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Electronic Supplementary Information

Lewis Base Assisted B-H Bond Redistribution in Borazine and Polyborazylene

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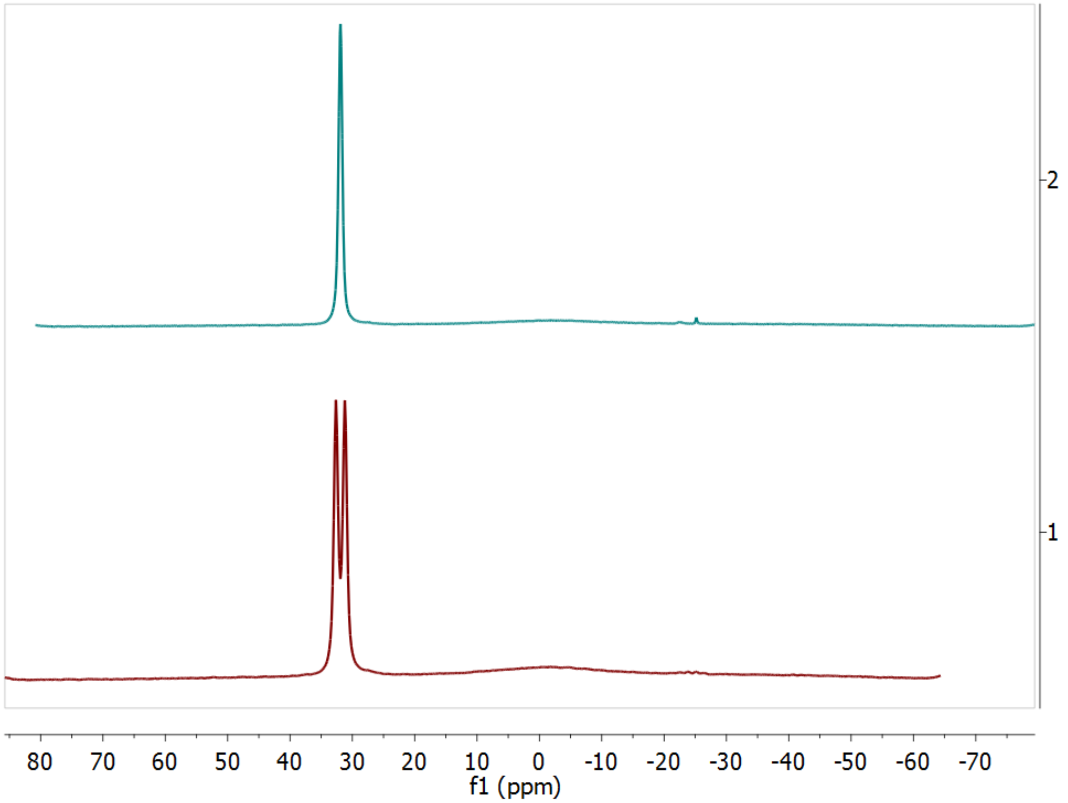
General

All reactions were performed under an inert atmosphere, using standard Schlenk line and glovebox techniques. Ethereal solvents were distilled from Na/benzophenone ketyl radical. Anhydrous NH_3 (Scott), borazine (Gelest, ^{11}B NMR spectra below), and ND_3 (Aldrich-Isotec, 99 atom % D; company certification – air: 400 ppm, CO_2: < 15 ppm, CH_4: < 15 ppm) were used as received. Ammonia borane (AB) was purchased from JSC Aviobor, dissolved in distilled THF, filtered thru a fine porosity frit to remove insolubles, and precipitated rapidly with hexanes. Polyborazylene (PB) was obtained from two sources 1) by extracting a container of Gelest borazine (that went unrefrigerated for several months) with distilled THF, then removing the solvent/volatiles under reduced pressure (this is the same PB used in reference 7) and 2) from an Fe(mirror) catalyzed dehydrocoupling of AB at Ottawa (details below). All spectra shown utilize the first source of PB unless explicitly detailed. Sodium tetraphenylborate was obtained from Aldrich and dried under vacuum overnight. ^{11}B (160 MHz) NMR spectra were recorded at 298K (unless otherwise noted) on Bruker Avance 300, 400, and 500 MHz spectrometers.



^{11}B and $^{11}B\{^1H\}$ NMR of Gelest borazine dissolved in C_6D_6

Experiments

Reaction of borazine in pyridine (neat):

Borazine (10 μL) was dissolved deuteropyridine (~500 μL) and heated to 90 °C in a NMR tube. After 23 h the tube was removed from the heat source and examined by ^{11}B NMR (128 MHz).

