazine, 7360-02-3.

Supplementary Material Available: Figures showing a typical TGA plot and a powder X-ray diffraction pattern (2 pages). Ordering information is given on any current masthead page.

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(19) The TEM micrographs are similar to those reported previously in our work,[8] except that the particles are larger and the lattice fringes are more well-defined.

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Inelastic Neutron-Scattering Study of $K[HCo_6(CO)_{15}]$: Implications for Location of the Hydride

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The study of transition-metal hydride complexes by vibrational spectroscopy has been of considerable utility in elucidating details of hydrogen–metal interactions.[2,3] Inelastic neutron-scattering (INS) techniques have in this context often proved invaluable[4] in assigning modes involving the hydrogen atoms because of the high sensitivity of INS to hydrogen. While many such systems where hydrogen atoms bridge two or more metal atoms have served as models for hydrogen chemisorbed on surfaces,[2,4] a much more limited number of metal complexes[5-8] are known to contain interstitial hydrogen. These in turn may be good representations of interstitial hydrogen either inside or just below the surface of bulk metals. An example of the latter, subsurface hydrogen, has been observed in Pd.[9] In fact, some of these compounds involve metal atoms (Co,[5] Ru[6]) that do not readily form hydride phases in the bulk and therefore are of particular importance in the study of metal hydrides.

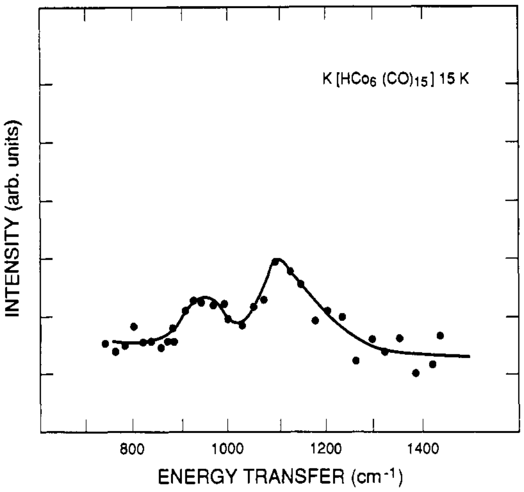

Figure 1. Neutron vibrational spectrum of the hydride in $K[HCo_6(CO)_{15}]$ obtained by subtraction of the spectrum of the deuterated form from that of the hydrogenated form. The line is drawn as a guide for the eye.

One such system is the ion $[HCo_6(CO_{15})]^-$, which is known from a single-crystal neutron diffraction study[5] to have a hydrogen atom located very nearly in the center of the Co_6 octahedron. One would therefore expect to observe a triply degenerate ν(M–H) mode, since the observed variation of metal–hydrogen distances is relatively small (i.e. 1.80 (2)–1.87 (2)Å). An INS study by Graham et al.[10] was indeed successful in assigning a single, relatively sharp band at 1056 cm^{-1} as ν(M–H). The compound used in the latter study used Cs$^+$ as the counterion, while the single crystal in the diffraction work contained $[(Ph_3P)_2N]^+$ instead.

Recently, Stanghellini and Longoni obtained IR vibrational spectra of several interstitial hydride clusters[11] including $K[HCo_6(CO)_{15}]$. They, however, assigned two bands, at 1086 and 949 cm^{-1}, respectively, to two ν(Co–H) modes. The experiments were performed at room temperature and at 100 K with the samples in Nujol mulls and, also, in alkali-metal halide disks. In the latter case, the spectra were found to change: repeated grinding and pressing of the sample in the alkali-metal halide disks caused the band at 949 cm^{-1} to virtually disappear whereas a rather weak line at ca. 1060 cm^{-1} increased considerably in intensity.[11] Changes were also observed in the CO deformation region with treatment of the alkali-metal halide disk samples.

The assignment of the two lines to ν(Co–H) was, however, unambiguous on account of the clearly observed isotope shift. We have, therefore, undertaken INS studies on the same compound $K[HCo_6(CO)_{15}]$ in an attempt to resolve the apparent discrepancy with the prior INS study by Graham et al.[10] The compound was prepared by the method described in ref 5. INS spectra were obtained for both the hydrogenated and deuterated compounds on the filter difference spectrometer (FDS)[12] at the Los Alamos Neutron Scattering Center. Since the neutron-scattering cross section for D is more than 1 order of magnitude less than that

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(1) (a) Los Alamos National Laboratory. (b) Universitá di Milano. (c) Universitá di Bologna.

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