Supporting Information

Facile Synthesis of Aminodiborane and Inorganic Butane Analogue NH$_3$BH$_2$NH$_2$BH$_3$

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Experimental.

All manipulations were carried out using a high vacuum line or in a nitrogen-filled glovebox or a nitrogen-filled glove bag. The ^{1}H and ^{1}H{^{11}B} NMR spectra were recorded on 500 MHz spectrometers and referenced to residual solvent protons. The ^{11}B and ^{11}B{^{1}H} NMR spectra were obtained at 160 MHz and externally referenced to BF$_3$·OEt$_2$ in D$_6$C$_6$ (δ = 0.00 ppm). Infrared (IR) spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer with 2 cm^{-1} resolution. Tetrahydrofuran (THF) and toluene were dried over sodium/benzolphenone and freshly distilled prior to use. Celite was dried overnight at 150 °C under a dynamic vacuum. Ammonia (Matheson), ammonia borane **2** (GFS Chemicals), and THF borane **3** (Aldrich) were used as received. Crystalline 18-crown-6 ether was purchased from Aldrich, ground to powder and dried over P$_2$O$_5$ in a vacuum for 5 days. Dry THF was condensed onto dry 18-crown-6. The mixture was warmed to room temperature, stirred for 10 min, and THF was evaporated under a dynamic vacuum. THF replacement was repeated twice, after which there was no observable water signal in the ^{1}H NMR spectrum of the crown ether.

Synthesis of Aminodiborane NH$_2$B$_2$H$_5$ 1.

Aminodiborane **NH$_2$B$_2$H$_5$ 1** was prepared on a variety of scales. In a typical large scale procedure, 10 g (0.32 mmol) ammonia borane **2** was loaded to a 500 ml flask with 300 ml (0.3 mmol) 1M THF borane **3** solution in a nitrogen-filled glove bag. Gas (presumably hydrogen, not measured) was produced while the mixture was stirring at room temperature. The reaction was monitored by ^{11}B NMR spectra. When the conversion rate reached ~90% based upon the integration of boron signals in the ^{11}B NMR spectra, the reaction was stopped and the mixture was filtered to remove a small amount of white precipitate. Most of **3** and solvent THF were

removed from the filtrate through fractionally condensation. The residual solution, ca. 40 ml, was evaporated by a dynamic vacuum and condensed into a flask which was submerged in an isopropyl alcohol/dry ice bath (-78 °C). A small amount of residual solvent was separated from a crystalline solid. The solid melted when warmed to room temperature (27 ml, yield 70 %). The liquid was identified as **1·THF** using ^{1}H NMR spectra. ^{1}H NMR (d_8-Toluene, 500 MHz): δ 3.47 (*m*, 4α-H of THF), 2.97 (*br t*, 2H of NH_2, J_{N-H} = 52.5 Hz), 1.52 (*m*, 4β-H of THF), 1.70~0.80 (*br m*, 4H of 2 BH_2, overlap with β–H of THF), -0.19 (*br s,* 1H of BHB) ppm. ^{1}H{^{11}B} NMR (d_8-Toluene, 500 MHz) δ 3.47 (*m*, 4α-H of THF), 2.97 (*br t*, 2H of NH_2), 1.51 (*m*, 4β-H of THF), 1.28 (*br s*, 4H of 2 BH_2), -0.21 (*br s*, 1 BHB) ppm. ^{11}B (d_8-Toluene, 160 MHz) δ -27.1 (br t) ppm. ^{11}B{^{1}H} (d_8-Toluene, 160 MHz) δ -27.1 (s) ppm (Figures S1 and S2). IR (toluene solution), ν(N-H): 3441(s), 3421(s, sh), 3350, (s, sh), 3397(s), 3254(s); ν(B-H): 2586(m, sh), 2557(s), 2520(s, sh), 2480(s, sh), 2470(s), 2455(s, sh), 2413(m), 2360(m), 2346(m), 2334(m), 2312(m) cm^{-1}.

Aminodiborane THF solution **1·THF** is unstable in air and it hydrolyzes very quickly in water.

Synthesis of an Adduct of 18-Crown-6 with Aminodiborane $C_{12}H_{24}O_6$·2NH$_2$B$_2$H$_5$ 5

A 10 ml THF solution of **1·THF** (0.11g, 1.0 mmol) was prepared and 0.13g (0.5 mmol) of 18-crown-6 was added to the solution in a dry box. The mixture was stirred for 5 min and filtered. X-ray quality crystals of **5** were obtained by slowly evaporating the THF from the filtrate.