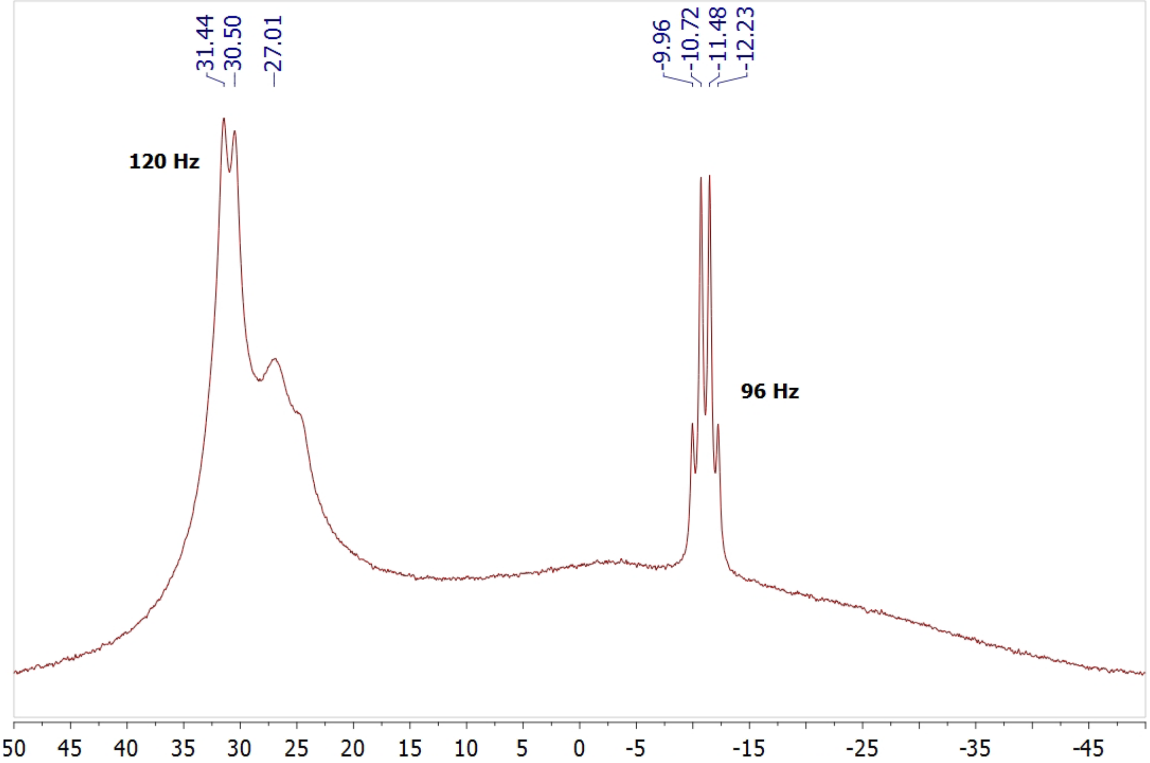


Figure S1 ^{11}B NMR (proton coupled) Products after heating borazine in neat pyridine @ 90 °C for 23h

Reaction of borazine in NH_3:

Borazine (10 μL) was injected into a cold high pressure NMR tube (-40 °C). This tube was quickly capped, removed from the glovebox, and immersed in 4-5 cm of a -90 °C bath. The NMR tube was attached to the Schlenk line and bottom 4-5 cm placed in a -196 °C bath. After ~5 min, the headspace was evacuated. Once equilibrium vacuum was achieved, NH_3 (~300 μL) was condensed into the tube. Within 5 minutes of thawing, the colorless solution was examined by ^{11}B NMR (96 MHz).

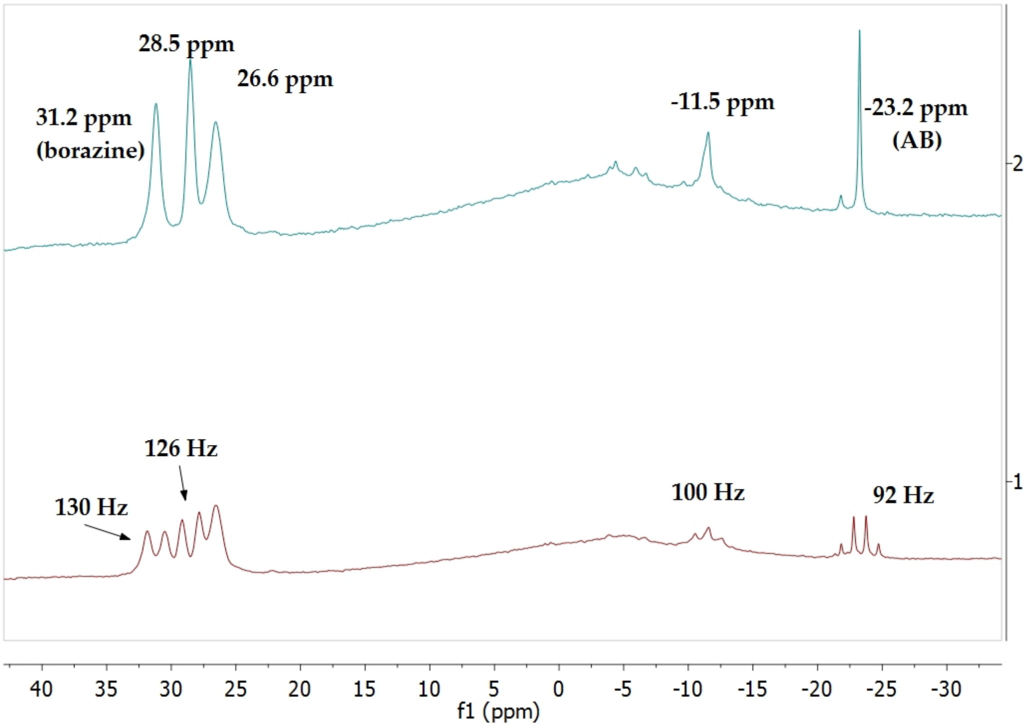


Figure S2 ^{11}B NMR of borazine in NH_3 (l)

Reaction of PB in NH_3:

PB (11.4 mg, 0.142 mmol) was loaded into a high pressure NMR tube. This tube was capped and removed from the glovebox. The NMR tube was attached to the Schlenk line and the headspace evacuated. Once equilibrium vacuum was achieved, NH_3 (~300 μL) was condensed into the tube. Within 5 minutes of thawing, the colorless solution was examined by ^{11}B NMR (96 MHz). For comparison the ^{11}B NMR of PB dissolved in THF is also provided.

