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Syntheses and Characterizations of Linear Triborazanes

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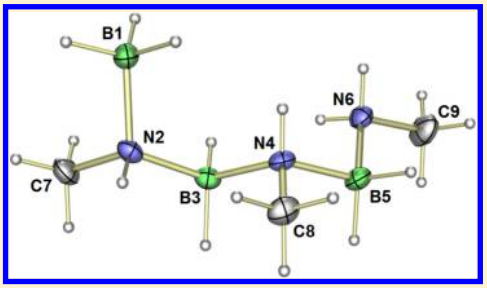
Supporting Information

ABSTRACT: Reaction of the amine boranes $NH_2(R)BH_3$, where R = H, Me, and Bz, with $^1/_3$ equiv of sodium hexamethyldisilazane produced the five-membered, linear aminoborane anions $Na^+[BH_3N(R)HBH_2N(R)HBH_3^-]$, where R = H (**1**), Me (**1Me**), and benzyl (**1Bz**). Reactions of **1** and **1Me** with ammonium chloride and methylammonium chloride, respectively, resulted in elimination of NaCl and H_2 to produce the linear triborazanes $BH_3(RNHBH_2)_2N(R)H_2$, where R = H (**2**) and Me (**2Me**), with the structure of **2** crystallographically confirmed. The reactions of **1** and **1Me** with pyridine–HCl produced the pyridine-capped aminoboranes $H_3B(RNHBH_2)_2(NC_5H_5)$, where R = H (**3**) and Me (**3Me**). **2** and **2Me** proved to be stable up to 90 °C but produced a mixture of products when heated above 90 °C. **2** was selectively monochlorinated at the terminal boron when treated with 1 equiv of HCl and dichlorinated when reacted with a second 1 equiv of HCl.



INTRODUCTION

The growth of aminoborane oligomers through the dehydrocoupling reactions of ammonia borane (AB, NH_3BH_3) has been a topic of recent research owing to the interest in amine boranes as potential hydrogen storage materials and/or chemical precursors to boron nitride ceramics.[1] While long-chain oligomers and polymers have been shown to be products of metal-catalyzed amine borane reactions,[2] only a few small linear oligomers have been characterized, including the four-membered parent diborazane $NH_3BH_2NH_2BH_3$[3] and its *N*-methyl-, *N*,*N*-dimethyl-, and *N*,*N*-(1,4-C_4H_8)diborazane derivatives.[4] We also recently reported[5] the syntheses of the five-membered, linear anionic chain $[BH_3NH_2BH_2NH_2BH_3^-]$ (**1**) and both linear $[BH_3NH_2BH_2NH_2BH_2NH_2BH_3^-]$ and branched $[HB(NH_2BH_3)_3^-]$ seven-membered chains via anionic AB chain growth initiated by deprotonation with Verkade's base (VB).[6] Herein, we report a greatly improved route to the **1** anion, as well as to its N-methylated and N-benzylated derivatives $Na^+[BH_3N(R)HBH_2N(R)HBH_3^-]$ (R = CH_3, **1Me**; R = $CH_2C_6H_5$, **1Bz**). We further demonstrate that **1** and **1Me** can be readily converted to the first examples of linear triborazanes $BH_3(RNHBH_2)_2N(R)H_2$, where R = H (**2**) and Me (**2Me**), by their reactions with ammonium and methyl ammonium chloride, respectively.

EXPERIMENTAL SECTION

Unless otherwise noted, all reactions and manipulations were performed in dry glassware under a nitrogen or argon atmosphere using the high-vacuum or inert-atmosphere techniques described by Shriver and Drezdzon.[7]

Materials. Ammonia borane (AB; Aviabor, 97% minimum purity) was ground into a free-flowing powder using a commercial coffee grinder. Sodium hexamethyldisilazane (NaHMDS; 0.6 M in toluene), BH_3–tetrahydrofuran (THF) (1 M in THF), methylamine (2 M in THF), HCl (1 M in diethyl ether), and benzylamine were used as received (Sigma-Aldrich). Methylamine borane and benzylamine borane were prepared by amine displacement from BH_3–THF with their purities confirmed by ^{1}H NMR. Pyridine–HCl and all ammonium chloride salts (Sigma-Aldrich) were dried in vacuo with heating prior to use. Fluorobenzene (Sigma-Aldrich) and acetonitrile (Fisher) were dried over CaH_2 and distilled prior to use. Glyme (1,2-dimethoxyethane) and THF (Fisher) were dried over sodium/benzophenone and distilled prior to use. Toluene and diethyl ether (Fisher) were HPLC-grade and were used as received.

Physical Methods. The ^{11}B NMR spectra at 128.4 MHz and ^{1}H NMR spectra at 400.1 MHz were obtained on a Bruker DMX-400 spectrometer equipped with appropriate decoupling accessories. All ^{11}B chemical shifts are referenced to external $BF_3{\cdot}O(C_2H_5)_2$ (0.0 ppm), with a negative sign indicating an upfield shift. All ^{1}H chemical shifts were measured relative to internal residual protons in the lock solvents and are referenced to Me_4Si (0.0 ppm). Elemental microanalysis of many of the very hydroscopic products proved difficult; however, satisfactory elemental analyses of **2Me** and **1Bz** were obtained at the MicroAnalytical Facility at University of California at Berkeley, Berkeley, CA. Thermal analysis was carried out on a TA Instruments SDT model 2960 instrument capable of simultaneous differential scanning calorimetry (DSC) and thermal gravimetry (TGA) measurements.

