Electronic Supplementary Material (ESI) for ChemComm.

Use of Crown Ethers to Isolate Intermediates in Ammonia-Borane Dehydrocoupling Reactions

Robert J. Less,* Raúl García-Rodríguez, Hayley. R. Simmonds, Lucy. K. Allen, Andrew D. Bond and Dominic S. Wright

Supplementary Information

Syntheses

General experimental procedures

All preparations were performed on a double-manifold vacuum line under a nitrogen atmosphere. The products were isolated and stored with the aid of a nitrogen-filled glove box (Saffron type b), equipped with Cu and molecular sieve columns in order to remove O_2 and moisture, respectively. All ^{11}B, ^{1}H and ^{13}C NMR spectra were recorded using a Bruker DPX 500 MHz NMR spectrometer (^{1}H, ^{13}C referenced to $SiMe_4$, ^{11}B referenced to $BF_3{\cdot}Et_2O$, ^{27}Al referenced to $AlCl_3{\cdot}6H_2O$-D_2O). Elemental (C, H, N) analyses were obtained using an Exeter CE-440 Elemental Analyser. Solvents and amine bases were dried by distillation over an appropriate drying agent: THF, Et_2O (both Na/benzophenone), CH_2Cl_2, CD_2Cl_2, Et_3N, $^{i}Pr_2EtN$ (all CaH_2), $CDCl_3$ (P_2O_5). $AlCl_3$ was sublimed before use. Ammonia borane and 18-crown-6 were used as supplied (Sigma-Aldrich).

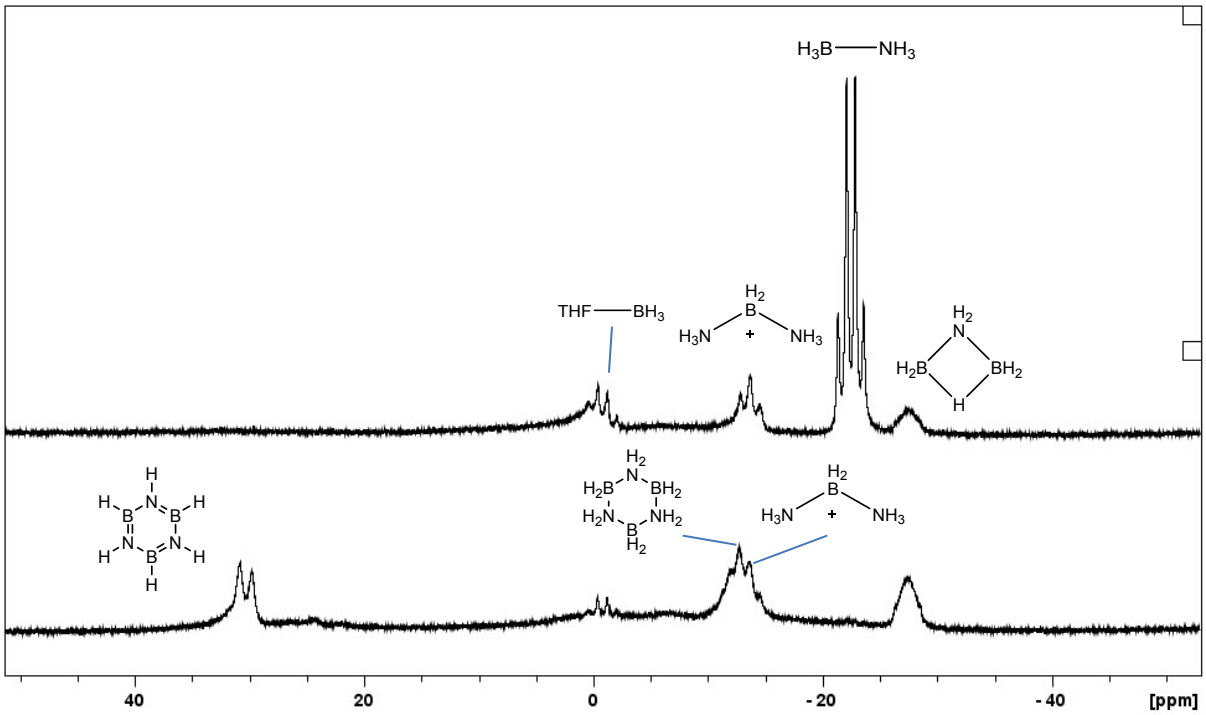

Figure S1 *In situ* ^{11}B NMR spectra of AB + $AlCl_3$ (1 eq.) in THF after 16h at room temperature (top) and after 16h reflux (bottom).

Synthesis of [(THF)BH_2NH_3(18-C-6)][$AlCl_4$] [**1**·THF(18-C-6)][$AlCl_4$]

$AlCl_3$ (864 mg, 6.48 mmol) was added to a solution of ammonia borane (50 mg, 1.62 mmol) and 18-crown-6 (428 mg, 1.62 mmol) in 3 ml THF at 0°C [AB(18-C-6) is only partially soluble]. The solution was allowed to warm to room temperature and was stirred for 16h. The reaction mixture was then filtered and layered with 10 ml diethyl ether in a 20 mm diameter tube. After 3d crystals were collected and recrystallised a second time in the same manner (THF-diethyl ether) to yield colourless needles (330 mg, 38 %).