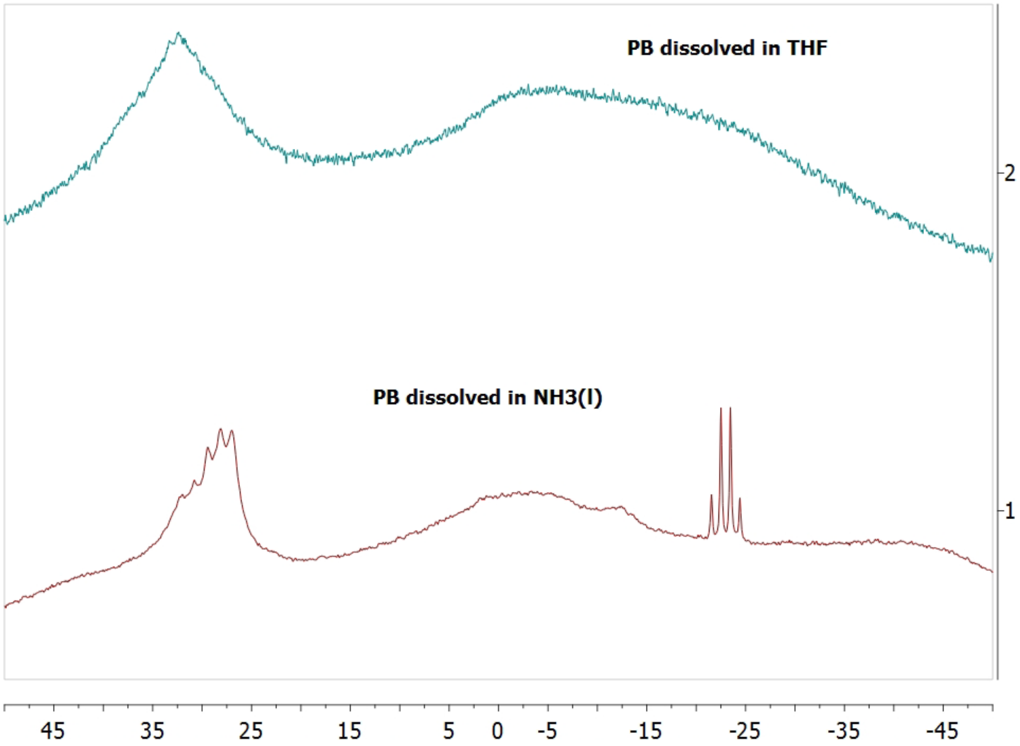


Figure S3 ^{11}B NMR Polyborazylene dissolved in THF (top) and NH_3 (bottom)

Reaction of borazine in ND_3:

Borazine (10 µL) was injected into a cold high pressure NMR tube (-40 °C). This tube was quickly capped, removed from the glovebox, and immersed in 4-5 cm of a -90 °C bath. The NMR tube was attached to the Schlenk line and bottom 4-5 cm placed in a -196 °C bath. After ~5 min, the headspace was evacuated. Once equilibrium vacuum was achieved, ND_3 (~300 µL) was condensed into the tube. Within 5 minutes of thawing, the colorless solution was examined by ^{11}B NMR (96 MHz).

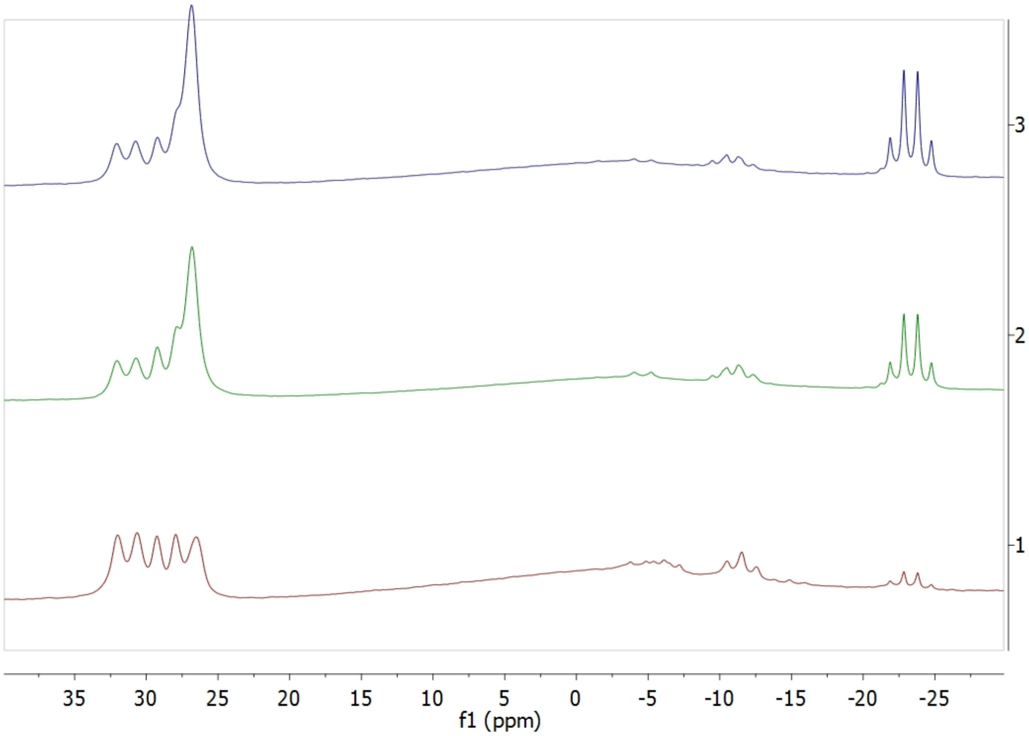


Figure S4 ^{11}**B NMR Borazine in ND$_3$ (l) after 5 min (bottom), 24 h (middle), and 5 days (top)**

Low Temperature reaction of borazine in NH$_3$:

Borazine (10 μL) was injected into a cold high pressure NMR tube (-40 °C). This tube was quickly capped, removed from the glovebox, and immersed in 4-5 cm of a -114 °C bath (ethanol/liquid N$_2$). The NMR tube was attached to the Schlenk line and the bottom 4-5 cm placed in a -196 °C bath. After ~5 min, the headspace was evacuated. Once equilibrium vacuum was achieved, NH$_3$ (~300 μL) was condensed into the tube. The NMR tube was kept frozen in the -114 °C bath before loading into the NMR spectrometer already cooled to -90 °C. The sample was warmed in 5 °C increments and allowed to equilibrate for 5 minutes before spectra were acquired.