$Na^+[BH_3NH_2BH_2NH_2BH_3^-]$ (1). NaHMDS (11.0 mmol) was added to a suspension of AB (1.02 g, 33.0 mmol) in fluorobenzene (30 mL) and the mixture stirred at 50 °C for 24 h. The solution was next diluted with 30 mL of toluene and frit-filtered. The retained solid was washed with toluene (2 × ~20 mL) and diethyl ether (3 × ~20 mL) and then dried in vacuo. The ^{1}H and ^{11}B NMR spectra of the resultant white solid (1.03 g, 10.8 mmol, 96%) were consistent with the literature values for $[BH_3NH_2BH_2NH_2BH_3^-]$.[5]

$Na^+[H_3BN(CH_3)HBH_2N(CH_3)HBH_3^-]$ (1Me). NaHMDS (11.1 mmol) was added to a suspension of methylamine borane (1.50 g, 33.4 mmol) in fluorobenzene (30 mL) and the mixture stirred at 60 °C for 24 h. In a nitrogen-filled glovebag, the solution was diluted with 30 mL of toluene and frit-filtered. The retained solid was washed with

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toluene (2 × ~20 mL) and diethyl ether (3 × ~20 mL) and then dried in vacuo. Yield: 1.03 g (10.8 mmol, 96%). ^{11}B NMR (THF-d_8, ppm, J in Hz): −3.3 (t, J = 98, BH_2), −18.2 (q, J = 87, $2BH_3$). Density functional theory (DFT)/gage invariant atomic orbital (GIAO)-calculated [B3LYP/6-311G(d)] ^{11}B NMR shifts: *S,R* isomer, −5.6, −20.0, −23.4 ppm; *R,R* isomer, −5.7, −19.1, −19.1 ppm. ^{1}H{^{11}B} NMR (THF-d_8, ppm, J in Hz): 2.60 (s, $2NH_2$), 2.11 (d, J = 6, $2CH_3$), 1.62/1.35 (q, J = 4, BH_2, diastereomers), 1.22 (d, J = 3, BH_3).

$Na^+[H_3BN(CH_2C_6H_5)HBH_2N(CH_2C_6H_5)HBH_3^-]$ (1Bz). NaHMDS (0.9 mmol) was added to a suspension of benzylamine borane (0.32 g, 2.6 mmol) in fluorobenzene (20 mL) and the mixture stirred at 60 °C for 24 h. In a nitrogen-filled glovebag, the solution was diluted with toluene (~20 mL) and frit-filtered. The retained solid was washed with toluene (2 × 15 mL) and cold diethyl ether (3 × ~15 mL) and then dried in vacuo for 12 h. Yield: 0.12 g (0.4 mmol, 49%). Anal. Calcd: C, 60.97; H, 8.77; N, 10.16. Found: C, 59.62; H, 8.89; N, 9.94. ^{11}B NMR (CD_3CN, ppm, J in Hz): −2.6 (t, J = 89, BH_2), −17.2 (q, J = 92, $2BH_3$). DFT/GIAO-calculated [B3LYP/6-311G(d)] ^{11}B NMR shifts: *S,R* isomer, −10.0, −17.4, −24.4 ppm; *R,R* isomer, −13.3, −20.0, −20.0 ppm. ^{1}H{^{11}B} NMR (CD_3CN, ppm, J in Hz): 7.28 (m, $2CH_2C_6H_5$), 3.49/3.40 (m, $2CH_2C_6H_5$, diastereomers), 2.52 (s, $2NH$), 1.85/1.77 (s, BH_2, diastereomers), 1.24 (d, J = 3, $2BH_3$).

Attempted Synthesis of $Na^+[H_3BN(CH_3)_2BH_2N(CH_3)_2BH_3^-]$. NaHMDS (1.4 mmol) was added to a suspension of dimethylamine borane (0.25 g, 4.2 mmol) in fluorobenzene (20 mL) and the mixture stirred at 60 °C for 12 h. Analysis by ^{11}B NMR indicated no formation of oligomeric products but instead showed a large peak near 28 ppm.

$BH_3(NH_2BH_2)_2NH_3$ (2). NH_4Cl (0.78 g, 14.6 mmol) was added to a solution of **1** (1.36 g, 14.3 mmol) in glyme (30 mL) and the mixture stirred at room temperature for 24 h. The solution was then filtered and the retained solid washed with glyme (4 × ~20 mL). The filtrate was vacuum-evaporated until ~5 mL of glyme remained. The product was precipitated from the concentrated glyme solution by the addition of diethyl ether (~25 mL), then filtered, and washed with diethyl ether (3 × ~20 mL). The remaining white solid was dried in vacuo for 18 h to remove all traces of glyme. Yield: 1.06 g (11.9 mmol, 84%), ^{11}B NMR (THF-d_8, ppm, J in Hz): −10.5 (t, J = 95, BH_2), −12.4 (t, J = 104, BH_2), −22.3 (q, J = 95, BH_3). DFT/GIAO-calculated [B3LYP/6-311G(d)] ^{11}B NMR shifts: −12.8, −13.5, −21.0 ppm. ^{1}H{^{11}B} NMR (CD_3CN, ppm, J in Hz): 4.69 (br s, NH_3), 2.97 (br s, NH_2), 2.15 (br s, NH_2), 2.08 (m, BH_2), 1.97 (quin, J = 4, BH_2), 1.31 (t, J = 4, BH_3).

$H_3B[(CH_3)NHBH_2]_2N(CH_3)H_2$ (2Me). CH_3NH_3Cl (0.26 g, 3.9 mmol) was added to a solution of **1Me** (0.5 g, 3.9 mmol) in acetonitrile (~20 mL) and the mixture stirred at 60 °C with careful monitoring by ^{11}B NMR. After ~6 h, **1Me** had been consumed, with the ^{11}B NMR spectrum showing only **2Me** resonances. In a nitrogen-filled glovebag, the solution was frit-filtered and the retained solid washed with acetonitrile (2 × ~20 mL). The solvent from the combined filtrates was evaporated on a high-vacuum line until crystallization was observed (~24 h). The crystals were washed two times with cold ether and then dried in vacuo. Yield: 0.5 g (3.4 mmol, 88%), Anal. Calcd: C, 27.58; H, 15.43; N, 32.16. Found: C, 27.90; H, 15.71; N, 31.93%. ^{11}B NMR (THF-d_8, ppm, J in Hz): −5.1 (t, J = 105, BH_2), −7.3 (t, J = 108, BH_2), −18.9 (q, J = 91, BH_3). DFT/GIAO-calculated [B3LYP/6-311G(d)] ^{11}B NMR shifts: *S,S* isomer, −8.2, −9.2, −17.5 ppm; *R,S* isomer, −6.8, −8.6, −21.4 ppm. ^{1}H{^{11}B} NMR (THF-d_8, ppm, J in Hz): 5.17 (br s, NH_2), 3.35 (br s, NH), 2.67 (br s, NH), 2.40 (t, J = 6, CH_3), 2.18 (d, J = 6, CH_3), 2.11 (d, J = 6, CH_3), 1.91 (m, BH_2), 1.80 (m, BH_2), 1.29 (d, J = 4, BH_3).

