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Synthesis of $LiBC_4N_4$, BC_3N_3, and Related C−N Compounds of Boron: New Precursors to Light Element Ceramics

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Abstract: The synthesis of a novel framework cyanide with composition $LiBC_4N_4$ (**1**) is described. X-ray powder diffraction as well as ^{7}Li, ^{11}B, and ^{13}C NMR of **1** reveal an ordered structure which consists of two interpenetrating diamond-like networks of BC_4 and LiN_4 tetrahedra linked by C−N bonds. The structure is simple cubic, symmetry $P4\bar{3}m$, $a = 5476(3)$ Å. In solution the presence of the $B(CN)_4$ anion has been established for the first time by spectroscopic methods. Molecular $B(CN)_3$ is isolated for the first time as a Lewis acid−base complex with bases such as NMe_3 and $SiMe_3CN$, and a single-crystal X-ray structure of $B(CN)_3NMe_3$ (**3**) has been obtained. The novel solid-state cyanide BC_3N_3 (**2**) is prepared from the thermal elimination of $NCSiMe_3$ from $B(CN)_3NCSiMe_3$ (**4**). In route to **4**, compounds $B(CN)_2(SMe)NCSiMe_3$ (**5**) and $B(CN)_2(SMe)$-NMe_3 (**6**) have also been isolated. A single-crystal X-ray structure of **6** reveals that the compound crystallizes in the monoclinic space group $P2_1/n$. The new crystalline solids **2** and **1** (isoelectronic to C) are promising precursors for high-pressure and high-temperature syntheses of novel phases with structures related to Si_3N_4, diamond, and graphite.

Introduction

Recent research on the development of new superhard materials has stimulated interest in the design and synthesis of first-row element (Li, Be, B, C, N, O) compounds that are isoelectronic to diamond or have compositions related to that of Si_3N_4.[1,2] Typical examples of such systems include metastable forms of planar (sp^2) and tetrahedral (sp^3) carbon nitride with C_3N_4 stoichiometry[3−5] and a phosphorus-substituted derivative with C_3N_3P composition.[6] The discovery of a related material with composition C_3N_3B and structure similar to that of the hypothetical β-C_3N_4 model is of interest because it is expected to be more stable and stronger than C_3N_4. A three-dimensional C_3N_3B structure would incorporate C in the tetrahedral sites, while sp^2-hybridized B replaces one-fourth of the trigonal N sites. There are several advantages to such an arrangement: (a) elimination of the destabilizing N−N lone pair interaction that exists in the hypothetical β-C_3N_4 model [7,8] and (b) an increase in cohesive energy because of the stronger B−C bonds. Furthermore, the development of the $LiBC_4N_4$ derivative is of particular interest because it is isoelectronic to carbon (i.e., four valence electrons per atom), and it might provide a unique synthetic route to new hard materials with diamond-like or graphite-like structures by high-pressure methods.

Our immediate objective is to develop pure and well-characterized materials with the desired elemental compositions C_3N_3B (**2**) and $LiBC_4N_4$ (**1**) by soft chemistry methods. The stoichiometric cyanides of boron, $B(CN)_3$ and $LiB(CN)_4$, present attractive targets since they are the molecular analogues of the extended stoichiometric solids C_3N_3B and $LiBC_4N_4$. The long-term goal is to use high pressure to transform these compounds into denser, stronger, and harder forms while maintaining their stoichiometry. In this study we present for the first time the synthesis of a novel solid-state cyanide material with composition C_3N_3B (**2**) and a crystalline derivative with the exact stoichiometry $LiBC_4N_4$ (**1**). These compounds are fundamentally interesting (they are typical examples of classical inorganic compounds with unique solid-state structures), but more importantly preliminary results indicated that they are also suitable as precursors for the proposed high-pressure studies.

Surprisingly, the existence of pure and crystalline $LiBC_4N_4$ (**1**) has not been established to date; previous attempts have only produced uncharacterized materials with a formula purportedly close to that of the desired product.[9] A molecular form of $B(CN)_3$ has also been known for a long time; however, the synthetic procedure is impractical and has not been reproduced. The reported preparation involved the reaction of AgCN with BCl_3 which was allowed to take place, unintentionally, over the course of 40 years. This experiment has not been since duplicated, to our knowledge.[10]

Results and Discussion

The synthetic methodology used for the synthesis of **1** utilizes a common reagent, $SiMe_3CN$, which undergoes metathesis with $LiBF_4$ to produce the desired composition at low temperatures in nonaqueous solvents (eq 1). The product is initially an

$$4SiMe_3CN + LiBF_4 \rightarrow LiBC_4N_4 + 4SiMe_3F \qquad (1)$$

amorphous brown solid that crystallizes upon heating at temperatures in excess of 250 °C. The amorphous and crystalline solid is readily purified by extraction with dry CH_3CN. The

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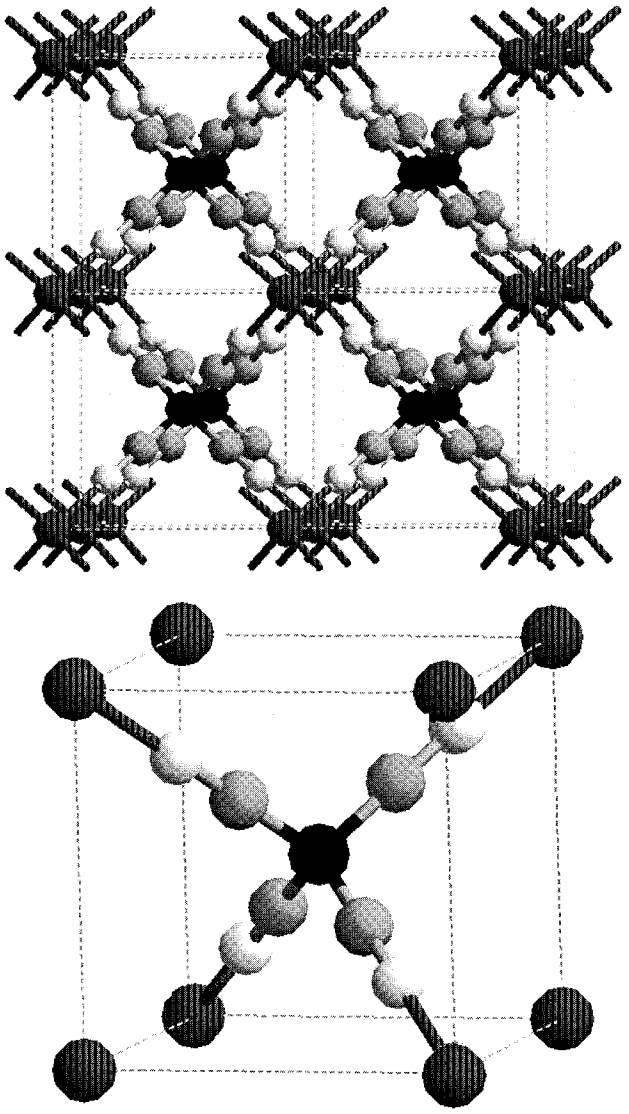