Found (%): C 35.55, H 6.91, N 2.88; Calculated for $C_{16}H_{37}AlBCl_4NO_7$: C 35.92, H 6.97, N 2.62.

^{11}B NMR (128.4 MHz, 25 °C, $CDCl_3$), δ/ppm = 1.2 (br).

^{1}H NMR (400.1 MHz, 25 °C, $CDCl_3$), δ/ppm = 5.63 (br s, 3H, NH_3), 4.36 (m, 4H, THF), 3.63 (s, 24H, 18-C-6), 2.60 (br, 2H, BH_2), 2.29 (m, 4H, THF).

^{13}C NMR (100.6 MHz, 25 °C, $CDCl_3$), δ/ppm = 79.77 (THF), 70.31 (18-C-6), 25.51 (THF).

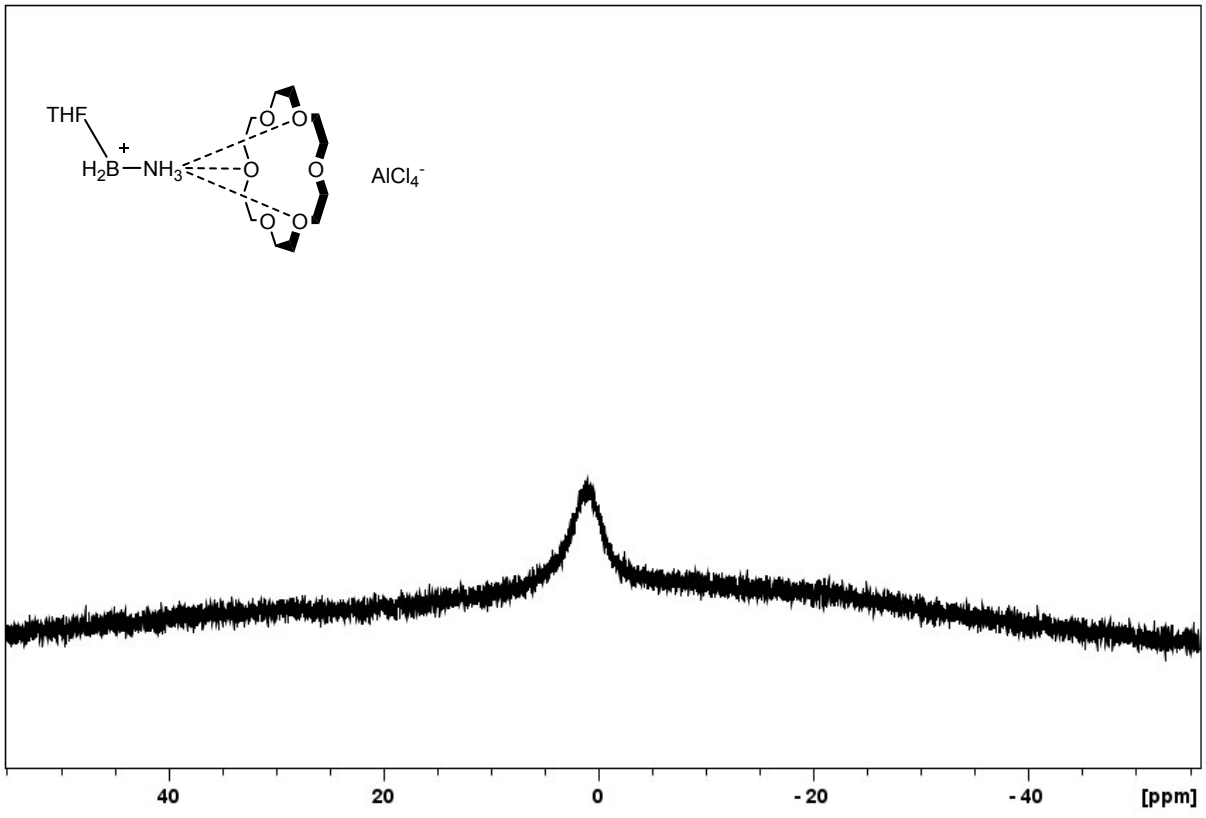

Figure S2 ^{11}B NMR spectrum of [(THF)BH_2NH_3(18-C-6)][$AlCl_4$] in $CDCl_3$.