$BH_3(NH_2BH_2)_2(NC_5H_5)$ (3). A solution of **1** (0.10 g, 1.1 mmol) in acetonitrile (15 mL) was cooled at −20 °C and then reacted with pyridine−HCl (0.12 g, 1.1 mmol). The solution immediately became cloudy. After stirring for 10 min, the solution was quickly filtered and the retained solid washed with cold acetonitrile. The solvent was vacuum-evaporated from the filtrate to leave the product as a white solid. Yield: 0.11 g (0.74 mmol, 68%). ^{11}B NMR (CD_3CN, ppm, J in Hz): −3.3 (t, J = 107, BH_2), −9.6 (t, J = 102, BH_2), −21.7 (q, J = 90, BH_3). DFT/GIAO-calculated [B3LYP/6-311G(d)] ^{11}B NMR shifts: −5.4, −11.0, −21.5 ppm. ^{1}H{^{11}B} NMR (CD_3CN, ppm, J in Hz): 8.62 (d, J = 1.2, $HCCH_2CH_2N$−), 8.25 (m, $HCCH_2CH_2N$−), 7.77 (t, J = 7, $HCCH_2CH_2N$−), 3.15 (br s, NH_2), 2.87 (s, BH_2), 2.09 (s, NH_2), 1.79 (quin, J = 4, BH_2), 1.12 (t, J = 5, BH_3).

$H_3B[(CH_3)NHBH_2]_2(NC_5H_5)$ (3Me). A solution of **1Me** (0.10 g, 0.78 mmol) in acetonitrile (15 mL) was cooled at −20 °C and then treated with pyridine−HCl (0.92 g, 0.78 mmol). The solution immediately became cloudy. After stirring for 10 min, acetonitrile was vacuum-evaporated and fluorobenzene (~10 mL) was then vacuum-transferred to the flask. The mixture was warmed to room temperature and quickly filtered and the retained solid washed with cold fluorobenzene. The solvent was vacuum-evaporated from the filtrate to leave the product as a white solid. Yield: 0.13 g (0.68 mmol, 87%). ^{11}B NMR (CD_3CN, ppm, J in Hz): −0.4 (t, J = 109, BH_2), −4.0 (t, J = 105, BH_2), −18.2 (q, J = 90, BH_3). DFT/GIAO-calculated [B3LYP/6-311G(d)] ^{11}B NMR shifts: *S,R* isomer, −1.3, −6.9, −17.7 ppm; *S,S* isomer, −0.6, −7.5, −23.2 ppm. ^{1}H{^{11}B} NMR (CD_3CN, ppm, J in Hz): 8.64 (d, J = 5, $HCCH_2CH_2N$−), 8.24 (m, $HCCH_2CH_2N$−), 7.77 (m, $HCCH_2CH_2N$−), 3.45 (s, NH), 2.87/2.75 (s, BH_2, diastereomers), 2.34 (m, NH), 2.20 (d, J 6, CH_3), 2.01 (d, J = 6, CH_3), 1.57/1.24 (s, BH_2, diastereomers), 1.12 (s, BH_3).

Attempted Thermal Cyclization of 2 and 2Me. A suspension of **2** (0.04 g, 0.4 mmol) in fluorobenzene (~10 mL) was heated at 100 °C for 12 h while being monitored by ^{11}B NMR. The solvent was vacuum-evaporated and the residue taken up in ether (~10 mL) and filtered. The ether was vacuum-evaporated, leaving 12 mg of a white solid, which ^{11}B and ^{1}H NMR analyses identified as a ~1:1 mixture of AB and cyclotriborazane (CTB).[8]

A solution of **2Me** (0.02 g, 0.2 mmol) in fluorobenzene (~10 mL) was heated at 100 °C for 12 h while being monitored by ^{11}B NMR. Fluorobenzene was vacuum-evaporated and the remaining white solid redissolved in THF-d_8. Analysis by ^{11}B and ^{1}H NMR identified this solid as a ~3:1 mixture of methylamine borane and tri-*N*-methylcyclotriborazane.[4b,c]

Chlorination of 2. A solution of **2** (0.05 g, 0.6 mmol) in glyme (~10 mL) was cooled at −30 °C, while a solution of HCl−etherate (0.6 mmol) was added via syringe. After the solution was stirred for 15 min at −30 °C, ^{11}B NMR analysis indicated formation of the monochlorinated product **2Cl**. Attempts to isolate the product by solvent vacuum evaporation resulted in product decomposition. ^{11}B NMR (glyme, ppm, J in Hz): −6.6 (d, J = 98, BH_2), −10.9 (t, J = 101, BH_2), −12.1 (t, J = 123, BH_2). DFT/GIAO-calculated [B3LYP/6-311G(d)] ^{11}B NMR shifts for 1-$ClB_3N_3H_{11}$: −6.1, −10.6, −11.4 ppm.

In a separate reaction, after 1 equiv of HCl−etherate (0.6 mmol) had been added to a sample of **2** (0.05 g, 0.6 mmol) in glyme at −30 °C, a second 1 equiv of HCl−etherate (0.6 mmol) was added and the mixture stirred for an additional 15 min at −30 °C. ^{11}B NMR analysis then indicated formation of a dichlorinated product, but attempts to isolate the product by solvent vacuum evaporation resulted in product decomposition. ^{11}B NMR (CD_3CN, ppm, J in Hz): −1.6 (d, J = 129, BH), −7.5 (t, J = 113, BH_2), −12.2 (t, J = 96, BH_2). The DFT/GIAO-calculated ^{11}B NMR shifts of the three possible isomers of $Cl_2B_3N_3H_{12}$ are given in Figure S5 in the Supporting Information (SI).