Figure 1. (Top) Structure of $LiBC_4N_4$ shown as interconnected LiN_4 and BC_4 tetrahedra. Black, gray, and white spheres are B, C, and N, respectively. Striped spheres with dangling bonds at the corners are the Li atoms. (Bottom) Unit cell of $LiBC_4N_4$.

pure material is a colorless solid, stable in air, and slightly soluble in polar organic solvents. Combustion analysis for C, H, and N is consistent with the proposed $LiBC_4N_4$ composition. The X-ray diffraction pattern revealed a simple cubic tetrahedral structure with a lattice parameter $a = 5.476(3)$ Å. Rietveld refinement indicated an ordered structure in which each Li is bonded to four N atoms and each B is bonded to four C atoms to form LiN_4 and BC_4 tetrahedra. These metal-centered tetrahedra are joined at the vertexes by C−N bonds to form two identical and interpenetrating networks (Figure 1). The observed and calculated diffraction patterns for this topology of $P4\bar{3}m$ symmetry are in good agreement. The C−N bond length was found to be 1.204(5) Å, which is within the range for metal cyanides.[11,12] The Li−N and B−C bond lengths are 1.982(5) and 1.555(4) Å, respectively. The structure is similar to that proposed for $LiGa(CN)_4$ ($a = 5.847$), in which LiN_4 and GaC_4 tetrahedra are also linked by C−N bonds.[11]

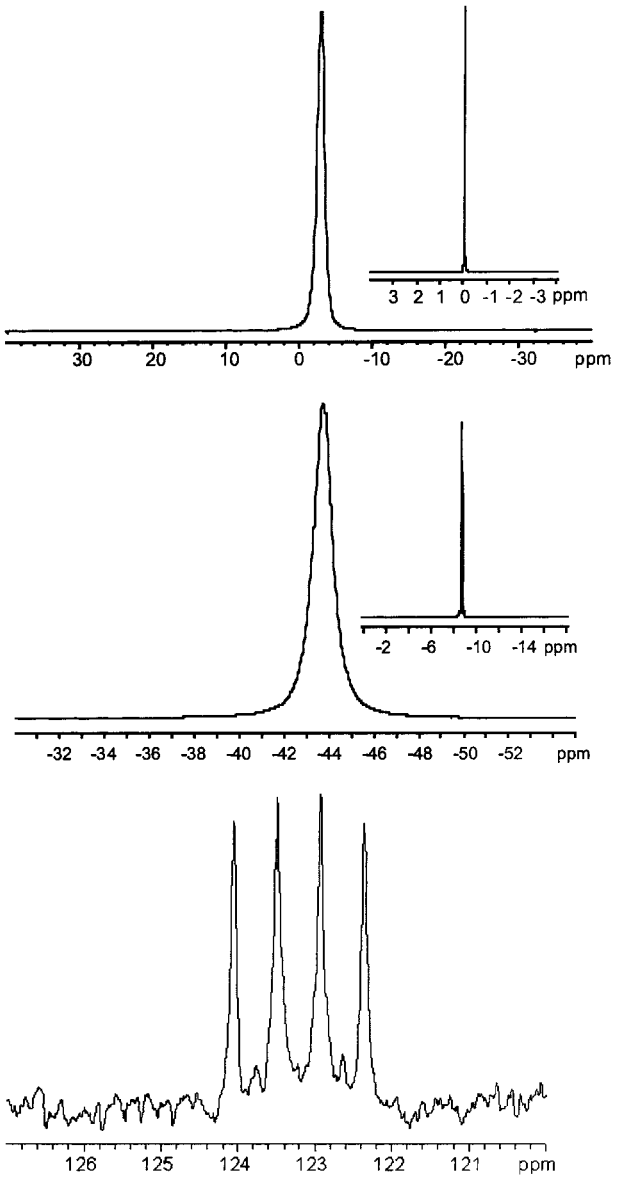

Figure 2. NMR spectra of $LiB(CN)_4$. (Top) ^{7}Li solid state, and solution (in the offset); (middle) ^{11}B solid state, and solution (in the offset); (bottom) ^{13}C solution spectra.

The infrared spectrum shows ν C≡N at 2270 cm^{-1} and a set of intense absorptions at 995−960, 530, and 400 cm^{-1} that are assigned to ν(^{10}B−C−^{11}B−C), ν(Li−N), and B−C (bending), respectively. The solid-state magic angle spinning (MAS) NMR spectra confirmed the presence of the CN ligands and revealed single resonances for both ^{11}B and ^{7}Li at δ −43 and δ −2.83, respectively, indicating single environments for these atoms in the solid state. The most plausible interpretation of the NMR and IR data (only B−C and Li−N absorptions) is that the B atom is in a single coordination environment in which it is bonded to only carbon, and the Li is in another environment in which it is bonded exclusively to nitrogen. These results are consistent with the ordered framework structure of LiN_4 and BC_4 tetrahedra found by X-ray diffraction.