Synthesis of Aminoborane Analogue of Butane, NH$_3$BH$_2$NH$_2$BH$_3$ 4

In a dry box, a 50 ml flask was charged with **1·THF** (1.95g, 17 mmol). The flask was connected to a vacuum line and ca. 15 ml toluene was condensed into it. A very rapid reaction was initiated when ammonia was bubbled into the flask at 0 °C. A white precipitate formed immediately and the reaction was followed by the ^{11}B NMR. The white solid was isolated by filtration, washed three times by toluene and dried overnight under a dynamic vacuum (yield 0.91 g, 90%). ^{1}H NMR (d_8-THF, 500 MHz) δ 4.57 (*br t*, 3H of NH_3), 2.35 (*br t*, NH_2), 2.35~1.73 (q, BH_2, overlap with NH$_2$ and β-H of THF), 1.58~1.03 (q, 3 H of BH_3, J_{B-H} = 92 Hz) ppm. ^{1}H{^{11}B} NMR (d_8-THF, 500 MHz) δ 4.57 (*br t*, 3H of NH_3), 2.34 (*br t*, 2H of NH_2), 2.06 (sextet, 2H of BH_2, $^3J_{H-H}$ = 5 Hz), 1.30 (*t*, 3H of BH_3, $^3J_{H-H}$ = 5 Hz) ppm. ^{11}B (d_8-THF, 160 MHz) δ -11.6 (*t*, BH_2, J_{B-H} = 103 Hz), -22.8 (q, BH_3, J_{B-H} = 92 Hz) ppm. ^{11}B{^{1}H} (d_8-THF, 160 MHz) δ -11.6 (*s*, BH_2), -22.8 (*s*, BH_3) ppm (Figures S3 and S4). IR (KBr): ν(N-H): 3313(s), 3293(s), 3274(s), 3241(s), 3212(m), 3176(m); ν(B-H): 2448(m,sh), 2388(s), 2370(s), 2317(s), 2290(s), 2208(m,sh) cm^{-1}.

The inorganic butane analogue **4** is less stable than ammonia borane, but it is stable enough not to catch fire when exposed to moist air. It is unstable in solutions.

Synthesis of an Adduct of 18-Crown-6 with 4, $C_{12}H_{24}O_6 \cdot N_2B_2H_{10}$ 6

A 10 ml THF solution of **4** (0.175 g, 0.5 mmol) was prepared and 0.13 g (0.5 mmol) of 18-crown-6 was added to the solution in a dry box. The mixture was stirred for 5 min and filtered. X-ray quality crystals of **6** were obtained by slowly evaporating the THF from the filtrate.

X-Ray Crystallography

Details of X-ray single crystal diffraction data and a summary of the intensity data collection parameters for **5** and **6** are listed in Table S1. Crystal structure data were collected on a Nonius Kappa CCD diffraction system, which employs graphite-monochromated Mo K_α radiation (λ = 0.71073 Å). Single crystals of **5** and **6** were mounted on the tips of glass fibers coated with Fomblin oil (pentafluoropolyether). Unit cell parameters were obtained by indexing the peaks in the first 10 frames and refined by employing the whole data set. All frames were integrated and corrected for Lorentz and polarization effects using the DENZO0SMN package (Nonius BV, 1999).[1] Absorption correction for the structures was accounted for using SCALEPACK. The structures were solved by direct methods and refined using the SHELXTL-97 (difference electron density calculations and full-matrix least-squares refinements) structure solution package.[2] Hydrogen atoms bonded to nitrogen and boron were located and refined isotropically and all non-hydrogen atoms were located and refined anisotropically. The hydrogen atoms of the 18-crown-6 ether were calculated assuming standard geometries. The structures of **5** and **6** are shown in Figures S5 and S6.

In the **4** moiety of **6**, the H–H distance of 2.50 Å observed between N–H and B–H in the terminal groups is slightly larger than the sum of two van der Waals radii of hydrogen, but the distance would fall within the range of dihydrogen bonds after applying a correction for the N–H and B–H bonds that always appear shorter in crystal structures obtained from X-ray diffraction than those from neutron diffraction. The correction would make the H–H distance 0.1-0.15 Å shorter. In addition, the 2.50 Å H–H distance reported here is for **4** in the adduct of **6**. The actual H–H distance in pure **4** without the crown ether should be shorter when the NH_3 group is not bonded to the crown ether in **6** thus would form a stronger dihydrogen bond with the terminal BH_3 group of **4**. The calculated dihydrogen bond distance in **4** is 1.925 Å.[3] This weak dihydrogen bond between N–H and B–H results in the formation of the gauche form of **4** instead of the anti-form.

Comparison with Theoretical Predictions

Electronic structure calculations[4,5] using various models with different degrees of accuracy showed that the reaction between NH_3BH_3 **2** and BH_3 may go through different transition states and forms either $BH_2BH_2 + H_2 + BH_3$ or $NH_2B_2H_5 + H_2$ as the final products. The calculations predicted $NH_2B_2H_5 + H_2$ as the most stable products.