Computational Studies. DFT/GIAO/NMR calculations were performed using the *Gaussian 09* program.[9] Geometry optimizations were carried out at the B3LYP/6-311G(d) level. All ^{11}B NMR chemical shifts were calculated at the B3LYP/6-311G(d) level using the GIAO option in *Gaussian 09* and are referenced to BF_3−OEt_2 using an absolute shielding constant of 102.2 ppm. Frequency analyses were carried out to ensure that each minimized structure was a true minimum with no imaginary frequencies.

Collection and Reduction of Crystallographic Data. X-ray-quality crystals of **2Me** formed as the material was under high vacuum. Crystallographic data and structure refinement information are summarized in Table 1. The X-ray intensity data were collected on a Bruker APEXII CCD area detector employing graphite-monochromatized Mo Kα radiation. Rotation frames were integrated using *SAINT*,[10] producing a list of unaveraged F and $\sigma(F^2)$ values that were then passed to the *SHELXTL*[11] program package for further processing and structure solution on a Dell Pentium 4 computer. The intensity data were corrected for Lorentz and polarization effects and for absorption using *SADABS*.[12]

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Table 1. Crystallographic Data

	2Me
empirical formula	$C_3B_3H_{20}N_3$
fw	130.65
cryst class	monoclinic
space group	$P2_1/c$ (No. 14)
Z	4
a, Å	5.7671(4)
b, Å	16.7609(12)
c, Å	10.4260(8)
β, deg	103.302(4)
V, Å^3	980.76(12)
D_{calc}, Mg/m^3	0.885
μ, mm^{-1}	0.051
λ(Mo Kα), Å	0.71073
cryst size, mm	0.26 × 0.14 × 0.04
F(000)	296
2θ angle, deg	4.70−50.74
temperature, K	143(1)
hkl collected	$-6 \le h \le 6$, $-19 \le k \le 20$, $-12 \le l \le 12$
no. of measd reflns	26815
no. of unique reflns	1796 (R_{int} = 0.0207)
no. of param	163
R indices ($F > 2\sigma$)	R_1 = 0.0340, wR_2 = 0.0911
R indices (all data)	R_1 = 0.0375, wR_2 = 0.0945
GOF[b]	1.056
final difference peaks, e/Å^3	+0.185, −0.104

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$. [b] GOF = $\{\sum w(F_o^2 - F_c^2)^2/(n - p)\}^{1/2}$, where n = number of reflections and p = number of parameters refined.

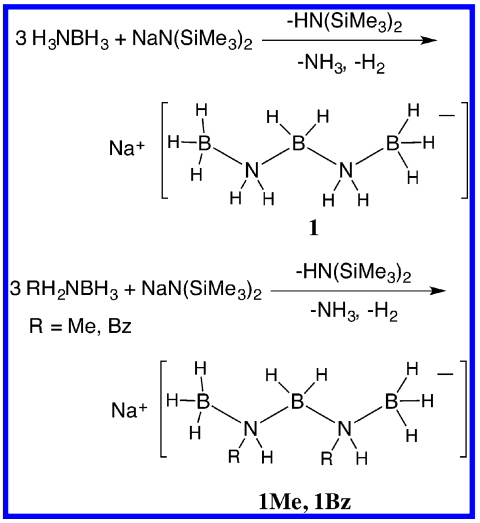
Solution and Refinement of the Structures. The structures were solved by direct methods (*SHELXS-97*[13]), and refinement was by full-matrix least squares based on F^2 also using *SHELXL-97*. All reflections were used during the refinement (values of F^2 that were experimentally negative were replaced with $F^2 = 0$). All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined isotropically.

RESULTS AND DISCUSSION

We recently demonstrated[14] that strong bases, such as bis(dimethylamino)naphthalene (Proton Sponge), can promote ammonia borane hydrogen release through anionic dehydropolymerization reactions. We proposed[5,14] that these reactions involve initial deprotonation to form $BH_3NH_2^-$, followed by reaction of this anion with another AB to form the $BH_3NH_2BH_3^-$ anion. This new anion can then react with successive equivalents of AB with H_2 elimination to produce $H_3BNH_2BH_2(NH_2BH_3)_x^-$ chains. Reaction of only 3 equiv of AB with VB (3 days at room temperature) allowed isolation (74% yield) and structural characterization of the $[VBH^+]$ salt of the $[BH_3NH_2BH_2NH_2BH_3^-]$ anion (**1**). It was further shown that **1** could be converted to both seven-membered linear and chain-branched anionic oligomers by reaction with an additional AB equivalent, thus providing strong evidence for the proposed anionic chain growth mechanism.[5]

We now report that **1** can be produced in both higher yields and larger scales with faster reaction times when NaHMDS is used as the base (Scheme 1). In a typical preparation, the reaction of 3 equiv of AB (33.0 mmol) with 1 equiv of NaHMDS (11.0 mol) in a fluorobenzene solution for 24 h at 50 °C gave a 96% isolated yield (10.8 mol) of salt **1**. The salt was largely insoluble in fluorobenzene and could be completely

Scheme 1. Syntheses of 1, 1Me, and 1Bz



precipitated from the reaction solution by the addition of toluene. **1** was isolated as an air-stable solid that was very soluble in glyme, *N*,*N*-dimethylformamide, and water and slightly soluble in acetonitrile and THF. Both the ^{11}B and ^{1}H NMR spectra of **1** were consistent with the previously reported values.[5]

VB proved to be inactive for inducing N-alkylated amine borane oligomerizations, but the reactions of methylamine borane and benzylamine borane with $^1/_3$ equiv of NaHMDS readily produced the **1Me** and **1Bz** (Scheme 1; R = CH_3, Bz) five-membered chains. **1Me** was obtained in an excellent 96% isolated yield, but **1Bz** was obtained in a much lower 49% yield owing to the formation of a side product, exhibiting a downfield (∼28 ppm) doublet resonance in its ^{11}B NMR spectrum characteristic of $(R_2N)_2BH$-type compounds.[15,16] Reaction of $(CH_3)_2NHBH_3$ with NaHMDS produced no oligomers, but instead gave a single product, again exhibiting a doublet ^{11}B NMR resonance near 28 ppm consistent with $(Me_2N)_2BH$ formation.[15,16]

1Me and **1Bz** are chiral compounds and are synthesized as mixtures of diastereomers. The DFT-optimized structures of **1** and the two possible diastereomers of **1Me** are shown in Figure 1, and their ^{11}B and ^{1}H NMR spectra are compared in Figures 2 and 3.