The solution NMR spectra of $LiBC_4N_4$ (**1**) demonstrated for the first time the existence of the tetrahedral anion, $B(CN)_4^-$ with B−C bonds (Figure 2). The ^{13}C spectrum in CD_3CN

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Table 1. Crystal Data for $B(CN)_2{\cdot}(SMe)NMe_3$ (**6**) at −130 °C

space group: $P2_1/n$		mol wt = 196.06
a = 6.3488(1) Å	α = 90.00°	ρ_{calcd} = 1.216 g cm^{-1}
b = 10.7251(6) Å	β = 90.45°	μ_{calcd} = 0.292 mm^{-1}
c = 13.5604(8) Å	γ = 90.00°	size = 0.15 × 0.06 × 0.04 mm
V = 923.32(8) Å^3	Z = 4	GOF = 0.970

diffractometer: SMART CCD
radiation: Mo Kα = 0.17069 Å
monochromator: graphite crystal
scan: ω (0.90°/min)
θ range: 1.5−23.25°
reflns: 3863 total, 1315 independent, 826 observed
R_{int}: 0.0906
residuals:[a] R = 0.0589; wR = 0.01261
all data: R = 0.1127

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. w$R = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w(F_o^2)^2]^{1/2}$.

showed a single resonance at δ 123 which is split into 1:1:1:1 pattern due to coupling to ^{11}B ($S = 3/2$). The observed $^{13}C-^{11}B$ coupling constant (71 Hz) is typical of those found in NMR studies of classical boron alkyl compounds such as BMe_3 and $MeB(OMe)_2$.[13] Coupling of ^{13}C to ^7Li (also $S = 3/2$) is not observed in this study at 30−60 °C (the reported values of $^{13}C-^7Li$ are less than 15 Hz[13,14]). The solution ^{11}B and ^7Li NMR spectra are sharp single resonances at δ −8.5 and δ 0.112, respectively (Figure 2). The NMR data are consistent with the presence of only B−C bonds and support the presence of a the anion $B(CN)_4^-$ and the implication of a solvated cation Li $(NCMe)_x$ in solution.

The successful preparation of **1** encouraged us to develop a suitable synthetic method for the related $B(CN)_3$. Our initial attempts to synthesize $B(CN)_3$ involved metathetical exchange of NMe_2 in $B(NMe_2)_3$ by cyanide using $SiMe_3CN$ as the cyanide source. Partial displacement is readily obtained at 22 °C, and a mixture of the $B(CN)(NMe_2)_2$ and $B(CN)_2(NMe_2)$ was formed. However, complete CN substitution on a single B center could not be accomplished using this methodology even when high temperatures and long reactions times were used. These extreme conditions lead to intractable polymeric materials rather than molecular solids. Alternatively, the reaction of the related thiomethoxyborane, $B(SMe)_3$, with $SiMe_3CN$ results in complete displacement of a SMe group by cyanide at 60 °C in solution to yield $B(CN)_3NCSiMe_3$ (**4**). This is the first example of a molecular compound that incorporates the elusive $B(CN)_3$ core (eq 2). At 22 °C the reaction of $B(SMe)_3$ with $SiMe_3CN$ yields the disubstituted derivative complex $B(CN)_2(SMe)NCSiMe_3$ (**5**) as the major product (eq 3). Compound **5** was characterized by spectroscopic methods and elemental analysis; see the Experimental Section for details. The $B(CN)_2(SMe)NMe_3$ (**6**) derivative of **5** was also prepared as a crystalline solid by reaction of $B(CN)_2(SMe)NCSiMe_3$ with NMe_3 (eq 4) and was characterized by single-crystal X-ray diffraction (Tables 1 and 2). An ORTEP diagram displaying the $B(CN)_2(SMe)$ core of **5** and **6** is shown in Figure 3.

$$B(SMe)_3 + 4Me_3SiCN \rightarrow B(CN)_3NCSiMe_3 + 3Me_3SiSMe \quad (2)$$

$$B(SMe)_3 + 3Me_3SiCN \rightarrow B(CN)_2(SMe)NCSiMe_3 + 2Me_3SiSMe \quad (3)$$

$$B(CN)_2(SMe){\cdot}CNSiMe_3 + NMe_3 \rightarrow B(CN)_2(SMe)(NMe_3) + CNSiMe_3 \quad (4)$$

The identity of **4** was established by elemental analysis for C, H, and N, the results of which are consistent with the proposed empirical formula, and by IR and NMR spectroscopies. The IR spectra revealed two sharp absorption bands at 2310 and 2232 cm^{-1} which are assigned to the coordinated ligand, $SiMe_3CN$, and the terminal cyanides of the $B(CN)_3$ fragment, respectively (Figure 4). Previous studies have considered the stretching frequencies of the cyanide ligand in many metal cyanide compounds and have demonstrated that bridging cyanide groups exhibit higher frequencies than do terminal cyanide groups, as we have also observed in this case.[15] The ^1H NMR spectrum reveals a single resonance corresponding to the Si−Me_3 protons at δ 0.04. In addition, the ^{13}C spectrum shows a resonance at δ 123 split into a 1:1:1:1 pattern by coupling to ^{11}B ($S = 3/2$), and the ^{11}B spectrum shows a single resonance at δ 143.

Table 2. Selected Distances (Å) and Angles (deg) for **6**

Distances			
S(1)−C(6)	1.824 (5)	S(1)−B(1)	1.894 (6)
B(1)−C(1)	1.594 (9)	B(1)−C(2)	1.600 (9)
B(1)−N(3)	1.620 (7)	C(1)−N(1)	1.147 (6)
C(2)−N(2)	1.151 (6)	N(3)−C(5)	1.484 (6)
N(3)−C(3)	1.497 (6)	N(3)−C(4)	1.512 (6)
Angles			
C(6)−S(1)−B(1)	105.8 (3)	C(1)−B(1)−C(2)	110.2 (5)
C(1)−B(1)−N(3)	107.7 (4)	C(2)−B(1)−N(3)	107.8 (4)
C(1)−B(1)−S(1)	111.2 (4)	C(2)−B(1)−S(1)	105.7 (4)
N(3)−B(1)−S(1)	114.2 (4)	N(1)−C(1)−B(1)	177.9 (5)
N(2)−C(2)−B(1)	176.8 (5)	C(5)−N(3)−C(3)	109.1 (4)
C(5)−N(3)−C(4)	108.1 (4)	C(3)−N(3)−C(4)	108.3 (4)
C(5)−N(3)−B(1)	110.5 (4)	C(3)−N(3)−B(1)	110.1 (4)
C(4)−N(3)−B(1)	110.6 (4)		

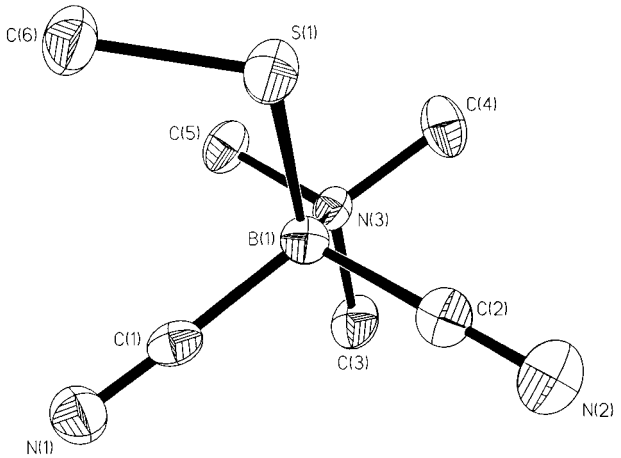

Figure 3. Molecular structure of $B(CN)_2(SMe)NMe_3$. The atoms are 50% probability ellipsoids. The hydrogen atoms are omitted for clarity.