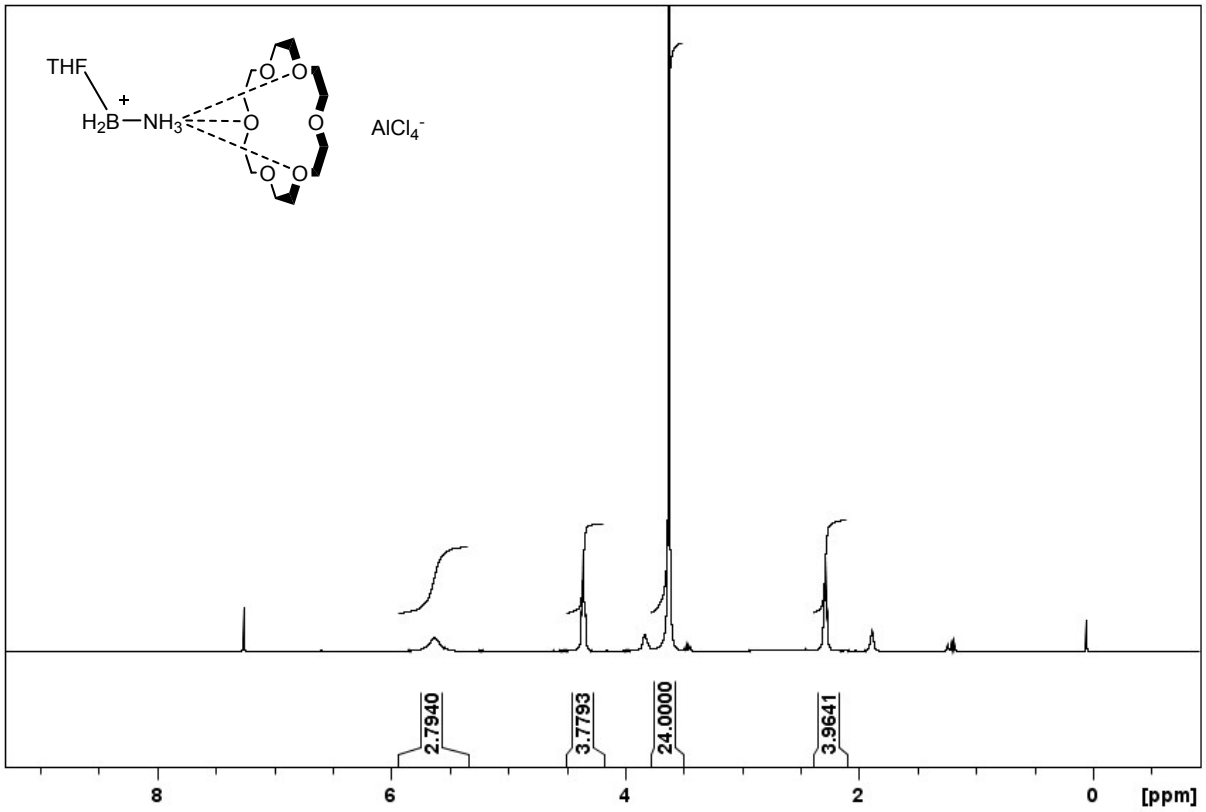

Figure S3 ^{1}H NMR spectrum of $[(THF)BH_2NH_3(18\text{-}C\text{-}6)][AlCl_4]$ in $CDCl_3$.