Another study by Nutt and McKee[3] using density functional theory (DFT) calculations showed the reaction between $NH_2B_2H_5$ and NH_3 may follow three different pathways to two different products (Figure S7). Our reaction at 0 °C ended with the formation of the chain compound $NH_3BH_2NH_2BH_3$ **4** (A2 in their article) as a white solid without further reactions to

form the predicted final products. The calculations showed the enthalpy and the free energy of the reaction $NH_2B_2H_5 + NH_3 \rightarrow NH_3BH_2NH_2BH_3$ (A2) at room temperature to be –8.1 and +1.6 kcal/mole respectively, which would indicate the reaction is thermodynamically slightly unfavorable based on the DFT calculations. It is noted that the free energy value is well within the accuracy of DFT calculations. The fact our Reaction 2 took place very quickly at 0 °C indicates that the free energy of this reaction has to be negative.

Table S1. Crystallographic data and structure refinement details for $C_{12}H_{24}O_6 \cdot 2NH_2B_2H_5$ **5** and $C_{12}H_{24}O_6 \cdot N_2B_2H_{10}$ **6**.

formula	$C_{12}H_{38}B_4N_2O_6$ **5**	$C_{12}H_{34}B_2N_2O_6$ **6**
fw	349.68	324.03
T (K)	150(2)	150 (2)
λ (Å)	0.71073	0.71073
cryst syst	Triclinic	Orthorhombic
space group	$P\bar{1}$	$P2_12_12_1$
a, (Å)	8.499(2)	8.872(2)
b, (Å)	8.572(2)	11.618(2)
c, (Å)	8.883(2)	18.212(2)
α, (deg)	117.05(3)	90
β, (deg)	97.77(3)	90
γ, (deg)	107.32(3)	90
V, ($Å^3$)	521.6(2)	1877.2(6)
Z	4	4
D_{calc}, (g/cm^3)	1.113	1.147
μ (mm^{-1})	0.081	0.087
F(000)	192	712