Heating of **4** at 200−250 °C results in complete loss of $SiMe_3$-CN from the adduct, affording a nonvolatile air-stable solid at a virtually quantitative yield based on the decomposition reaction depicted by eq 5. Dissolution of this material with an excess of $SiMe_3CN$ at 80 °C regenerated $(SiMe_3CN)B(CN)_3$ in nearly quantitative yield, indicating that the reaction is reversible.

$$B(CN)_3NCSiMe_3 \underset{80\ °C}{\overset{250\ °C}{\rightleftharpoons}} BC_3N_3 + SiMe_3CN \quad (5)$$

Elemental analysis on BC_3N_3 showed an insignificant amount of H, consistent with compete elimination of $SiMe_3CN$, and a lower than expected N content (see Experimental Section for

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(15) Kawaguchi, M. *Adv. Mater.* **1997**, *9*, 615

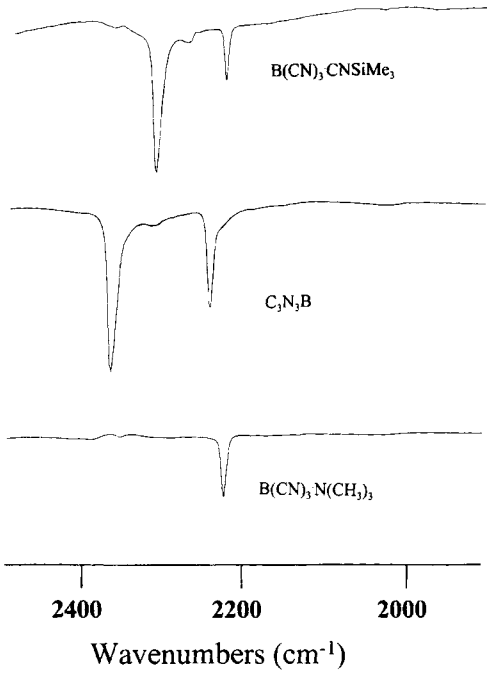

Figure 4. Infrared spectra of $B(CN)_3NCSiMe_3$, BC_3N_3, and $B(CN)_3$-NMe_3, showing C−N stretching bands. The higher frequencies bands for $B(CN)_3NCSiMe_3$ and BC_3N_3 correspond to the bridged CN ligands.

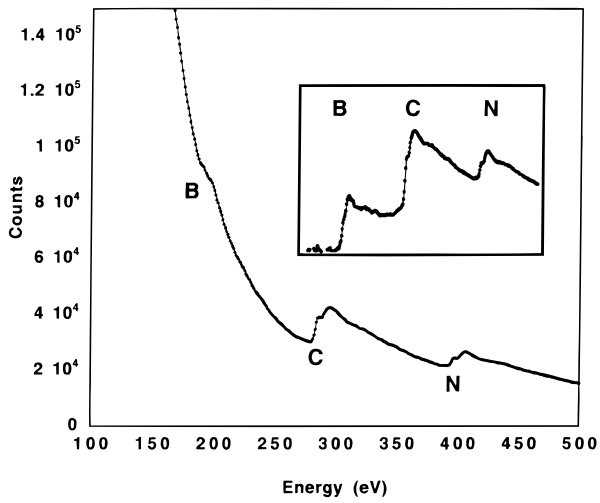

Figure 5. EELS spectrum for C_3N_3B featuring the K-shell ionization edges for B, C, and N. Inset shows the spectrum after background subtraction.

details). This is presumably due to formation of refractory nitrides during combustion analysis. The material is polycrystalline, and all the reflections in the X-ray diffraction pattern could be indexed using a tetragonal cell with $a = 8.214$ Å and $c = 13.832$ Å. Electron diffraction confirmed that C_3N_3B is polycrystalline. Examination of individual crystallites by electron energy loss spectroscopy (EELS) revealed only B, C, and N and verified the absence of oxygen or other impurities. The IR spectrum (Figure 5) shows sharp absorptions at 2376 and 2250 cm^{-1} that are assigned to bridging (B−NC−B) and terminal cyanide groups, respectively, and a strong absorption at 1015−984 cm^{-1} corresponding to [($^{10}B-^{11}B$)−CN,NC]. The spectrum is different from that of the black residue[10] generated from decomposition of BF_2CN. The solid-state ^{11}B NMR spectrum revealed two closely spaced and narrow peaks, at δ −35.13, −40.64, in the ratio of approximately 1:1. This indicates the presence of at least two possible types of B sites and suggests

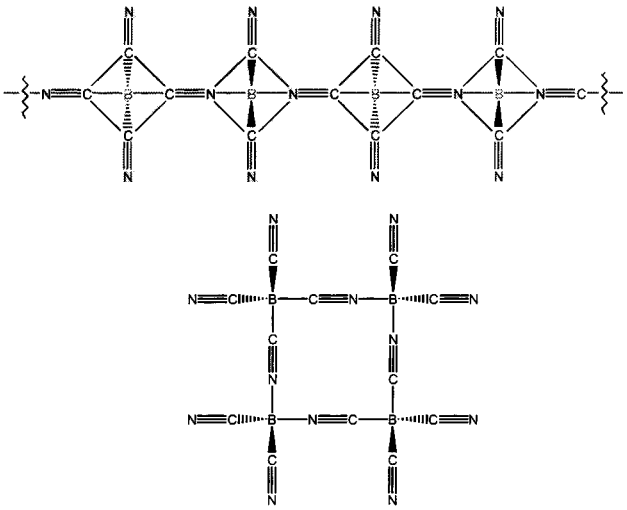

Figure 6. Schematic of model structures for BC_3N_3. The structure shown as a square array of B atoms bridged by CN ligands is also adopted by tetranuclear clusters such as $[R_2MCN]_4$, where R = allyl or alkyl and M = Au, Pd.[16]