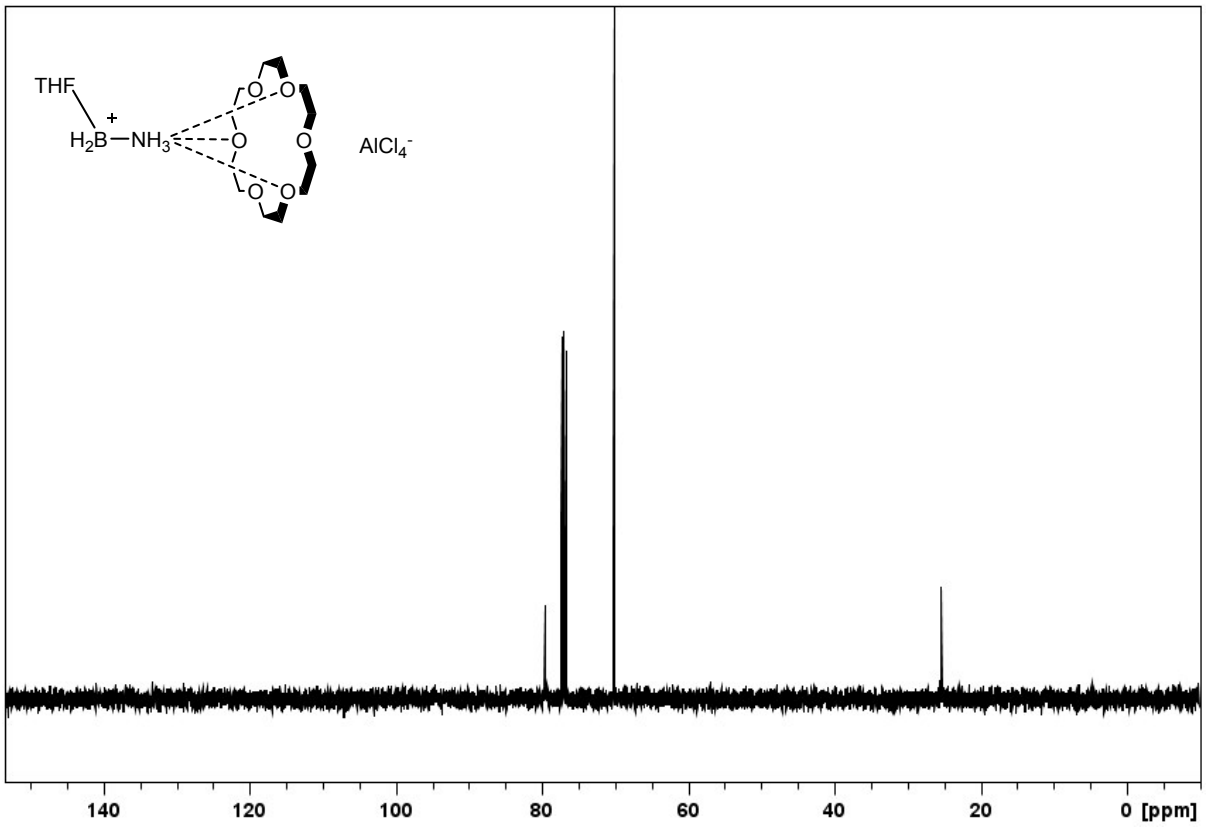

Figure S4 $^{13}C\{^{1}H\}$ NMR spectrum of $[(THF)BH_2NH_3(18\text{-}C\text{-}6)][AlCl_4]$ in $CDCl_3$.

Synthesis of $[BH_2(NH_3)_2(18\text{-}C\text{-}6)_2][AlCl_4]$ $[\mathbf{2}(18\text{-}C\text{-}6)_2][AlCl_4]$

$AlCl_3$ (108 mg, 0.81 mmol) was added to a solution of ammonia borane (25 mg, 0.81 mmol), NH_4Cl (43 mg, 0.81 mmol) and 18-crown-6 (426 mg, 1.62 mmol) in 5 ml THF and the mixture heated to reflux for 16h. The solution was filtered and layered with 10 ml diethyl ether in a 20 mm diameter tube. After 3d the crystals were collected and dried *in vacuo* (370 mg, 61 %).

Found (%): C 38.72, H 8.01, N 3.70; Calculated for $C_{24}H_{56}AlBCl_4N_2O_{12}$: C 38.73, H 7.58, N 3.76.

^{11}B NMR (128.4 MHz, 25 °C, $CDCl_3$), δ/ppm = -13.7 (br).

^{1}H NMR (400.1 MHz, 25 °C, $CDCl_3$), δ/ppm = 5.90 (br s, 6H, NH_3), 3.66 (s, 48H, 18-C-6), 2.06 (br, 2H, BH_2).

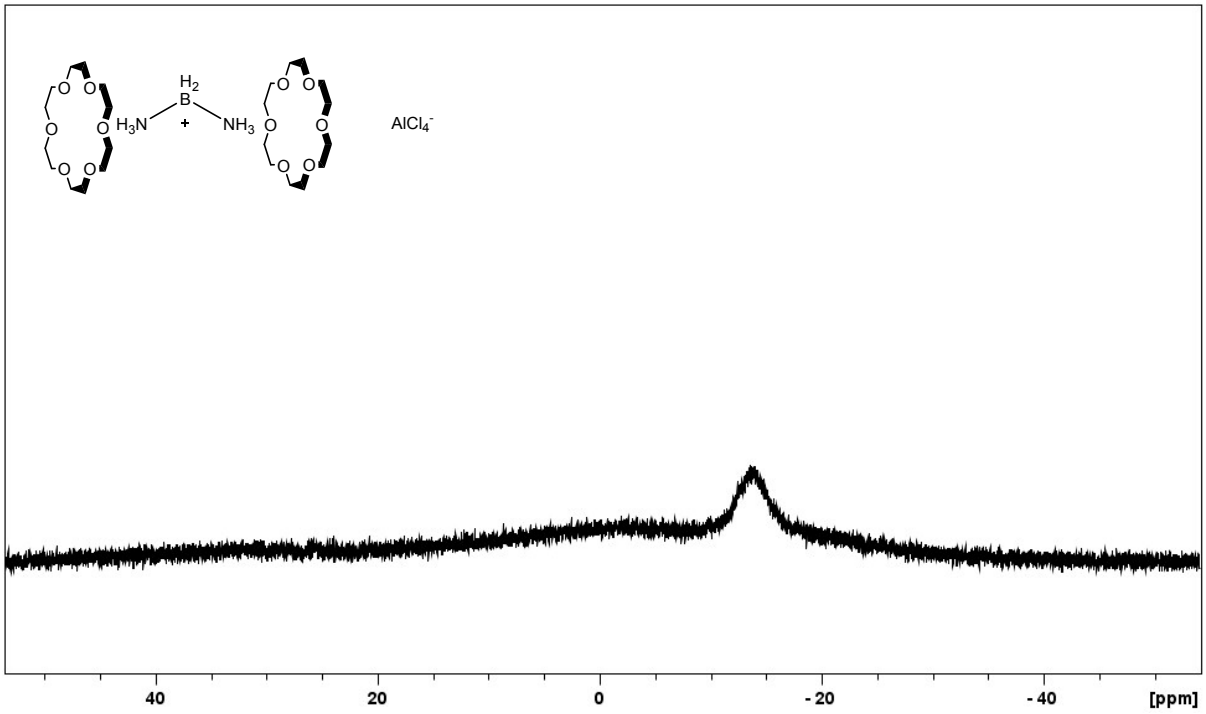

Figure S5 ^{11}B NMR spectrum of $[BH_2(NH_3)_2(18\text{-}C\text{-}6)_2][AlCl_4]$ in $CDCl_3$.