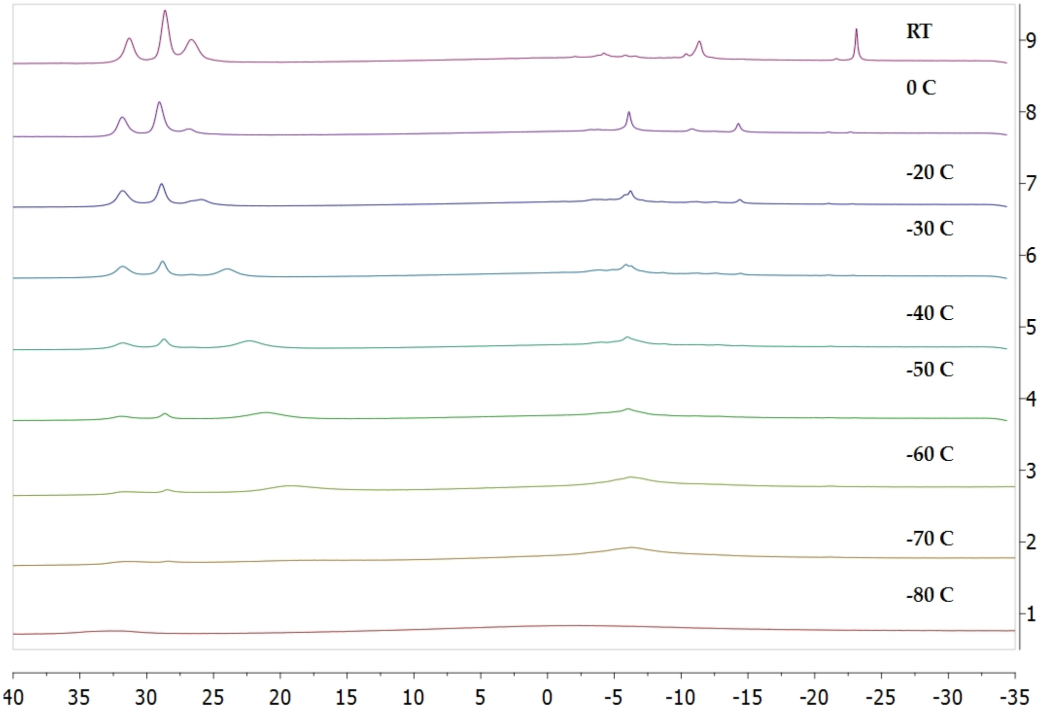


Figure S5 $^{11}B-\{^1H\}$ NMR of borazine in liquid NH_3, gradually warmed from -80 °C to RT