C,N orientational disorder between bridging cyanides in the structure. The ^{13}C MAS NMR spectrum, on the other hand, revealed a weak and rather broad C−N resonance centered at δ 118, but the line width of the signal did not allow determination of the exact number of C sites with certainty. The spectroscopic evidence suggests that B is four-coordinated with two shared and two terminal CN groups associated with each B atom, an arrangement which is consistent with the idealized BC_3N_3 formula. The stability of this material toward hydrolysis and oxidation is also consistent with boron using its s and p orbitals in the coordination polymer. Figure 6 displays possible structures of BC_3N_3 which are consistent with the stoichiometry of the compound as well as the IR and NMR data.

Further evidence for the existence of BC_3N_3 is provided by the treatment of the material with trimethylamine (NMe_3), which leads quantitatively to the formation of a volatile and air-stable molecular adduct with composition $B(CN)_3NMe_3$. A correct elemental analysis for this compound was obtained and ^1H NMR, ^{13}C NMR, and IR spectra showed the presence of the coordinated NMe_3 molecule and the $B(CN)_3$ core. The mass spectra displayed isotopic envelopes for the molecular ion M^+ [M = $B(CN)_3NMe_3$] as the highest mass peak at 148 amu as well as mass peaks for $M^+ - Me$, $M^+ - CN$, $M^+ - (CN)_2$, NMe_3^+ (the strongest peak), $B(CN)_2^+$, and $(CN)_2^+$. The experimental isotopic patterns are in excellent agreement with the calculated patterns for the compound. A single-crystal X-ray diffraction structure of $B(CN)_3NMe_3$ (Tables 3 and 4) reveals that it is a Lewis acid−base complex between Me_3N and $B(CN)_3$. The compound crystallizes in space group *Pnma* with four molecules in the unit cell. Each molecule lies on a crystallographic mirror plane, and the Me and the CN groups are staggered. An ORTEP diagram showing the molecular conformation and the atom numbering scheme is presented in Figure 7. The B−N bond distance [1.596(3) Å] and the B−C bond distance [1.594(4) Å] are identical. The C−N bond length of the cyanide ligand [1.143(3) Å] is within the range found for similar cyanides,[16] and it is slightly shorter than the C−N bond length in LiB(CN)4 [1.204(5) Å]. The geometry at the B atom is very close to tetrahedral [109.6(12)−109.03(13)°], and the B−C≡N branches of units are nearly linear [178.90(17)°].

(16) Dunbar K. R.; Heinz, R. A. *Prog. Inorg. Chem.* **1997**, *45*, 283.

Table 3. Crystal Data for $B(CN)_3 \cdot NMe_3$ (**3**) at −130 °C

space group: *Pnma*	mol wt = 147.97
a = 12.0366(15) Å	ρ_{calcd} = 1.151 g cm^{-3}
b = 10.2805(13) Å	μ_{calcd} = 13.81 cm^{-1}
c = 6.9085(9) Å	size = 0.12 × 0.15 × 0.21 mm
V = 854.0(4) Å^3	GOF = 1.83
Z = 4	

diffractometer: SMART CCD
radiation: Mo Kα = 0.17069 Å
monochromator: graphite crystal
scan: ω (0.3° per frame)
$2\theta_{max}$: 49.4°
reflns: 4274 total, 1026 unique
R_{int}: 0.039
residuals:[a] R = 0.036; wR = 0.043
all data: R = 0.052

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. $wR = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table 4. Selected Distances (Å) and Angles (deg) for **3**

Distances			
N(1)−C(1)	1.143(3)	N(2)−C(2)	1.146(2)
N(3)−C(3)	1.501(3)	N(3)−C(4)	1.505(2)
N(3)−C(4)	1.505(2)	N(3)−B(1)	1.596(3)
C(1)−B(1)	1.594(4)	C(2)−B(1)	1.586(2)
C(3)−H(1)	0.95(2)	C(3)−H(2)	0.980(16)
C(3)−H(2)	0.980(16)	C(4)−H(3)	1.036(18)
C(4)−H(4)	0.873(12)	C(4)−H(5)	0.947(17)
Angles			
C(3)−N(3)−C(4)	108.37(12)	C(3)−N(3)−C(4)	108.37(12)
C(3)−N(3)−B(1)	110.18(17)	C(4)−N(3)−C(4)	108.2(2)
C(4)−N(3)−B(1)	110.81(12)	C(4)−N(3)−B(1)	110.81(12)
N(1)−C(1)−B(1)	178.0(2)	N(2)−C(2)−B(1)	178.90(17)
N(3)−C(3)−H(1)	107.6(14)	N(3)−C(3)−H(2)	108.1(9)
N(3)−C(3)−H(2)	108.1(9)	H(1)−C(3)−H(2)	112.3(11)
H(1)−C(3)−H(2)	112.3(11)	H(2)−C(3)−H(2)	108.2(18)
N(3)−C(4)−H(3)	107.7(10)	N(3)−C(4)−H(4)	99.8(8)
N(3)−C(4)−H(5)	107.2(10)	H(3)−C(4)−H(4)	112.1(15)
H(3)−C(4)−H(5)	111.2(13)	H(4)−C(4)−H(5)	117.9(16)
N(3)−B(7)−C(4)	109.93(18)	N(3)−B(1)−C(2)	109.63(12)
N(3)−B(1)−C(2)	109.63(12)	C(1)−B(1)−C(2)	109.03(13)
C(1)−B(1)−C(2)	109.03(13)	C(2)−B(1)−C(2)	109.6(2)

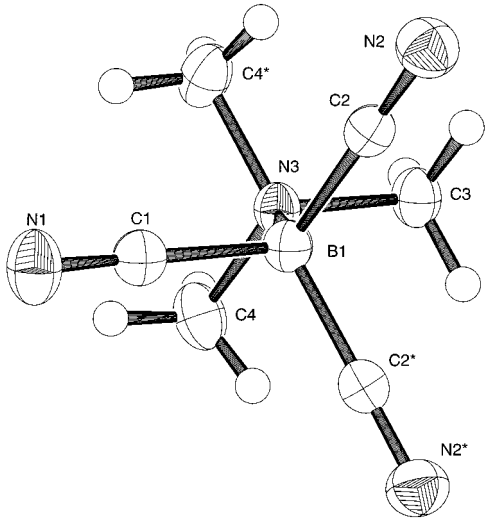

Figure 7. Molecular structure of $B(CN)_3 \cdot NMe_3$. The heavy atoms are 50% probability ellipsoids, and the hydrogen atoms are of arbitrary size.