As reported,[5] the ^{11}B NMR spectrum (Figure 2a) of **1** consists of a triplet at −8.8 ppm and a quartet at −22.3 ppm in a 1:2 ratio. The spectra of **1Me** (Figure 2b) and **1Bz** (Figure S1 in the SI) are similar, but, as predicted by the DFT/GIAO chemical shift calculations, with peaks shifted slightly downfield relative to **1** as a result of the N-alkylation. The internal BH_2 protons of **1** appear as a single pentet at 1.78 ppm in its ^{1}H NMR spectrum, but because of **1Me** and **1Bz** both being diastereotopic mixtures, their internal BH_2 protons give rise to two peaks, at 1.62 and 1.35 ppm for **1Me** and at 1.85 and 1.77 ppm for **1Bz** (Figures 3 and S1 in the SI). Unlike the BH_2 protons, the CH_3 protons of **1Me** do not show diastereomeric differences but appear as a single doublet (split by the adjacent N−H) at 2.11 ppm.

While the cyclic dehydrotrimer of AB (CTB) has been known for decades,[17] no linear triborazanes have heretofore been reported. Nevertheless, we found that the parent triborazane **2** and its methyl derivative **2Me** were readily produced (Scheme 2) in 84 and 88% isolated yields by the

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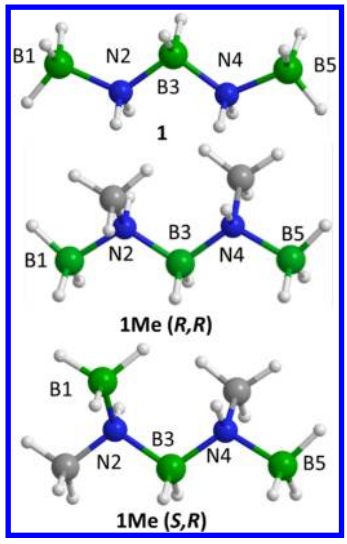


Figure 1. DFT-optimized [B3LYP/6-311G(d)] geometries of **1** and the *R,R*/*S,S* and *S,R* isomers of **1Me.**.

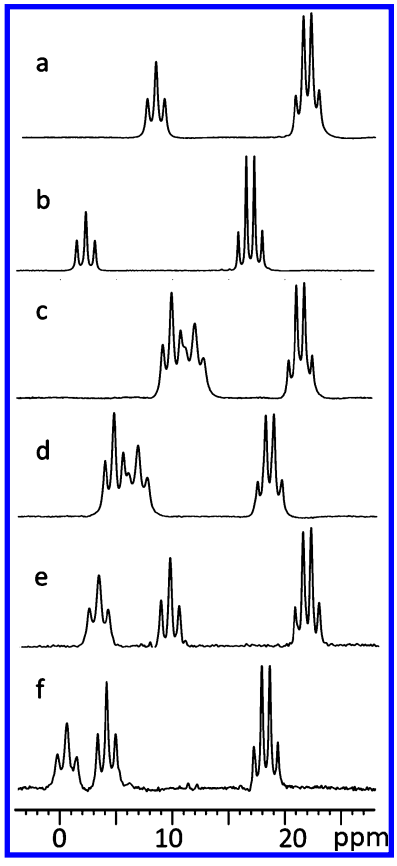


Figure 2. Comparisons of the ^{11}B NMR spectra of (a) **1**, (b) **1Me**, (c) **2**, (d) **2Me**, (e) **3**, and (f) **3Me**.

glyme solution reactions of **1** and **1Me** with NH_4Cl and CH_3NH_3Cl, respectively.

2 was soluble and stable in glyme and water at room temperature and slightly soluble in THF and acetonitrile. However, at even mildly elevated temperatures, **2** decomposed in ethereal solvents to give ^{11}B NMR spectra characteristic of trigonal B−O compounds (singlets, ∼18−20 ppm).[15] For the reaction of **1Me** with CH_3NH_3Cl, it was necessary to carefully monitor the reaction by ^{11}B NMR to determine the point at

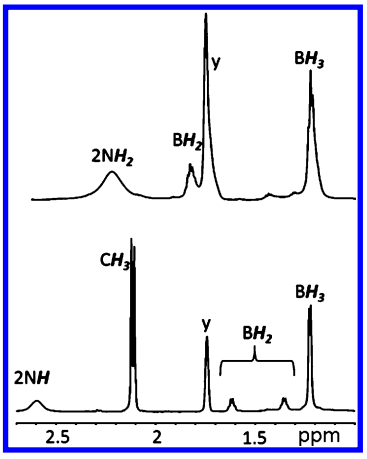
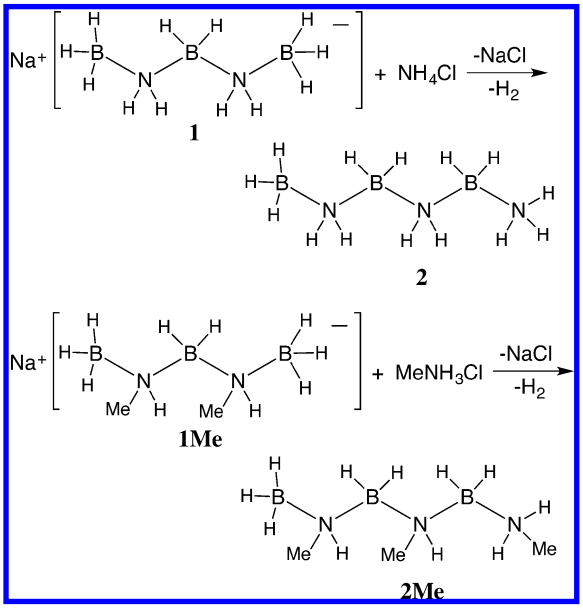


Figure 3. Comparison of the ^{1}H{^{11}B} NMR spectra of **1** (top) and **1Me** (bottom). y = residual protons in THF-d_8.