cryst size (mm)	$0.19 \times 0.15 \times 0.15$	$0.35 \times 0.27 \times 0.27$
2θ range, (deg)	2.65-24.94	2.55-25.01
reflns collected	3530	3319
indep reflns/R_{int}	1821/0.0190	3319/0.0001
params	185	240
GOF on F^2	1.032	1.040
R_1, wR_2 [I>2σ(I)]	0.0458, 0.1143	0.0318, 0.0810
R_1, wR_2 (all data)	0.0652, 0.1278	0.0373, 0.0847
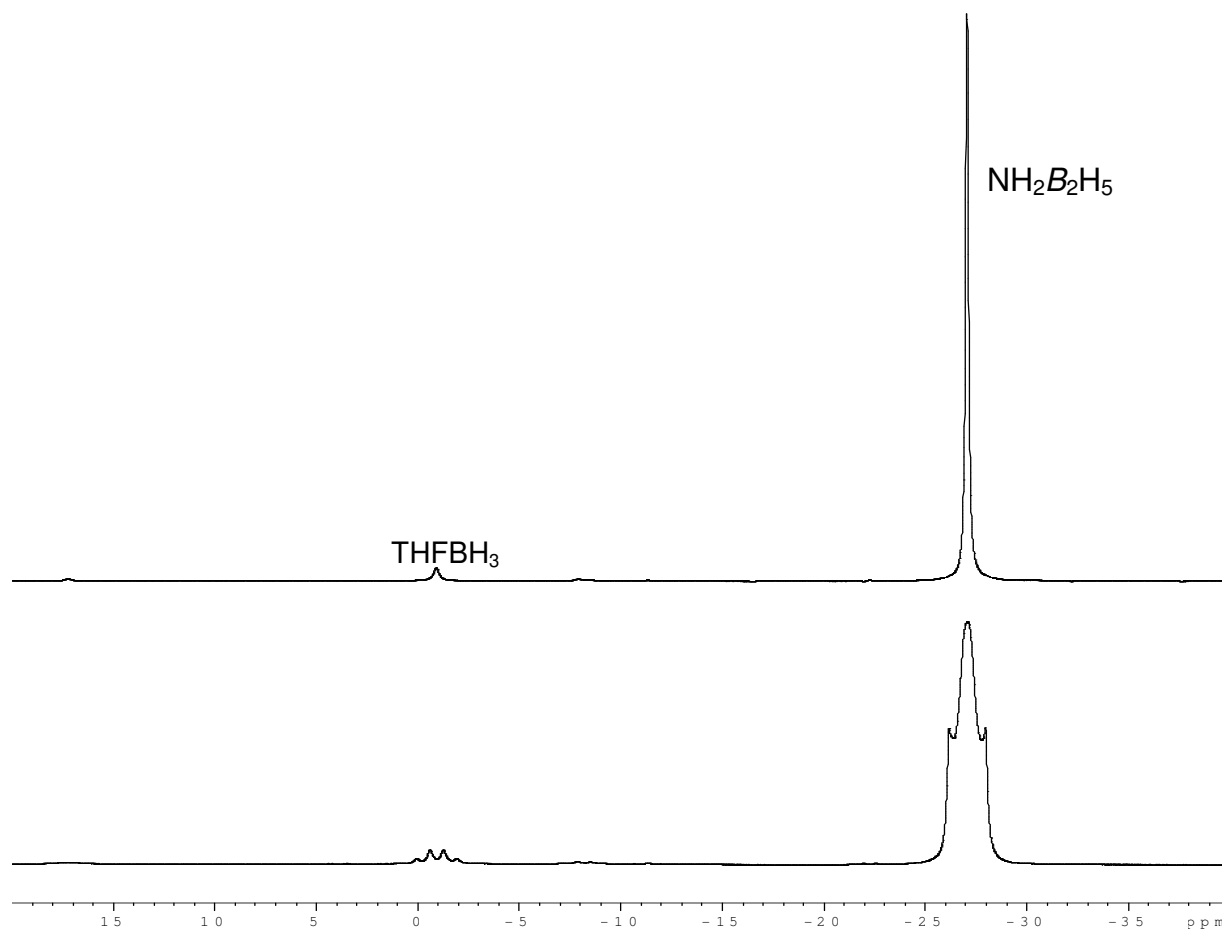
Figure S1. ^{11}B (bottom) and $^{11}B\{^1H\}$ (top) NMR spectra of $NH_2B_2H_5 \cdot THF$ (**1·THF)** in d_8-Toluene.
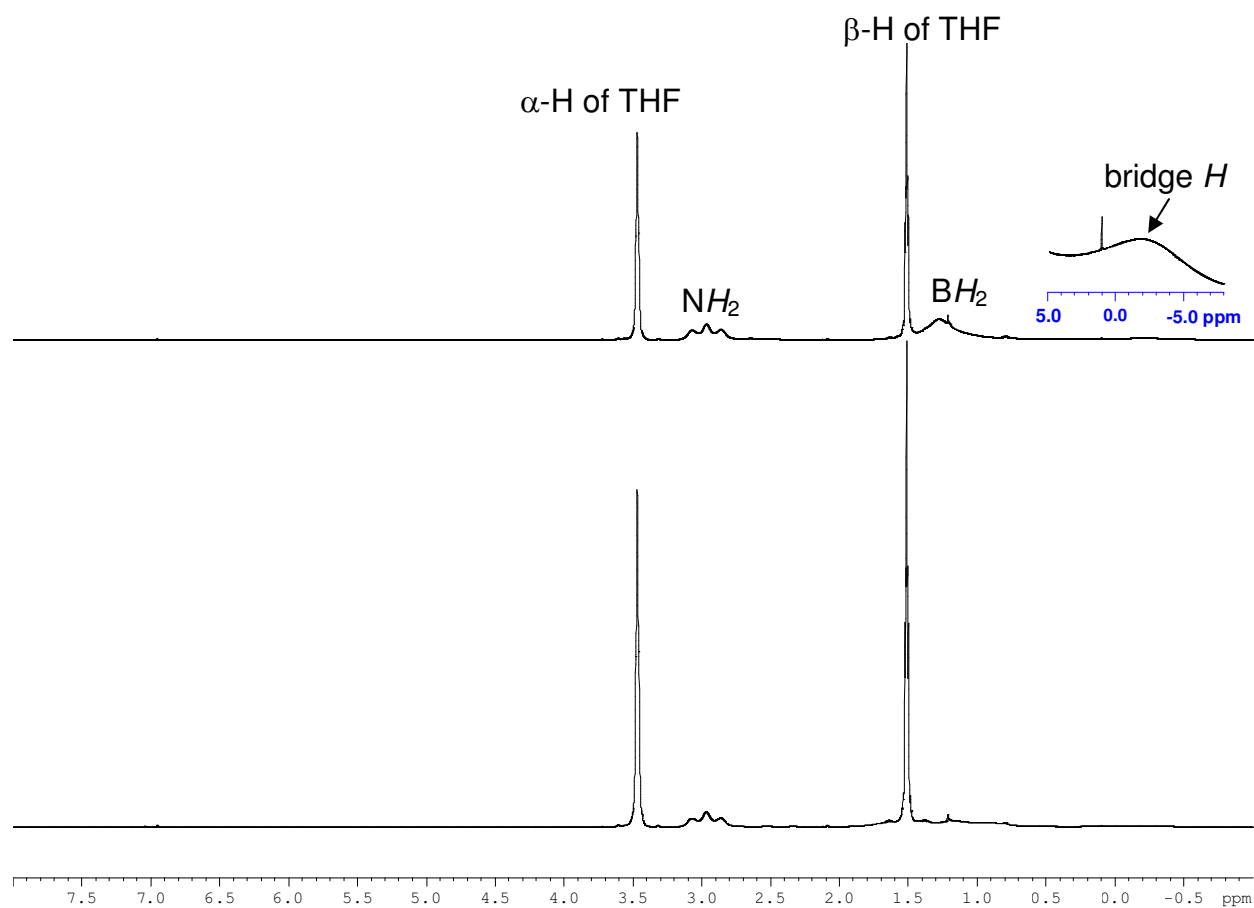