All angles around the N atom of the NMe_3 group are within 109.5 ± 1°. Selected bond lengths and angles are listed in Table 4.

Thermolysis of BC_3N_3 has been performed under a variety of conditions. Heating in situ in the inlet of the mass spectrometer and under high vacuum in a flask revealed that the compound is thermally stable up to about 450 °C. However,

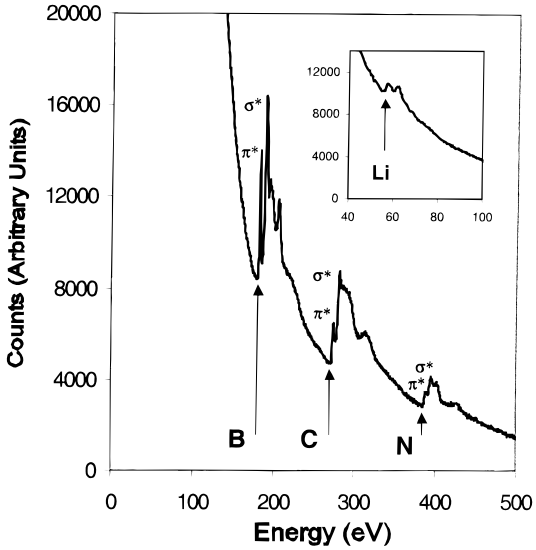

Figure 8. Typical EELS spectra of B−C−N phase and Li phase (inset) featuring the K-shell ionization edges for B, C, and N, and Li, respectively. The presence of π^* and σ^* features indicates that the B−C−N material is graphitic.

at higher temperatures loss of $(CN)_2$ is observed in the mass spectrum. The thermal dissociation of C_3N_3B via elimination of $(CN)_2$ is likely to yield a stoichiometric material with composition BCN (eq 6).

$$C_3N_3B \rightarrow BCN + (CN)_2 \quad (6)$$

Heating C_3N_3B in an atmosphere of nitrogen did not result in elimination of $(CN)_2$. However, it transformed the crystalline cyanide into a polymeric network, perhaps via cyclization of the (C≡N) groups to form (C_3N_3) triazene-type rings. The presence of C_3N_3 moieties is indicated by the appearance of the characteristic C−N ring modes in the IR and the strong π-to-π^* transitions in the EELS spectrum, indicating substantial sp^2 hybridization for both carbon and nitrogen. A possible structure of a stoichiometric C_3N_3B polymer incorporates C_3N_3 rings linked together at the carbon sites by trigonal planar B to form a two-dimensional network similar to that of graphitic C_3N_4. Such a structure should be an ideal precursor for the high-pressure synthesis experiments proposed in the Introduction. Our preliminary results are certainly consistent with formation of a planar C_3N_3B. The vibrational and EELS spectra are consistent with a layered model structure, and the X-ray diffraction pattern is reminiscent of highly turbostatic amorphous carbon. High-pressure studies are currently in progress.

A brief survey of preliminary high-pressure experiments on $LiB(CN)_4$ in the multianvil have shown that a transparent glassy material, which is extremely hard but amorphous and has a composition close to that of the starting material, is produced at 100 kbar and 400 °C. Further reactions at 900 °C and 100 kbar resulted in a crystalline black solid with platelet-like morphology. High-resolution electron diffraction and EELS examinations at the nanometer scale revealed that most crystals in the sample have a graphite-like layered structure and consist of sp^2-hybridized B, C, and N atoms (Figure 8), indicating that the development of a planar B−C−N network has been achieved. EELS was also used to identify a different set of particles which are extremely beam sensitive (thus difficult to analyze) and are found to incorporate primarily Li and a small amount of C. The formation of separate B−C−N and Li phases from the compression of LiB_4CN_4 at 100 kbar and 900 °C

suggests that the compound is disproportionating under these conditions, presumably by elimination of LiCN. A systematic search and characterization for high-pressure phases in the Li−B−C−N system is currently in progress. The primary objective remains the determination of the synthetic conditions that favor formation of single-phase $LiBC_4N_4$ with diamond-like tetrahedral structure.

Concluding Remarks

The preparation of a novel framework cyanide with composition $LiBC_4N_4$, the BC_3N_3 derivative, and related molecular cyanides of boron such as $M{\cdot}B(CN)_3$ and $M{\cdot}B(CN)_2(SMe)$ (M = $SiMe_3CN$, NMe_3) has been achieved. In solution, the existence of the $B(CN)_4^-$ moiety has also been established for the first time.[17] The synthesis of new families of compounds based on this species should be possible and awaits exploration.

It is of considerable interest in materials science to discover synthetic pathways leading to new semiconductors and new host materials based on the graphite network as well as superhard diamond-like systems that incorporate boron, carbon, and nitrogen. Previously synthesized B−C−N materials suffer from poor crystallinity and often incorporate impurities which impede accurate characterization and reliable determination of their physical properties.[15] Preliminary studies show that $LiBC_4N_4$ can be used as a starting material for high-pressure synthesis of pure and crystalline B−C−N with graphite-like structure. Stoichiometric $LiBC_4N_4$ and BC_3N_3 might also be highly suitable as precursors to other novel structures such as cubic and hexagonal B/C/N (as large crystals), B/C/N clusters and nanotubes, and C−N-rich B−C−N phases with structures related to C_3N_4.