Scheme 2. Syntheses of 2 and 2Me



which the starting material was consumed (∼5−6 h) so that workup could be immediately undertaken. When **2Me** was allowed to remain in solution for longer periods, decomposition resulted to form a mixture of products that included methyldiborazane ($BH_3NH(CH_3)BH_2N(CH_3)H_2$)[4] and methylamine borane.

Similar reactions of the sodium borazane salts with other Lewis base hydrochlorides afforded base-capped borazane chains. For example, when pyridine−HCl was reacted with **1** and **1Me** in cold acetonitrile, H_2 and NaCl were quickly eliminated to form the pyridine-substituted derivatives **3** and **3Me** (Scheme 3). Similar capped aminoborane oligomers (L−$H_2BNH_2BH_3$) have been recently reported as the product of the reactions of Lewis bases with μ-aminodiborane.[18]

The DFT-optimized structures of **2** and **3** and the two possible diastereomers of both **2Me** and **3Me** are shown in Figures 4 and S2 in the SI. In agreement with their proposed linear structures, the ^{11}B NMR spectra (Figure 2c−f) of all of these compounds displayed two low-field triplets and a high-field quartet in 1:1:1 ratios with the resonances of **2Me** and **3Me** again shifted downfield, as predicted by the DFT/GIAO

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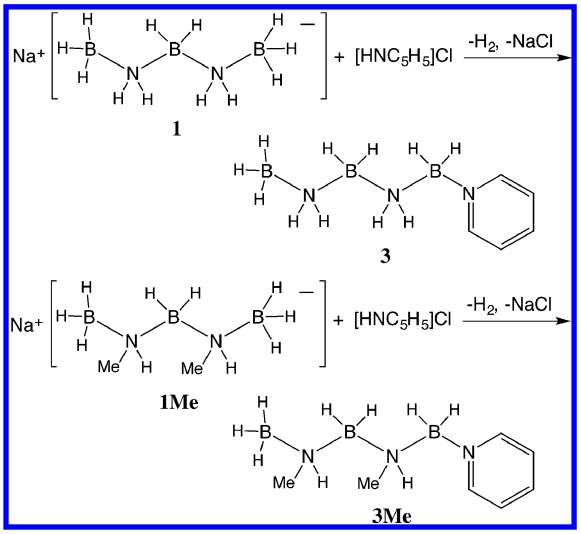
Scheme 3. Syntheses of 3 and 3Me



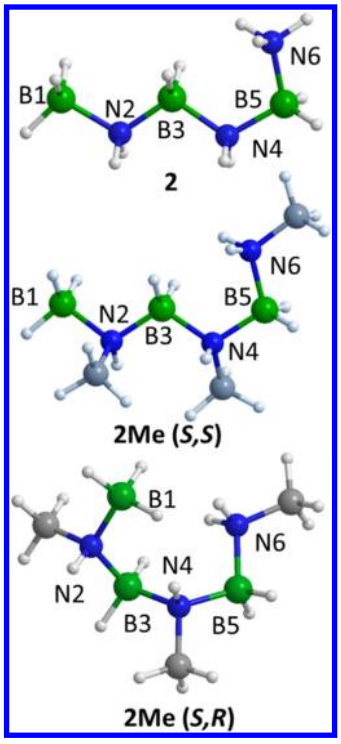


Figure 4. DFT-optimized [B3LYP/6-311G(d)] geometries of **2** and the *S,S*/*R,R* and *S,R* isomers of **2Me**.

chemical shift calculations, compared to those of **2** and **3**. The comparison of the ^{1}H NMR spectra of **3** and **3Me** in Figure 5 shows that the two sets of internal BH_2 resonances observed in **3** (at 2.87 and 1.79 ppm) became four resonances in the spectrum of **3Me**, owing to its synthesis as a diastereomeric mixture. However, despite the fact that **2Me** should also be a diastereomeric mixture, the expected two sets of BH_2 resonances were not resolved and only three CH_3 resonances were evident in its ^{1}H NMR spectrum (Figure S2 in the SI).

The proposed linear triborazane structure for **2Me** was confirmed by the crystallographic determination depicted in the ORTEP diagram in Figure 6. As discussed earlier, **2Me** is formed as a mixture of diastereomers with the structure in Figure 6 corresponding to the calculated *R,S* isomer shown in

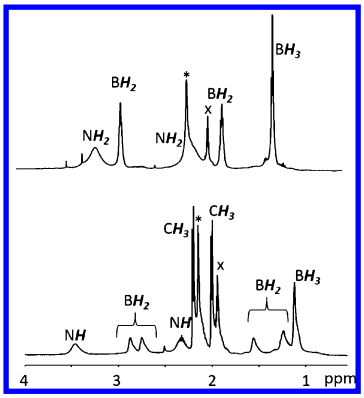


Figure 5. Comparison of the ^{1}H{^{11}B} NMR spectra of **3** (top) and **3Me** (bottom). * = residual H_2O; x = residual protons in CD_3CN.

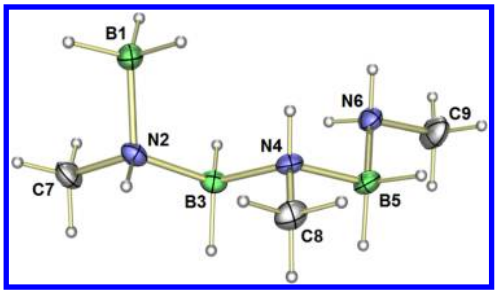


Figure 6. Crystallographically determined structure of **2Me** (*R,S*). Selected distances (Å) and angles (deg): B1–N2, 1.5838(13); C7–N2, 1.4820(13); N2–B3, 1.5819(13); B3–N4, 1.5766(13); C8–N4, 1.4845(12); N4–B5, 1.5749(13); B5–N6, 1.5898(14); N6–C9, 1.4820(13); B1–N2–C7, 111.58(8); B1–N2–B3, 115.65(7); C7–N2–B3, 108.45(8); N2–B3–N4, 111.06(7); B3–N4–C8, 112.24(8); C8–N4–B5, 108.90(7); B3–N4–B5, 112.68(7); N4–B5–N6, 108.41(7); B5–N6–C9, 113.43(8).