Replacement of NH_3 for THF

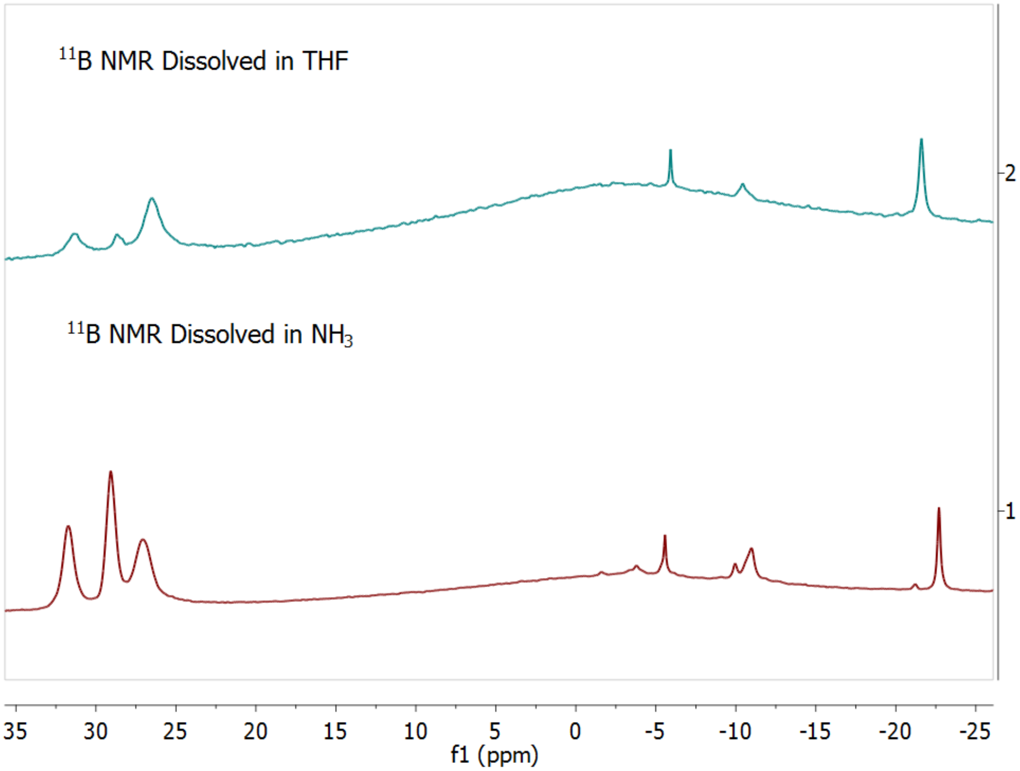


Figure S6 Evidence for short term stability in THF

Quantitative ^{11}B NMR Measurements

Typical Set Up: Solids were weighted out and added to a high pressure NMR tube (Wilmad, Part # 522-PV-8). Residual solids were washed into the tube using THF. The tube was then sealed and attached to a Schlenk line. The solvent was removed using a slow vacuum and a 0 °C bath to eliminate bumping. After all of the solvent was removed, NH_3 was condensed into the tube.

Data Collection: T1 relaxation measurements were performed on samples containing $NaBPh_4$ and H_3NBH_3 using a standard inversion recovery experiment. Data were processed and analyzed using Bruker TOPSPIN 1.3 software. The T1 for $NaBPh_4$ was the longest at ~15 seconds, so a relaxation delay of 110 seconds (> 7 *T1) was chosen for quantitative experiments. Spectra were recorded using a calibrated 90 degree pulse with transmitter offset equidistant from resonance frequencies. 32 scans yielded a signal/noise > 150 for the smallest peak (usually $NaBPh_4$) in all experiments. In the case of run #1, 5 independent measurements were taken to assess variance.

Data Processing: MestReNova versions 5.3 and 8.1 were used for data processing. FIDs were apodized with an exponential function at 2 Hz, zero-filled to 128k points, Fourier transformed, and then manually phased. All obtained results were within the error of measurements when line broadening between 1 and 3 Hz was employed. For LB below 1 Hz, integration became less accurate due to the S/N degradation. The baseline was corrected using the Full Auto mode (Whittaker Smoother). This is necessary to 1). correct for DC offset observed on all NMR instruments; and 2). correct for the broad 'hump' originating from borosilicates in NMR tube glass. Results were identical whether the Whittaker Smoother or linear function fitting points near the peaks of interest were used for baseline correction. The use of Whittaker smoother was preferred because of its consistency between experiments and absence of potential operator bias. Peaks were integrated using MNova's automatic integration algorithm. Quantification of known AB/$NaBPh_4$ mixtures using this method resulted in replication of the predicted ratios within ~5% (AB/$NaBPh_4$ control below). A 3% difference was observed between software versions, attributable to the manual phasing employed. Quantification using line fitting gave results within the SD of measurements as determined from multiple repeats for the same sample, so the above method was utilized.

For quantitative measurements it is important that the entire FID is collected (no truncation, acquisition time >5*T2*). In our experiments, line fitting indicated the narrowest line in the spectrum > 2Hz, corresponding to T2* of <160 ms; with acquisition time of 1.3 s, this ensured that 99.97% of the FID was collected. It is also important that 'reference' spectra of the glass tube are not subtracted to remove the borosilicate hump, or that deconvolution/FID shifting procedures are not used to remove the broad borosilicate 'hump' since both of these procedures have the potential of introducing significant errors in effect changing the measurements from quantitative to qualitative.

AB/$NaBPh_4$ Control:

Run #1: (#51) AB (0.0021 g, 0.068 mmol) and $NaBPh_4$ (0.0048 g, 0.014 mmol) were loaded into a NMR tube. After 18 hours, an AB/$NaBPh_4$ ratio of 5.27, 5.26, 5.35, 5.23, and 5.19 were collected (ave = 5.26). Theoretical Ratio: 4.95.

PB Evaluations:

Run #1: (#51) PB (0.0059 g, 0.073 mmol) and $NaBPh_4$ (0.0048 g, 0.014 mmol) were loaded into a NMR tube. After 18 hours, an AB/$NaBPh_4$ ratio of 1.24, 1.28, 1.27, 1.28, 1.28 were collected. B-H bond Yield: 48.7%

Run #2: (#43) PB (0.0053 g, 0.066 mmol) and $NaBPh_4$ (0.0044 g, 0.013 mmol) were loaded into a NMR tube. After 18 hours, an AB/$NaBPh_4$ ratio of 1.23 was collected. B-H bond Yield: 48.5%

Run #3: (#67, Ottawa) PB (0.0056 g, 0.070 mmol) and $NaBPh_4$ (0.0027 g, 0.0079 mmol) were loaded into a NMR tube. After 18 hours, an AB/$NaBPh_4$ ratio of 2.14 was collected. B-H bond Yield: 48.2%

Run #4: (#63) PB (0.0071 g, 0.088 mmol) and $NaBPh_4$ (0.003 g, 0.0088 mmol) were loaded into a NMR tube. After 6 days, an AB/$NaBPh_4$ ratio of 2.75 was collected. B-H bond Yield: 54.8%

Yield Calculations: A gas evolution measurement apparatus (Chemglass item: CG-1818) was employed with a mineral oil working fluid to measure evolved hydrogen. The apparatus was attached to a *ca.* 1 L cold trap with the body submerged in a Dewar containing a dry ice/acetone bath (-78 °C) and covered with a hard foam insulator. This was connected to a three-way valve attached to a sample flask as well as a gas/vacuum manifold. All connections were made using VWR "Select Grade" PVC tubing. Temperature measurements were made using an ethanol thermometer and the pressure was determined using a manometer. The system was tested using known quantities (9-12 mg) of $NaBH_4$ as a standard; the results were within 3% of the theoretical amount.