Figure S2. ^{1}H (bottom) and ^{1}H{^{11}B} (top) NMR spectra of $NH_2B_2H_5 \cdot THF$ (**1·THF)** in d_8-Toluene.
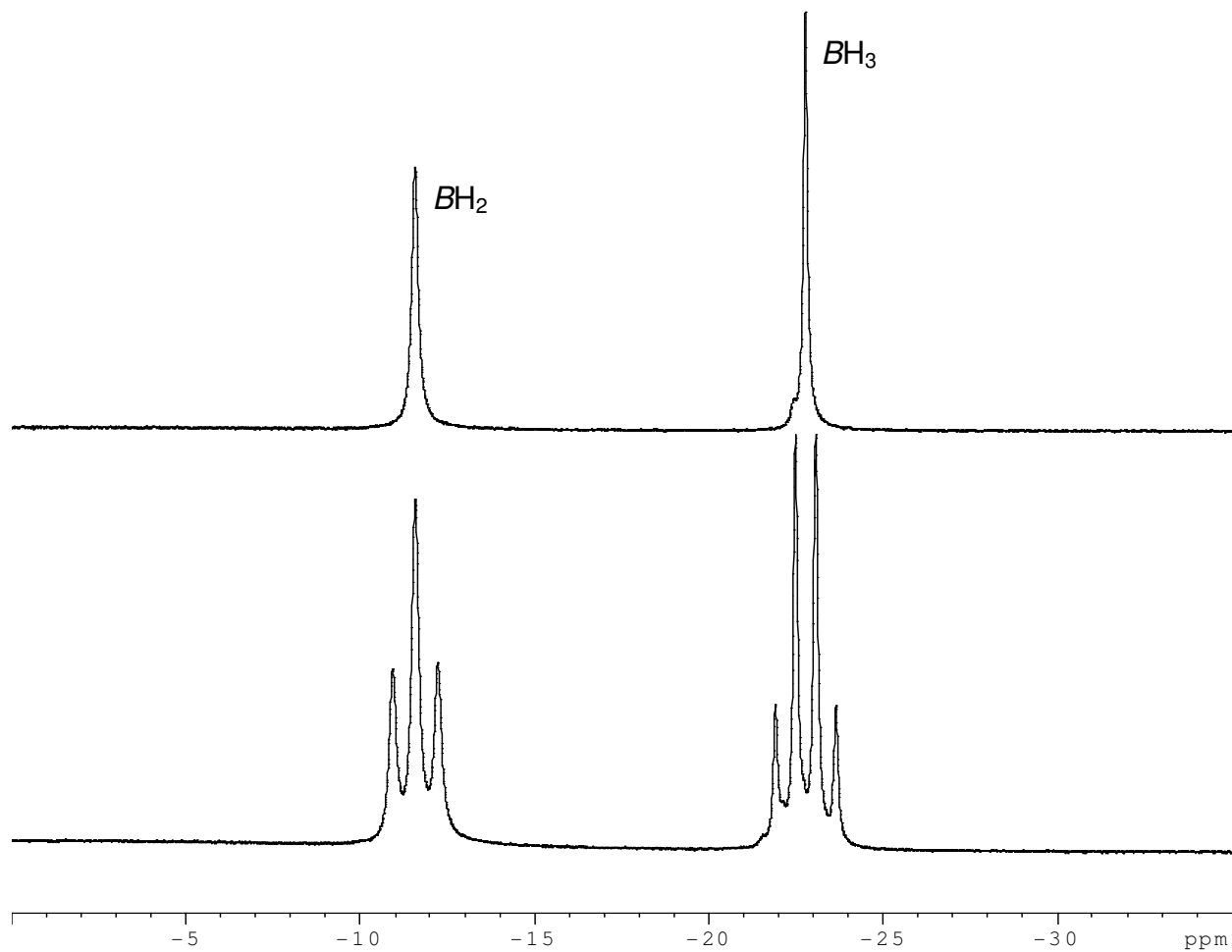
Figure S3. ^{11}B (bottom) and ^{11}B{^{1}H} (top) NMR spectra of $NH_3BH_2NH_2BH_3$ **4** in d_8-THF.
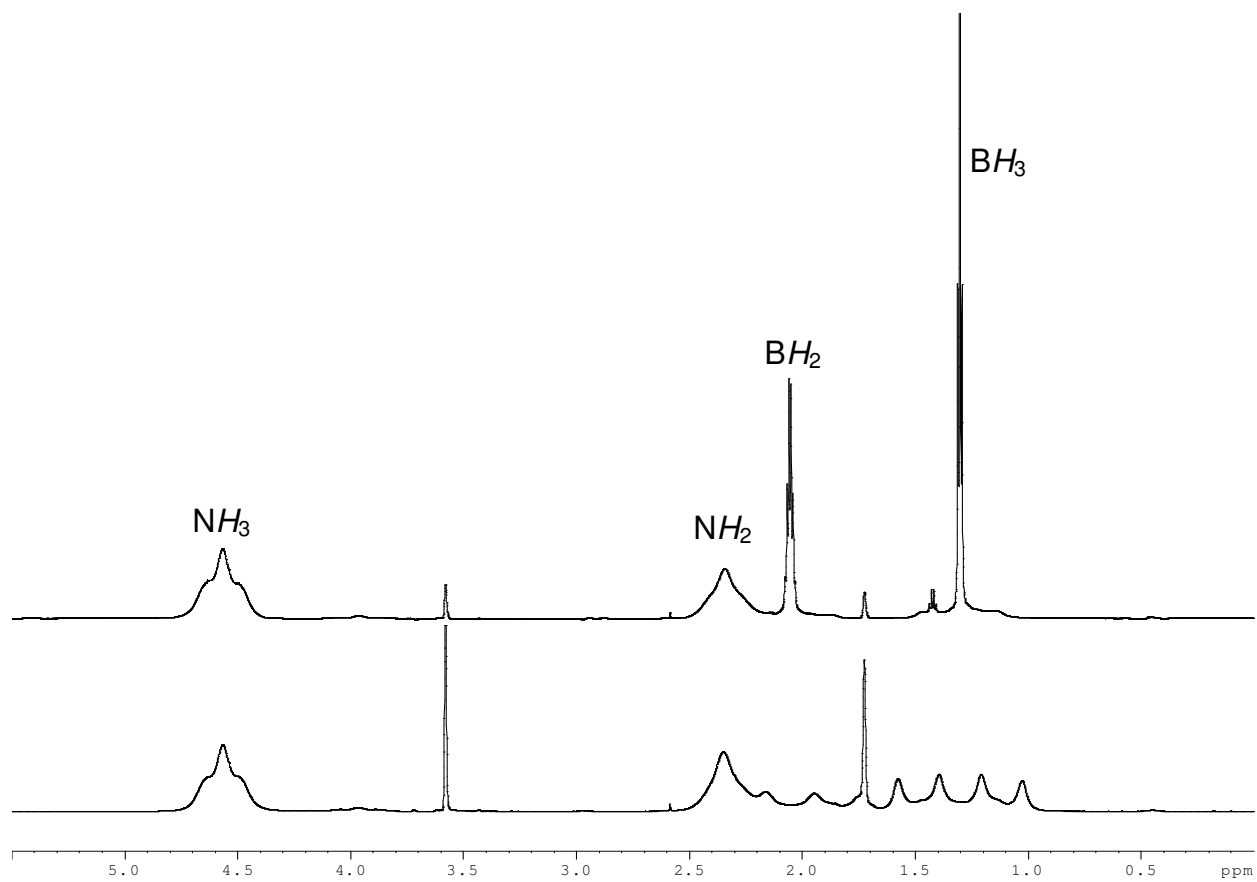
Figure S4. ^1H (bottom) and $^1H\{^{11}B\}$ NMR (top) spectra of $NH_3BH_2NH_2BH_3$ **4** in d_8-THF.
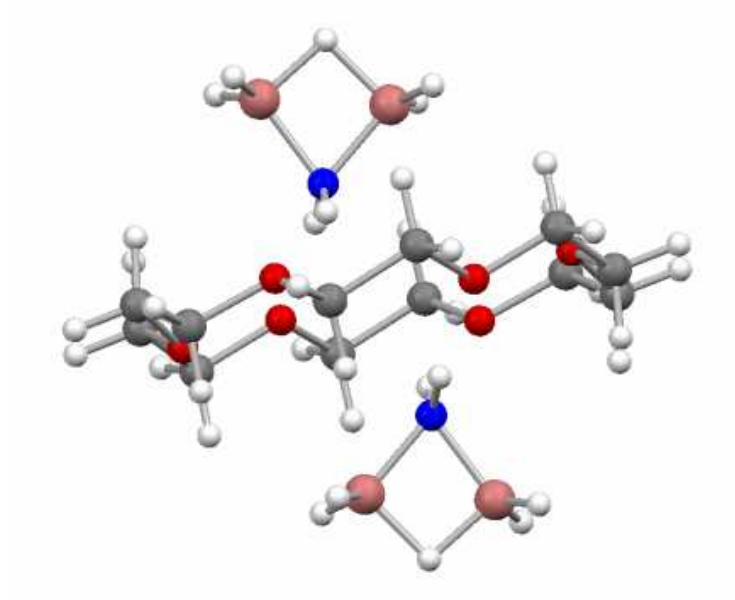
A
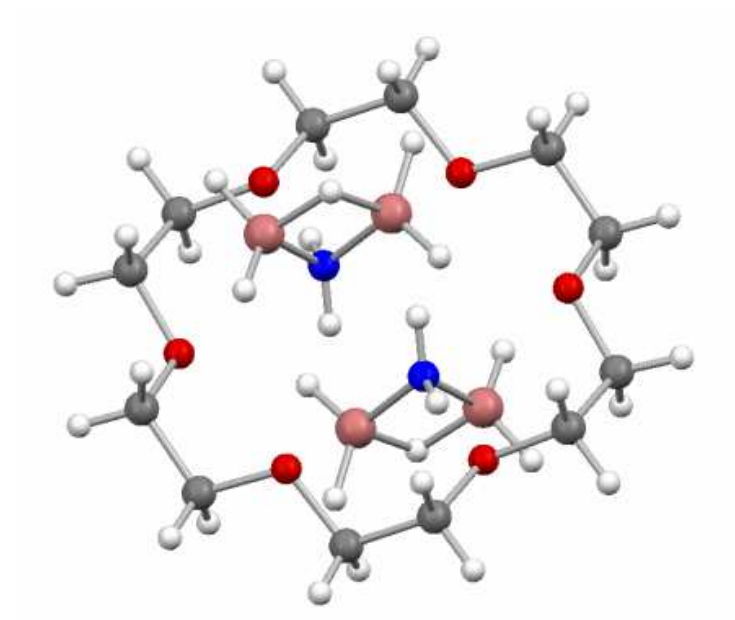
B