Figure 4. The N–B–N, B–N–B, and C–N–B angles (108–115°) are all consistent with sp^3 hybridization. In contrast to the structures of **1**[5] and $H_3BNH_2BH_2NH_3$,[3] where the B–N distances were greater at the terminal boron atoms (~1.59 Å) than at the internal boron atoms (~1.57 Å), the B–N lengths in **2Me** are reasonably homogeneous, averaging 1.581 Å. This value is similar to the B–N length in methylamine borane [1.587(3) Å][19] but longer than the 1.549 Å average B–N bond length reported for the methyldiborazane $H_3BN(CH_3)HBH_2N(CH_3)H_2$.[4]

Intermolecular dihydrogen bonding between hydridic B–H (δ^-) and protonic N–H (δ^+) hydrogen atoms has been shown to be important in many boron–nitrogen–hydrogen compounds, as characterized by B–H---H–N dihydrogen-bonding distances of ~1.7–2.2 Å and with H---H–N angles of 117–171°, usually larger than the B–H---H angles, 95–120°.[4,5,20] The ORTEP plot presented in Figure 7 shows the head-to-tail orientation of two chains that is adopted by **2Me** (*R,S*) in the solid state, with B1–H hydrogen atoms on each chain directed toward the N6–H or N4–H hydrogen atoms on the adjacent chain. The most significant interactions are between the N6–H6b and both B1–H1a and B1–H1c hydrogen atoms, with the H6b---H1a and H6b---H1c distances [2.06(2) and 2.20(2) Å] and the N6–H6b---H1a [151.7(11)°] and N6–H6b---H1c [150.5(11)°] angles, as well as the H6b---H1a–B1 [97.7(7)°] and H6b---H1c–Ba [90.9(8)°] angles, falling in the ranges indicated above for B–H---H–N bonding.[20]

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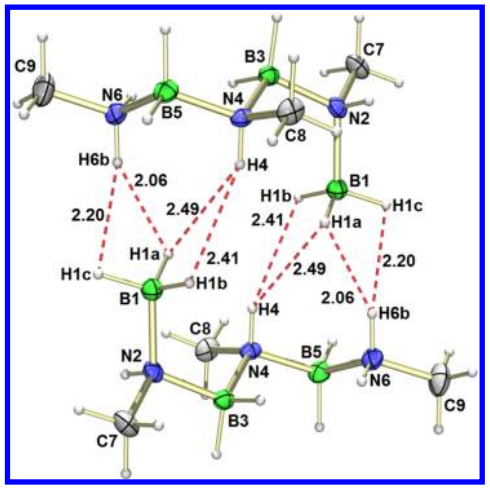


Figure 7. ORTEP drawing showing interchain dihydrogen interactions in **2Me** (*R*,*S*). Selected distances (Å) and angles (deg): H6b---H1a, 2.06(2); H6b---H1c, 2.20(2); H4---H1a, 2.49(2); H4---H1b, 2.41(2); N6–H6b---H1a, 151.7(11); H6b---H1a–B1, 97.7(7); N6–H6b---H1c, 150.5(11); H6b---H1c–B1, 90.8(8); N4–H4---H1a, 142.3(9); H4---H1a–B1, 98.0(7); N4–H4---H1b; 144.4(9); H4---H1b–B1, 102.7(7).

Despite the fact that the enthalpy of dehydrogenative cyclization of **2** to CTB was calculated to be −12.2 kcal/mol,[21] **2** is surprisingly thermally stable. The TGA measurements shown in Figure 8 showed that in the solid state **2**

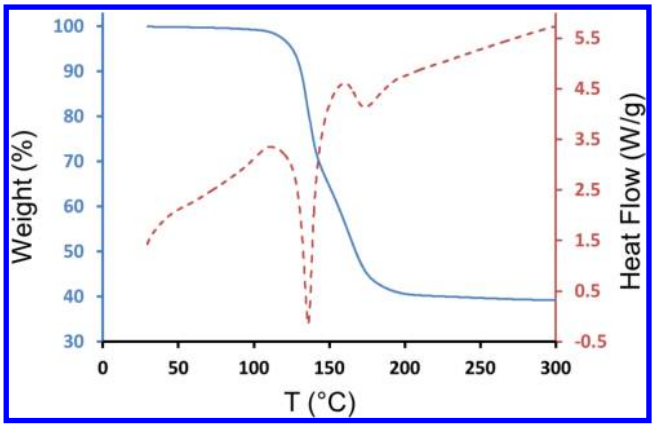
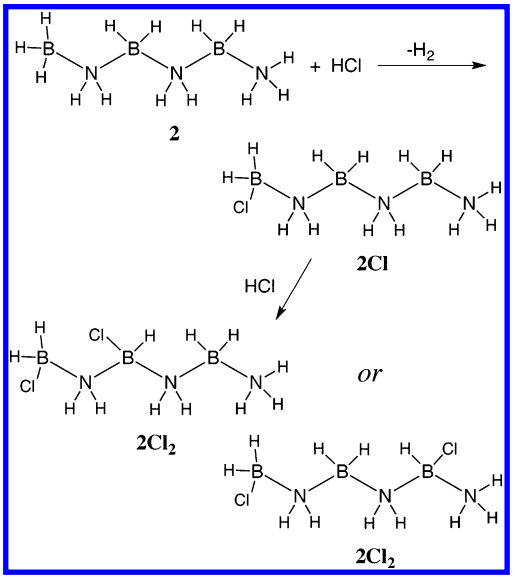


Figure 8. TGA (left axis, blue —) and DSC (right axis, red ---) analyses of **2**. Measurements were carried out on 2.32 mg of **2** under nitrogen with a ramp rate of 10 °C/min.