Inside of a glove box, a 10 mL Schlenk reaction flask was charged with *ca.* 43 mg (*ca.* 0.547 mmol) of polyborazylene, *ca.* 680 mg (7.23 mmol) of crystalline phenol, and *ca.* 250 mg (1.31 mmol) of crystalline *p*-toluenesulfonic acid monohydrate. The reaction flask was connected to the hose (attached to the three-way valve) and purged (x3) using the manifold. Argon was purged through the system for 5 minutes and then the gas was allowed to equilibrate for 5 minutes. Excess pressure was then allowed to purge until all three working fluid menisci were level. The sample flask was then placed in an oil bath and heated to 85 °C for 55 minutes with moderate stirring (*ca.* 700 rotations/min). The reaction flask was then removed from the oil bath and the residual oil on the flask was wiped-off using acetone. The flask was cooled back to room temperature. The volume of the gas was determined by allowing it to bubble into the graduated cylinder until the three working fluid menisci were once again level.

Using the above method, the amount of B-H bonds per B_3N_3 ring within PB was determined:

Mass PB mg	Measured Volume mL	Temp C	Ambient Pressure torr	B-H/B_3N_3 Ratio
44.0	26.9 mL	26.5	592	1.554
42.8	26.7 mL	29.7	590	1.564

Using the average B-H/B_3N_3 ratio, the yield of AB was calculated as follows:

(moles AB in equilibrated sample)/[(moles of PB added)*([B-H/B_3N_3]/3)] * 100

Borazine Evaluation:

Run #1: (#59) Borazine (0.0111 g, 0.138 mmol) and $NaBPh_4$ (0.003 g, 0.0088 mmol) were loaded into a NMR tube. After 18 hours, an AB/$NaBPh_4$ ratio of 5.73, 5.73, 5.89, 5.92, and 5.86 were collected (ave = 5.83). B-H bond Yield (18 h): 37.0% B-H bond Yield (6 days): 55.2%

Total Mass Balance of System

Run #1: (#71) Borazine (0.0088 g, 0.109 mmol) and $NaBPh_4$ (0.003 g, 0.0088 mmol) were loaded into a NMR tube. After 3 days, quantitative data was obtained using the long delay time as above. T1 measurements were performed as a precaution, yielding 12 ms for $B(NH_2)_3$, 38 ms for $HB(NH_2)_2$, and 68 ms for AB. Baseline correction was performed as described and integrals were obtained.