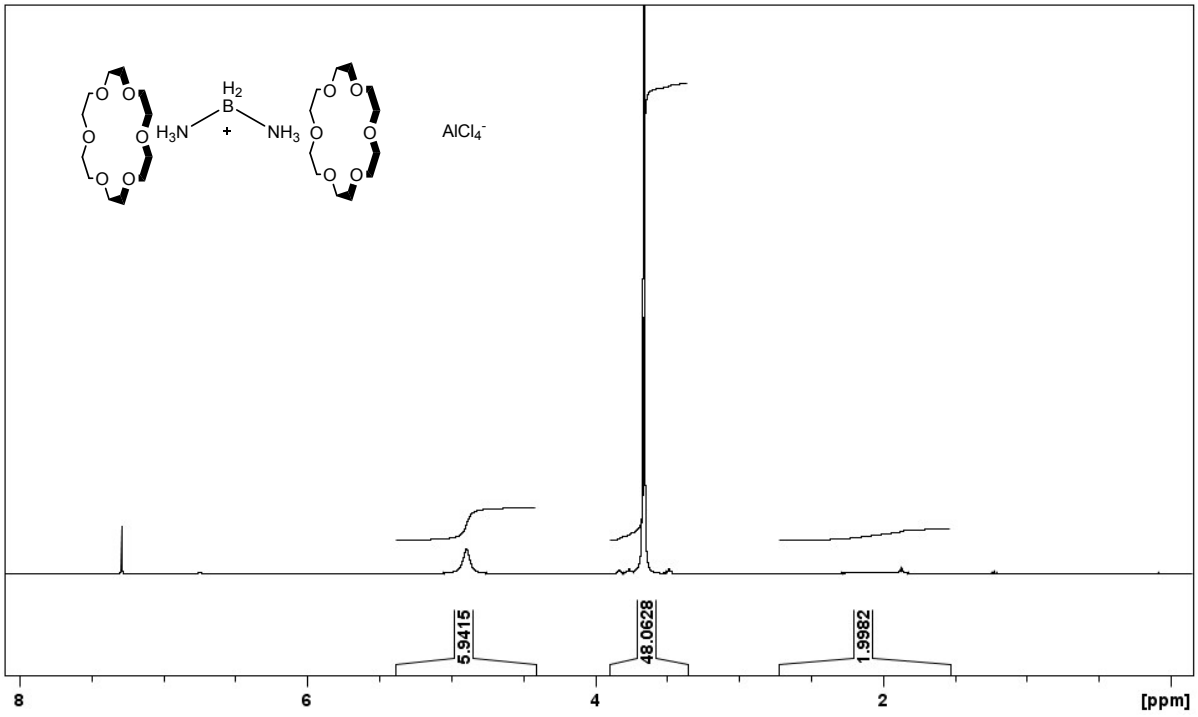

Figure S6 ^{1}H NMR spectrum of $[BH_2(NH_3)_2(18\text{-C-}6)_2][AlCl_4]$ in $CDCl_3$.

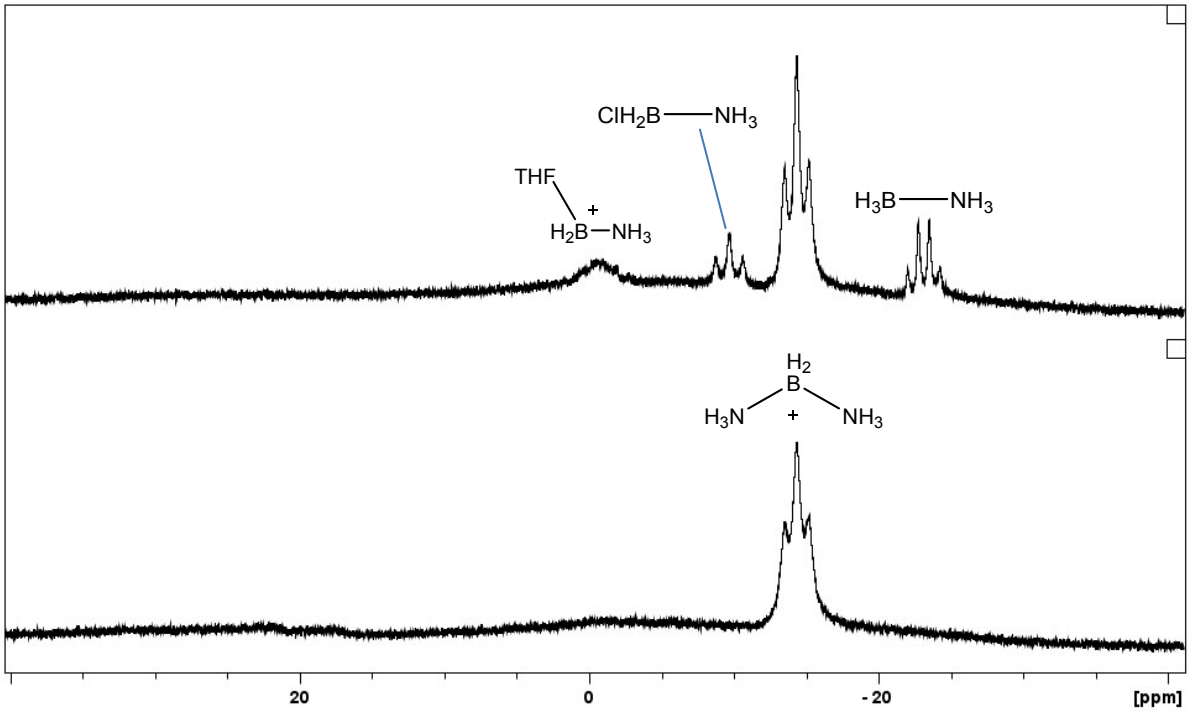

Figure S7 *In situ* ^{11}B NMR spectra of reaction of AB, NH_4Cl and $AlCl_3$ (1:1:1) in refluxing THF after 2h (above), 16h (below).