Experimental Section

General Procedures. Reactions were performed under prepurified nitrogen using standard Schlenk and drybox techniques. Dry, air-free solvents were distilled prior to use. ^{1}H NMR (300 MHz) and ^{13}C NMR (125.7 MHz) spectra were recorded on a Varian Gemini 300 and a Varian Unity 500 spectrometer, respectively. FTIR spectra were recorded on a Nicolet Magna-IR 550 spectrometer. Elemental analyses were performed by Desert Analytics (Tucson, AZ). Electron impact mass spectra were obtained on a Finnigan-MAT model 312 mass spectrometer (IE = 70 eV) in the Arizona State University departmental mass spectrometry facility. $LiBF_4$ and NaSMe (Aldrich) were used as received, and NMe_3 was dried over P_2O_5. $SiMe_3CN$ (Aldrich 98%) was purified by distillation, and its purity was checked by NMR and gas-phase IR. The CD_3CN NMR spectra for ^{13}C, ^{11}B, and ^{7}Li were referenced to TMS, BF_3 (Et_2O), and LiCl, respectively. The (MAS) NMR spectra for ^{13}C, ^{11}B, and ^{7}Li were referenced to hexamethylbenzene, B_2O_3, and LiCl, respectively. The PEELS spectra (Figure 5) were collected on a Philips CM200FEG 200 kV high-resolution and analytical TEM with information limit to 1.4 Å, focused probe size down to ∼0.5 nm, and equipped with an EDX detector, PEELS, and facilities for electron holography. PEELS spectra (Figure 8) were collected on a Vacuum Generators HB501 dedicated STEM equipped with Gatan dixiPEELS, focused probe size down to ∼0.5 nm.

$LiBC_4N_4$ (1). Me_3SiCN (4.8 g, 0.048 mol) was added dropwise to a stirred mixture of $LiBF_4$ (1.0 g, 0.011 mol) in 50 mL of Bu_2O at −78 °C. The mixture was stirred at 22 °C for 18 h and then refluxed for 4 h. After filtration the resulting white solid residue was heated at 250 °C for 18 h in vacuo and then extracted with warm CH_3CN. The solution was evaporated to dryness to yield a colorless solid. Anal. Calcd for C_4BliN_4: C, 39.34; H, 0.00; N, 45.50. Found: C, 39.25; H, <0.05; N, 43.10. The low value obtained for N is attributed to the formation of refractory nitrides during combustion analysis. $LiB(CN)_4$: IR (Nujol, cm^{-1}) 2271 (w), 995 (s), 961 (s), 530 (s), 398 (s); ^{13}C NMR (CD_3CN) δ −8.63 (1:1:1:1 quartet, $^1J_{C^{11}B}$ = 70.9 Hz); ^{11}B NMR (CD_3CN) δ −8.5 (s); ^{7}Li NMR (CD_3CN) δ 0.112 (s); ^{13}C MAS NMR δ 120.5 (s, br); ^{11}B MAS NMR δ −43.7 (s); ^{7}Li MAS NMR δ −2.83 (s).

C_3N_3B (2). A sample of pure $B(CN)_3{\cdot}CNSiMe_3$ was heated in a Pyrex tube at 250 °C for 1.5 h under dynamic vacuum. A nonvolatile brown solid (C_3N_3B) formed near the bottom of the tube, and modest amounts of starting material sublimed to the top of the tube. The only byproduct was $SiMe_3CN$. Anal. Calcd for C_3BN_3: C, 40.4; H, 0.0; N, 47.2. Found: C, 38.0; H, 0.9; N, 37.6. IR (Nujol, cm^{-1}): 2376 (m), 2250 (w), 1015 (s, br), 984 (s, br). ^{11}B MAS NMR: δ 35.13, −40.64. ^{13}C MAS NMR: δ 117.9 (br). The X-ray diffraction pattern gave peaks with the following diameter values and percent relative intensity: [d (Å), (I/I_o)] 5.79 (100), 4.44 (77.9), 3.46 (39.1), 3.29 (36.5), 2.91 (39.7), 2.84 (47.9), 2.77 (39.2), 2.68 (48.5), 2.55 (28.7), 2.31 (21.9), 1.96 (19.2). The tetragonal unit cell parameters are a = 8.214 Å and c = 13.832 Å

$B(CN)_3{\cdot}NMe_3$ (3). An excess of dry NMe_3 (0.25 g, 4.0 mmol) was combined at −196 °C with $B(CN)_3{\cdot}NCSiMe_3$ (0.25 g, 1.0 mmol). The mixture was stirred at 22 °C for 1 h, and then the volatile materials were removed in a vacuum to yield a light orange solid. The solid was purified by extraction with hexane (2 × 20 mL) followed by sublimation at 90 °C, 0.03 Torr, to afford a colorless crystalline solid. Anal. Calcd for $C_6H_9BN_4$: C, 48.64; H, 6.08; N, 37.83. Found: C, 48.20; H, 6.16; N, 37.17. IR (Nujol, cm^{-1}): 2225 (w), 1460 (vs), 1270 (s), 977 (m), 933 (s), 865 (s), 815 (s), 651 (m), 579 (w), 499 (w). ^{1}H NMR ($CDCl_3$): δ 3.03 (s). ^{13}C NMR ($CDCl_3$): δ 50.9 (1:1:1:1 quartet, $^1J_{C^{11}B}$ = 70.9 Hz), 123. ^{11}B NMR ($CDCl_3$): δ 8.543. EIMS (m/e): isotopic envelopes centered at 148 (M^+), 133 (M^+ − Me), 122 (M^+ − CN), 106 (M^+ − CN−CH_3), 95 [M^+ − $(CN)_2$], 81 [M^+ − Me−$(CN)_2$], 63 $[B(CN)_2]^+$, 59 $(NMe_3)^+$, 52 $[(CN)_2]^+$.

$B(CN)_3NCSiMe_3$ (4). A toluene solution (15 mL) of Me_3SiCN (1.8 g, 18.0 mmol) was added to a toluene solution (15 mL) of $B(SMe)_3$ (0.87 g, 6.0 mmol) at 22 °C. The reaction was heated at 60 °C for 18 h, during which time a red-brown crystalline precipitate developed. After filtration the solid was extracted with hexane (20 mL), the hexane was evaporated, and the solid was dried in vacuo. Sublimation at (160 °C/0.03 mmHg) yielded 222 mg of the product (20% yield). Anal. Calcd for $C_7H_9BN_3Si$: C, 43.5; H, 3.7; N, 30.2. Found: C, 41.8; H, 3.7; N, 29.1. IR (Nujol, cm^{-1}): 2310 (s), 2232 (m), 1272 (s), 985 (m), 951 (s), 926 (m), 859 (s), 781 (m), 640 (w), 597 (w), 529 (w), 495 (w). ^{1}H NMR (CD_3COCD_3): δ 0.04 (s). ^{13}C NMR (CD_3COCD_3): δ 122.9 (1:1:1:1 quartet, ($^1J_{C^{11}B}$ = 70.9 Hz), 1.9 (s).^{11}B NMR (CD_3CN): δ −7.527 (s).