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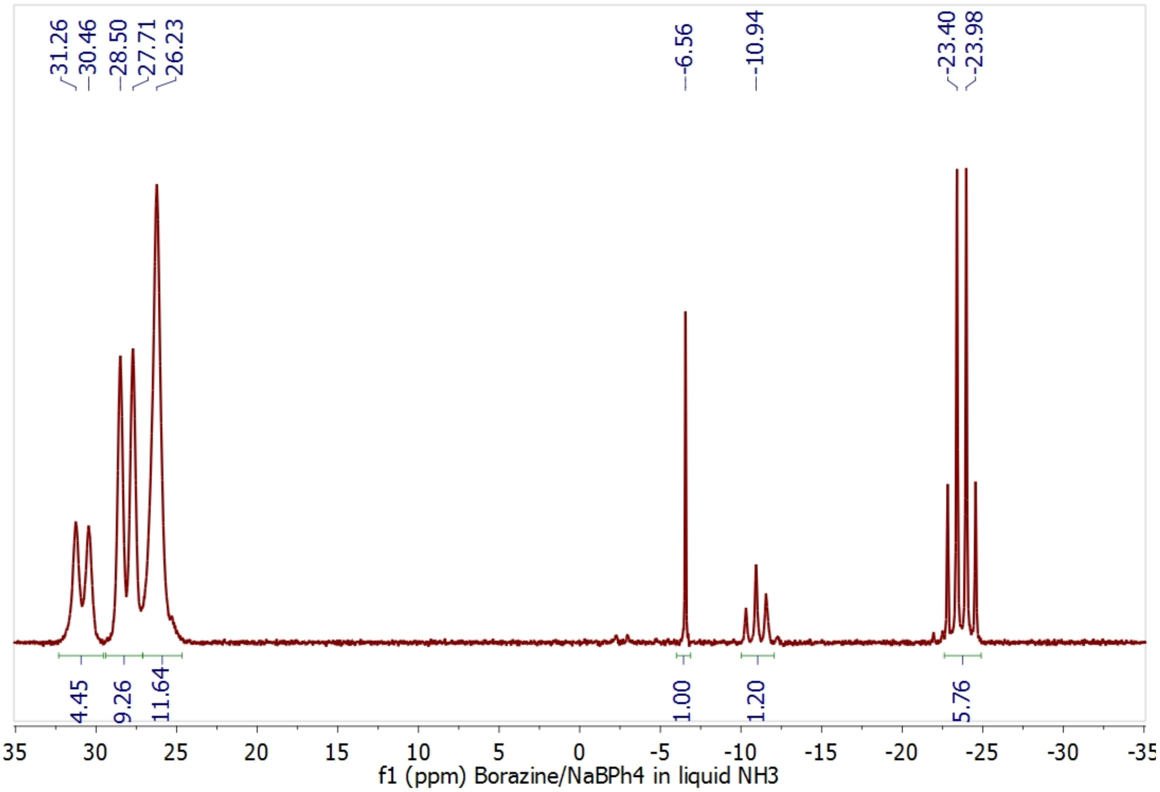
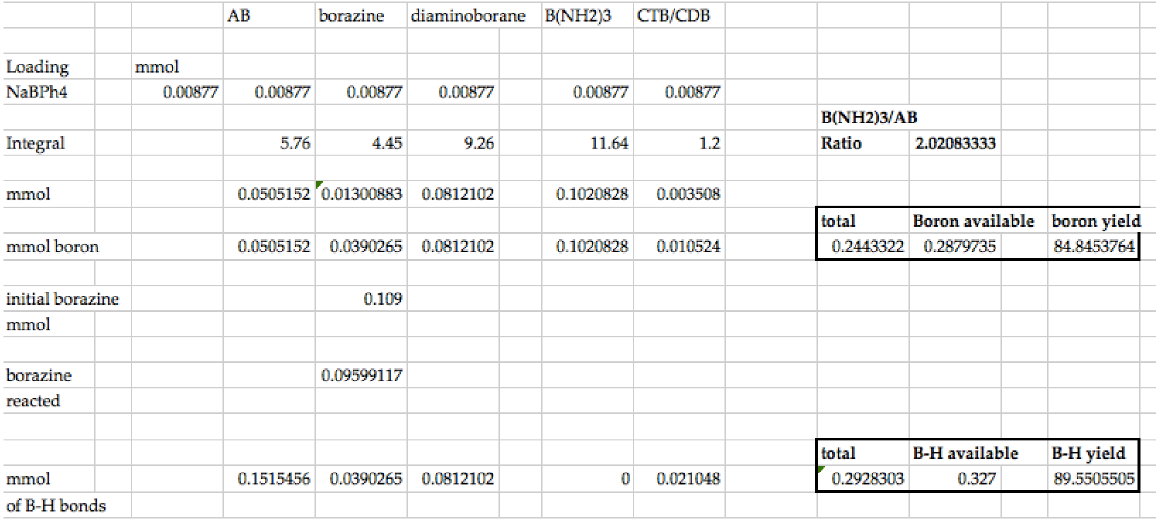
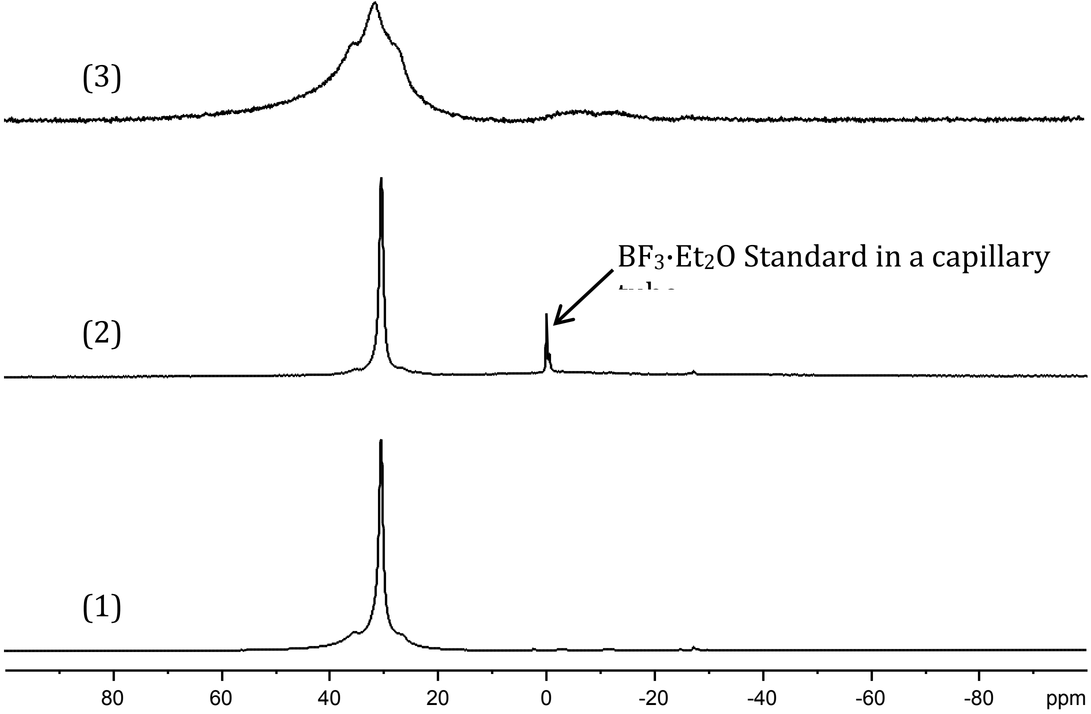




		AB	borazine	diaminoborane	B(NH2)3	CTB/CDB			
Loading	mmol								
NaBPh4	0.00877	0.00877	0.00877	0.00877	0.00877	0.00877			
							B(NH2)3/AB		
Integral		5.76	4.45	9.26	11.64	1.2	**Ratio**	**2.02083333**	
mmol		0.0505152	0.01300883	0.0812102	0.1020828	0.003508			
							total	**Boron available**	**boron yield**
mmol boron		0.0505152	0.0390265	0.0812102	0.1020828	0.010524	0.2443322	0.2879735	84.8453764
initial borazine			0.109						
mmol									
borazine			0.09599117						
reacted									
							total	**B-H available**	**B-H yield**
mmol		0.1515456	0.0390265	0.0812102	0	0.021048	0.2928303	0.327	89.5505505
of B-H bonds									

Alternative PB Synthesis



AB (1.3 g), $FeCl_2$ (0.260 g, 5 mol%) and DME (14 mL) were added to a Schlenk flask. The mixture was heated at 75 °C for 6 h in a glove box. A black precipitate was formed on the walls of the flask after around 20 min. ^{11}B NMR after 6 h shows a full conversion of AB to mostly borazine with some PB. (Figure 1 Spectrum 1). The colorless solution containing the products was decanted. The black precipitate in the flask was washed with THF (3×10 mL) and the collected THF was added to the original solution.