Synthesis of [(Et_3N)BH_2NH_3(18-C-6)][$AlCl_4$] [**1**·Et_3N(18-C-6)][$AlCl_4$]

Triethylamine (60 μl, 43 mg, 0.43 mmol) was added to a solution of [(THF)BH_2NH_3(18-C-6)][$AlCl_4$] (230 mg, 0.43 mmol) in 2 ml DCM at -78°C. The reaction mixture and allowed to warm to room temperature and was stirred for 16h, filtered and layered with 10 ml hexane in a 20 mm diameter tube. After 3d crystals were collected and dried *in vacuo* (114 mg, 47 %).

Found (%): C 37.90, H 8.12, N 4.96; Calculated for $C_{18}H_{44}AlBCl_4N_2O_6$: C 38.32, H 7.86, N 4.97.

^{11}B NMR (128.4 MHz, 25 °C, $CDCl_3$), δ/ppm = -9.2 (br).

^{1}H NMR (400.1 MHz, 25 °C, $CDCl_3$), δ/ppm = 5.11 (br s, 3H, NH_3), 3.66 (s, 24H, 18-C-6), 2.90 (q, *J* = 7.3 Hz, 6H, NCH_2CH_3), 1.96 (br, 2H, BH_2), 1.24 (t, 9H, *J* = 7.3 Hz, 9H, NCH_2CH_3).

^{13}C NMR (100.6 MHz, 25 °C, $CDCl_3$), δ/ppm = 70.18 (18-C-6), 48.98 (NCH_2CH_3), 8.10 (NCH_2CH_3).

Note: When this reaction was performed in THF rather than DCM, subsequent layering with hexane resulted in crystallisation of [**2**(18-C-6)$_2$][$AlCl_4$] instead.

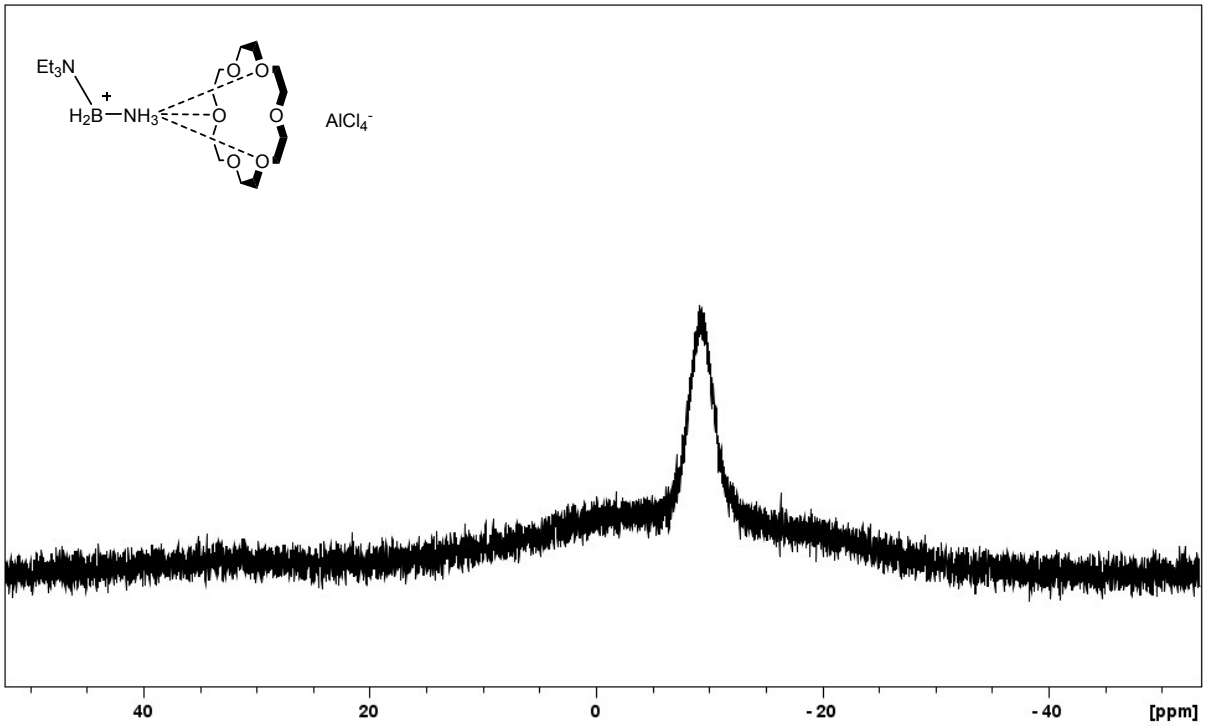

Figure S8 ^{11}B NMR spectrum of [(Et_3N)BH_2NH_3(18-C-6)][$AlCl_4$] in $CDCl_3$.