undergoes a two-step decomposition with an initial ∼30% weight loss beginning at ∼110 °C, followed by a second ∼30% loss beginning at ∼142 °C. Decomposition is complete by 200 °C, with an overall char yield of 39%. A complete conversion to boron nitride would correspond to an 84.2% char; thus, decomposition must involve the loss of molecular fragments larger than H_2. The apparent endothermic peak in the DSC at 135 °C and the overlapping exothermic process peaking at ∼160 °C most probably arise from a combination of **2** decomposition and decomposition-product evaporation/sublimation that is accompanying the initial weight loss. The second overlapping endothermic process near 170 °C could then result from further product evaporation/sublimation associated with the second weight loss event. The TGA of **2** is similar to that of AB, which showed an initial weight loss beginning at 110 °C, followed by a second loss with onset at 130 °C, and a final char yield of ∼45%.[22] The thermal behavior of **2** is notably different from that observed for CTB, which decomposes via three exothermic steps between 150 and 220 °C.[23] This difference suggests that **2** does not undergo cyclization to CTB during its solid-state pyrolysis, which is in agreement with recent computational work that predicted a high activation energy of cyclization (49.4 kcal/mol).[24]

In noncoordinating solvents, solutions of **2** heated to 80 °C also showed no trace of cyclization. After the solutions were held at 100 °C for 12 h in fluorobenzene, ^{11}B NMR analysis showed the formation of equivalent small amounts of CTB and AB but a larger amount of a white solid that, when dissolved in DMSO, was shown by ^{11}B NMR to contain **2**, oligomerized AB, and borohydride anion. Heating **2Me** at 100 °C in fluorobenzene similarly resulted in the formation of a ∼3:1 mixture of methylamine borane and *N*-methylcyclotriborazane (Scheme 4).[4b,c]

Scheme 4. Chlorination Reactions of 2



Recently, Shore et al. reported the synthesis of NH_3BH_2Cl via the treatment of AB with anhydrous HCl at −40 °C. He then showed that the reaction of NH_3BH_2Cl with sodium amide produced CTB.[25]

The reaction of **2** with 1 equiv of HCl in glyme at −30 °C yielded a product (**2Cl**) that exhibited three triplets in its ^{11}B NMR spectrum (Figure 9b), with the disappearance of the quartet in the spectrum of **2** and the emergence of a new triplet at −6.6 ppm consistent with terminal-boron chlorination. The DFT/GIAO-calculated shifts also strongly support the formation of a 1-$ClBH_2(NH_2BH_2)_2NH_3$ product. When a second 1 equiv of HCl was added to a glyme solution containing **2Cl** at −30 °C, ^{11}B NMR showed the disappearance (Figure 9c) of the higher field triplet resonance and the emergence of a new doublet at −1.6 ppm with the new doublet–triplet–triplet pattern (Figure S4b in the SI) possible for any of the 1,1-, 1,3-, and 1,5-$Cl_2B_3N_3H_{12}$ dichlorinated products. A comparison of the experimentally observed shifts for these resonances with the DFT/GIAO-calculated ^{11}B NMR chemical shifts for each isomer (Figure S5 in the SI) ruled out formation of the 1,1-dichlorinated product, but the predicted shifts for the 1,3 and 1,5 derivatives are nearly coincident and thus either product is possible. Reactions with additional

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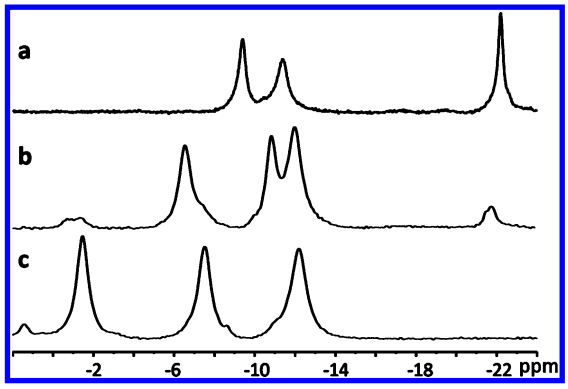

Figure 9. $^{11}B\{^{1}H\}$ NMR spectra of (a) **2**, (b) **2** after reaction with 1 equiv of HCl, and (c) **2** after reaction with 2 equiv of HCl. The ^{1}H-coupled ^{11}B NMR spectra corresponding to parts b and c are given in Figure S4 in the SI.

equivalents of HCl led to the formation of complex mixtures of polychlorinated derivatives. Unfortunately, these products could not be further characterized because they rapidly decomposed when their solutions were concentrated or warmed to room temperature.

Chlorination of the terminal boron in **2Cl** might be expected to facilitate its cyclization via the elimination of HCl. However, when allowed to come to room temperature, **2Cl** decomposed not to CTB but rather to a white insoluble material, suggesting intermolecular HCl elimination to form longer insoluble aminoborane oligomers. Likewise, as opposed to the cyclization observed in the treatment of NH_3BH_2Cl with sodium amide,[25] the treatment of **2Cl** with sodium amide led to chain fragmentation.

In summary, the improved synthetic method reported herein employing the reactions of NaHMDS with amine boranes now provides an efficient high-yield method for the syntheses of the sodium salts of the anionic five-membered aminoborane chains $[BH_3N(R)HBH_2N(R)HBH_3^-]$, where R = H, Me, and Bz. The reactions of the R = H and Me anions with ammonium chlorides also provide high-yield routes to the previously unknown linear triborazanes **2** and **2Me**, as well as the corresponding linear pyridine-capped chains **3** and **3Me**. The isolation and ready availability of these new linear aminoborane chains will undoubtedly make them useful as new starting materials and/or intermediate models for the numerous ongoing studies into the growth of aminoborane polymers via the dehydropolymerization reactions of amine boranes.

■ ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data in CIF format, figures of DFT-optimized geometries, tables of the coordinates and energies of all DFT-optimized structures, the ^{1}H NMR spectrum of **2Me**, the ^{1}H and ^{11}B NMR spectra of **1Bz**, and the proton-coupled ^{11}B NMR spectra for Figure 9. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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