The black precipitate/iron catalyst was dried under vacuum and fresh AB (1.066 g) was added to the flask and the reaction was performed under the same conditions. The collected solution was filtered and vacuum distilled. The remaining oily material was evacuated under high vacuum (~5 μtorr) for 4 h; a white solid (.290 g, 14%) resulted that was completely soluble in THF (Figure 1, Spectrum 3).

Additional Calculations

Additional calculations were run using the Gaussian09 code.[1] The additional reaction energies were calculated at the G3MP2 level.[2] The NMR calculations were done in the gauge invariant atomic orbital (GIAO) approach[3] at the density functional theory level using the B3LYP exchange-correlation functional[4] and the DZVP2 basis set.[5]

Reaction energies in kcal/mol at the G3MP2 level.

Reaction	ΔH 0K	ΔH 298K	ΔG 298K	$\Delta G_{solv,NH3}$ 298K[a]
$B_3N_3H_6 + NH_3 \rightarrow H_2 + B_3N_3H_5(NH_2)$	-19.6	-18.8	-17.9	-17.1
$B_3N_3H_6 + 2NH_3 \rightarrow 2H_2 + B_3N_3H_4(NH_2)_2$	-38.6	-36.9	-34.3	-31.7
$B_3N_3H_5(NH_2) + NH_3 \rightarrow H_2 + B_3N_3H_4(NH_2)_2$	-19.0	-18.1	-16.4	-14.7
$B_3N_3H_6 + 3NH_3 \rightarrow 3H_2 + B_3N_3H_3(NH_2)_3$	-57.1	-54.4	-50.4	-45.9
$B_3N_3H_4(NH_2)_2 + NH_3 \rightarrow H_2 + B_3N_3H_3(NH_2)_3$	-18.5	-17.5	-16.1	-14.2

[a] H_2 is a gas and there is no free energy of solvation.

G3MP2 Total Energies in Hartrees

Molecule	ΔH (0K)	ΔH (298K)	ΔG (298K)
H_2	-1.170135	-1.166831	-1.181590
NH_3	-56.470153	-56.466344	-56.488149
$B_3N_3H_6$	-242.255015	-242.248547	-242.281637
$B_3N_3H_5(NH_2)$	-297.586243	-297.578001	-297.616725
$B_3N_3H_4(NH_2)_2$	-352.916606	-352.906417	-352.949427
$B_3N_3H_3(NH_2)_3$	-408.246141	-408.233795	-408.281640

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NMR chemical shifts in ppm

Molecule	Atom	isotropic	σ
BH_3NH_3	B_1	123.5	-22.9
BH_2NH_2	B_1	59.0	41.6
$BH(NH_2)_2$	B_1	75.1	25.6
$B(NH_2)_3$	B_1	77.4	23.2
$B_3N_3H_6$	B_1	74.6	26.1
$B_3N_3H_5(NH_2)$	$B_{1,3}$	68.9	31.8
	B_2	77.0	23.6
$B_3N_3H_4(NH_2)_2$	$B_{1,3}$	76.6	24.0
	B_2	68.9	31.7
$B_3N_3H_3(NH_2)_3$	B_1	76.1	24.6

σ calculated with respect to $BF_3 \cdot OEt_2$

Cartesian Coordinates (x, y, z) in Angstroms.

$B_3N_3H_5(NH_2)$

H	-2.913500	0.000000	-0.000067
H	-1.809042	-2.292602	-0.000301
H	0.700407	-2.113175	-0.000211
H	0.700407	2.113175	0.000248
H	-1.809042	2.292602	0.000205
B	-1.211142	-1.254195	-0.000176
B	0.978834	0.000000	0.000027
B	-1.211142	1.254195	0.000111
N	0.212136	-1.226128	-0.000144
N	0.212136	1.226128	0.000154
N	-1.901844	0.000000	-0.000048
H	2.951533	0.843002	0.000225
H	2.951534	-0.843002	-0.000030
N	2.398280	0.000000	0.000056

$B_3N_3H_4(NH_2)_2$

H	0.000000	2.008714	0.000051
H	2.089443	-1.656168	0.000188
H	-2.089443	-1.656168	-0.000272
B	1.267368	0.313406	0.000147
B	0.000000	-1.864482	-0.000047
B	-1.267368	0.313406	-0.000132
N	1.223272	-1.132906	0.000106
N	-1.223272	-1.132906	-0.000163
N	0.000000	0.995869	0.000025
H	-2.566793	2.025652	-0.000232
H	-3.400446	0.560555	-0.000361
H	3.400446	0.560555	0.000389
H	2.566793	2.025652	0.000335
N	-2.502900	1.019532	-0.000250
N	2.502900	1.019532	0.000301
H	0.000000	-3.064291	-0.000078

$B_3N_3H_3(NH_2)_3$

H	2.430962	-0.000006	-0.000058
H	-1.215476	2.105277	-0.000206
H	-1.215487	-2.105271	0.000261
B	0.730581	1.265394	-0.000158
B	-1.461154	0.000004	0.000036
B	0.730574	-1.265398	0.000122
N	-0.709301	1.228553	-0.000118
N	-0.709308	-1.228549	0.000154
N	1.418610	-0.000004	-0.000034

H	-3.440658	-0.842653	0.000207
H	-3.440654	0.842671	0.000021
N	-2.887620	0.000007	0.000064
H	2.450088	-2.558370	0.000219
H	0.990551	-3.401027	0.000349
H	0.990569	3.401022	-0.000408
H	2.450101	2.558357	-0.000351
N	1.443803	-2.500754	0.000241
N	1.443816	2.500747	-0.000312

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