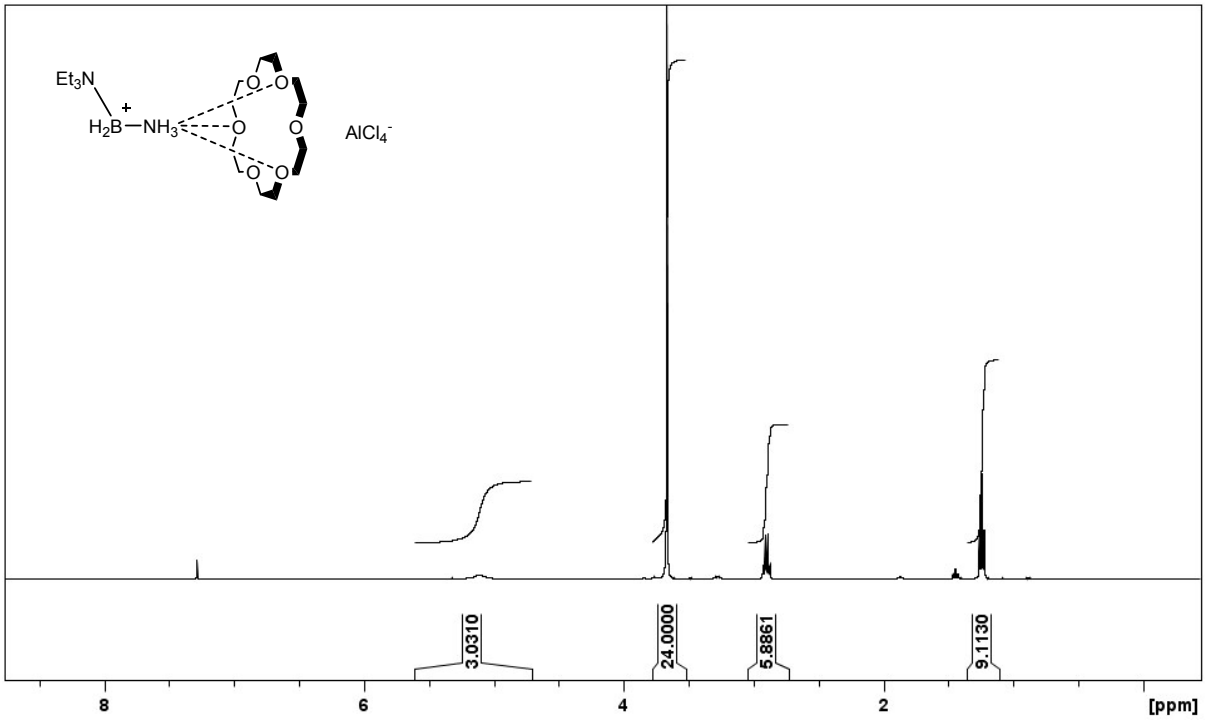

Figure S9 ^{1}H NMR spectrum of $[(Et_3N)BH_2NH_3(18\text{-}C\text{-}6)][AlCl_4]$ in $CDCl_3$.