$B(CN)_2(SMe)NCSiMe_3$ (5). A toluene solution (15 mL) of Me_3SiCN (1.8 g, 17.0 mmol) was added to a toluene solution (15 mL) of $B(SMe)_3$ (0.75 g, 5.0 mmol) at 22 °C. The product precipitated as colorless crystals in about 10 min. The solid was collected by filtration to yield 570 mg (58%) of $B(CN)_2(SMe)NCSiMe_3$. Mp: 82 °C dec. Anal. Calcd for $C_7H_{12}BN_3SSi$: C, 40.0; H, 5.2; N, 20.1. Found: C, 39.5; H, 4.8; N, 20.9. IR (Nujol, cm^{-1}): 2276 (s), 2223 (w), 1261 (s), 1019 (m), 995 (m), 971 (m), 951 (s), 873 (s), 800 (s), 781 (m), 636 (w), 597 (w), 533 (w), 495 (w), 422 (w). ^{1}H NMR ($CDCl_3$): δ 2.03 (s, 3H, $-SCH_3$), 0.59 (s, 9H, $-Si(CH_3)_3$). ^{13}C NMR ($CDCl_3$): δ 126.3, 12.1 (s), −0.8 (s). ^{11}B NMR ($CDCl_3$): δ 0.341 (s). EIMS (m/e): isotopic envelopes centered at 207 (M^+), 181 (M^+ − CN), 147 ($MeSSiMe_3^+$), 84 (Me_2SiCN^+), 73 (Me_3Si^+), and 63 (M^+ − $MeSSiMe_3$).

$B(CN)_2(SMe){\cdot}NMe_3$ (6). An excess of NMe_3 (0.20 g, 3.4 mmol) was condensed directly onto solid $B(CN)_2(SMe)NNSiMe_3$ (0.20 g, 0.95 mmol) at −196 °C. The mixture was warmed slowly to room temperature, and the volatiles were removed in vacuo, leaving behind a pale yellow solid. The solid was washed with hexane (2 × 20 mL) and dried in vacuo. Yield: 0.15 g (93%). Colorless single crystals for X-ray diffraction were grown by slow sublimation of the crude material in a sealed tube under vacuum. IR (Nujol, cm^{-1}): 2211 (w), 1473 (vs), 1264 (s), 999 (m), 972 (s), 932 (m), 907 (m), 864 (s), 807 (s), 648 (m), 576 (w), 362 (w). ^{1}H NMR ($CDCl_3$): δ 2.87 (s, 9H, NMe3), 2.14 (s, 3H, SMe). ^{13}C NMR ($CDCl_3$): δ 126.9 (1:1:1:1 quartet, J_{CB} = 72 Hz), 49.7 (s), 13.1 (s).

Structure of $B(CN)_3{\cdot}NMe_3$ (3) and $B(CN)_2(SMe)NCSiMe_3$ (6). A colorless polyhedral crystal of $N_4C_6H_9B$ (0.12 × 0.15 × 0.21 mm)

(17) The synthesis of $LiBC_4N_4$ was described by Darrick Williams in a dissertation entitled "The Synthesis and Characterization of Binary and Ternary group 11−12 and 13 Cyanides", Arizona State University, Tempe AZ, 1998; *Diss. Abstr., Int., B* **1999**, *59*, 10.

was mounted on a glass fiber using Paratone N hydrocarbon oil. All measurements were made on a SMART CCD area detector with graphite-monochromated Mo Kα radiation. Cell constants were obtained from a least-squares refinement using the measured positions of 1690 reflections in the range $3.00° < 2\theta < 45.00°$, corresponding to a primitive orthorhombic cell. Based on the systematic absences of $0kl$, $k + l \neq 2n$ and $hk0$, $h \neq 2n$, packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be *Pnma* (No. 62). The data were collected at -133 ± 1 °C. Frames corresponding to an arbitrary hemisphere of data were collected using ω scans of 0.3° counted for a total of 20.0 s per frame. The data were integrated to a maximum 2θ value of 49.4° and were corrected for Lorentz and polarization effects and analyzed for agreement and possible absorption. An empirical absorption correction based on comparison of redundant and equivalent reflections is applied ($T_{max} = 0.96$, $T_{min} = 0.69$). The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were refined with isotropic thermal parameters. The final cycle of full-matrix least-squares refinement was based on 574 observed reflections [$I > 3.00\sigma(I)$] and 76 variable parameters and converged with unweighted and weighted agreement factors of $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.036$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum_w F_o^2)]^{1/2} = 0.043$. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.16 and -0.13 $e^-/Å^3$, respectively. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corp.

The data for $B(CN)_2SMe{\cdot}CNSiMe_3$ (**6**) were collected at -124 °C using a SMART CCD system and a colorless crystal with dimensions 0.15, 0.06, 0.04 mm. Frames were collected by ω scans and of 0.3° counted for 20 s per frame. The data were integrated using Siemens SAINT with box parameters of 1.6 × 0.6, which yielded 3863 reflections to a resolution of 0.9 Å. The sample did not degrade during the data collection. The cell constants were obtained using 741 reflections taken from the data set with $I > 10\sigma(I)$. The data were corrected for absorption using SADABS following the removal of eight σ outliers ($T_{max} = 0.98$, $T_{min} = 0.61$). The crystal was twinned with twinning law $a,b,-c$. The minority twin component refined to be 15% of the structure. The structure was solved using Patterson synthesis and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were refined isotropically using a riding model. The final cycle of full-matrix least-squares refinement was based on 826 observed reflections [$I > 2.00\sigma(I)$] and 105 variable parameters and converged with unweighted and weighted agreement factors of $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.0589$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)]^{1/2} = 0.1261$. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.342 and -0.270 $e^-/Å^3$, respectively. All calculations were performed using the SHELXTL version 5.03 of Siemens Analytical X-ray Instruments.

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Supporting Information Available: Full tables of bond lengths and angles, atomic coordinates, and displacement parameters for **3** and **6** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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