Figure S5. (**A** – top view and **B** – side view) Structure of $C_{12}H_{24}O_6 \cdot 2NH_2B_2H_5$ **5**.
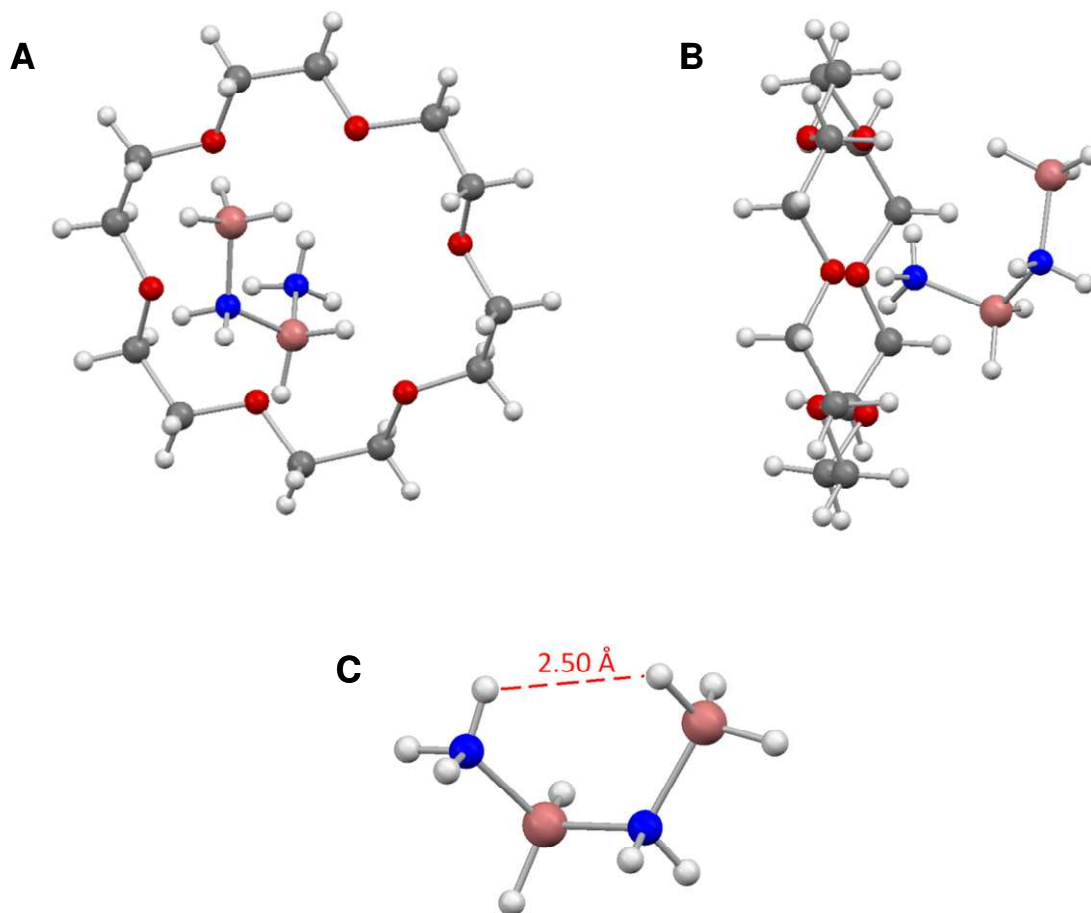
Figure S6. Structure of $C_{12}H_{24}O_6 \cdot N_2B_2H_{10}$ **6** (**A** and **B** – adduct of **4** and the 18-crown-6 ether viewed from two orientations; **C** – gauche conformer of **4**).
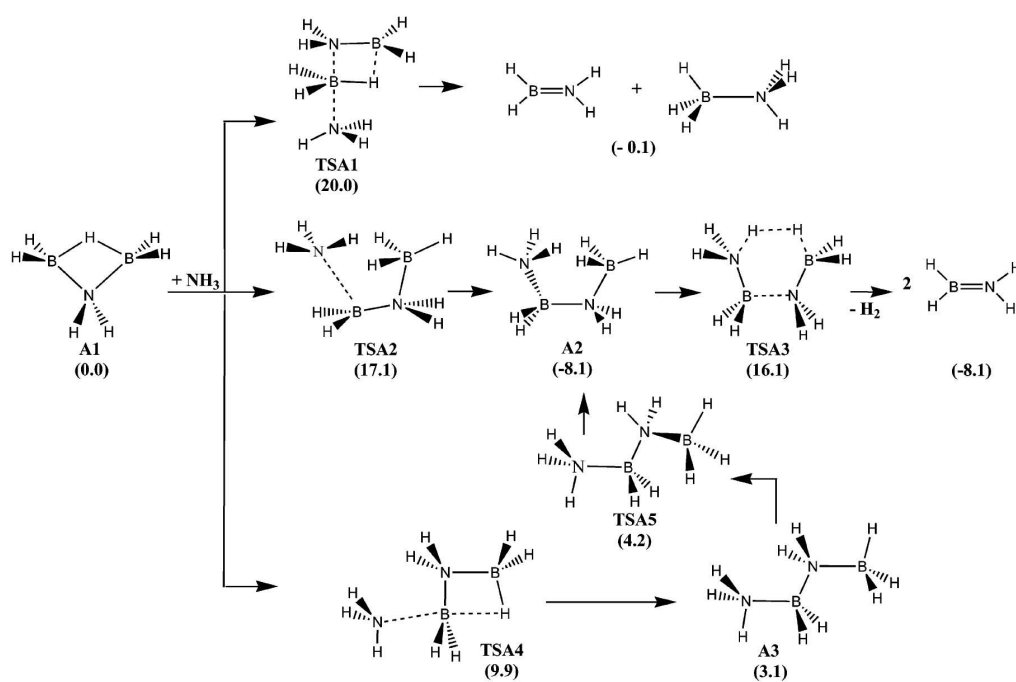
Figure S7. Predicted pathways of the reaction between $NH_2B_2H_5$ **1** and NH_3 based on density functional theory (DFT) calculations.[3] Enthalpies (kcal/mol) are relative to $NH_2B_2H_5$ + NH_3 at 298.15 K. The reaction depicted in Reaction 2 ends with the formation of the inorganic chain compound $NH_3BH_2NH_2BH_3$ **4** (A2 in this figure) without further reactions at 0 °C.

References

(1) Otwinowsky, Z; Minor, W. *Processing of X-Ray Diffraction Data Collected in Oscillation Mode.* In *Macromolecular Crystallography, Part A*, Carter, Jr., C.W.; Sweet, R. M. Eds. *Methods in Enzymology 276*, Academic Press, New York, 1997, p. 307.
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