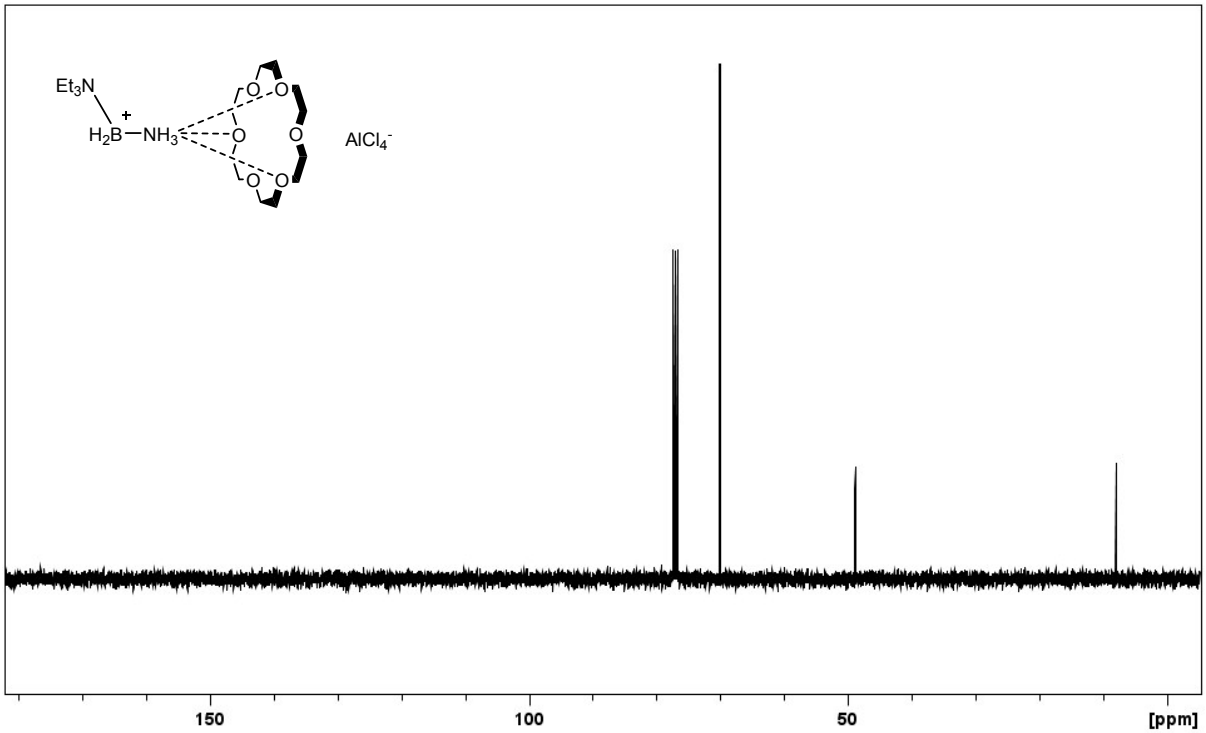

Figure S10 $^{13}C\{^{1}H\}$ NMR spectrum of $[(Et_3N)BH_2NH_3(18\text{-}C\text{-}6)][AlCl_4]$ in $CDCl_3$.

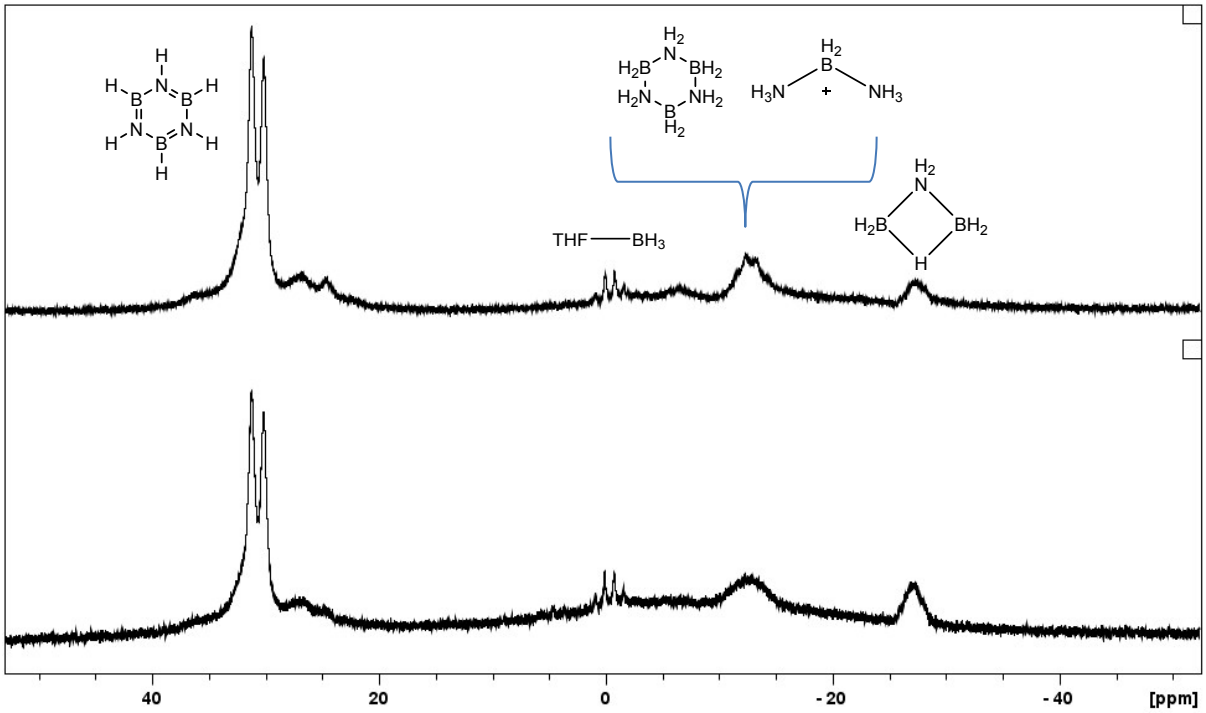

Figure S11 *In situ* ^{11}B NMR spectra of: AB + $AlCl_3$ (33% eq.) 16h reflux in THF (above); AB + $[(THF)BH_2NH_3(18\text{-}C\text{-}6)][AlCl_4]$ (10 % eq.) 16h reflux in THF (below).

***In situ* variable-temperature NMR study of reaction of AB + 18-C-6 (1 eq.) with $AlCl_3$ (4 eq.).**

A solution of $AlCl_3$ (85 mg, 0.64 mmol) in 0.3 ml d_8-THF was injected into an NMR tube containing a solution of amine borane (5 mg, 0.16 mmol) and 18-crown-6 (42 mg, 0.16 mmol) in 0.2 ml d_8-THF held at -78°C and shaken before transferring to the spectrometer. ^{11}B and ^{1}H spectra were collected at -40°C and at further 10°C intervals until room temperature.

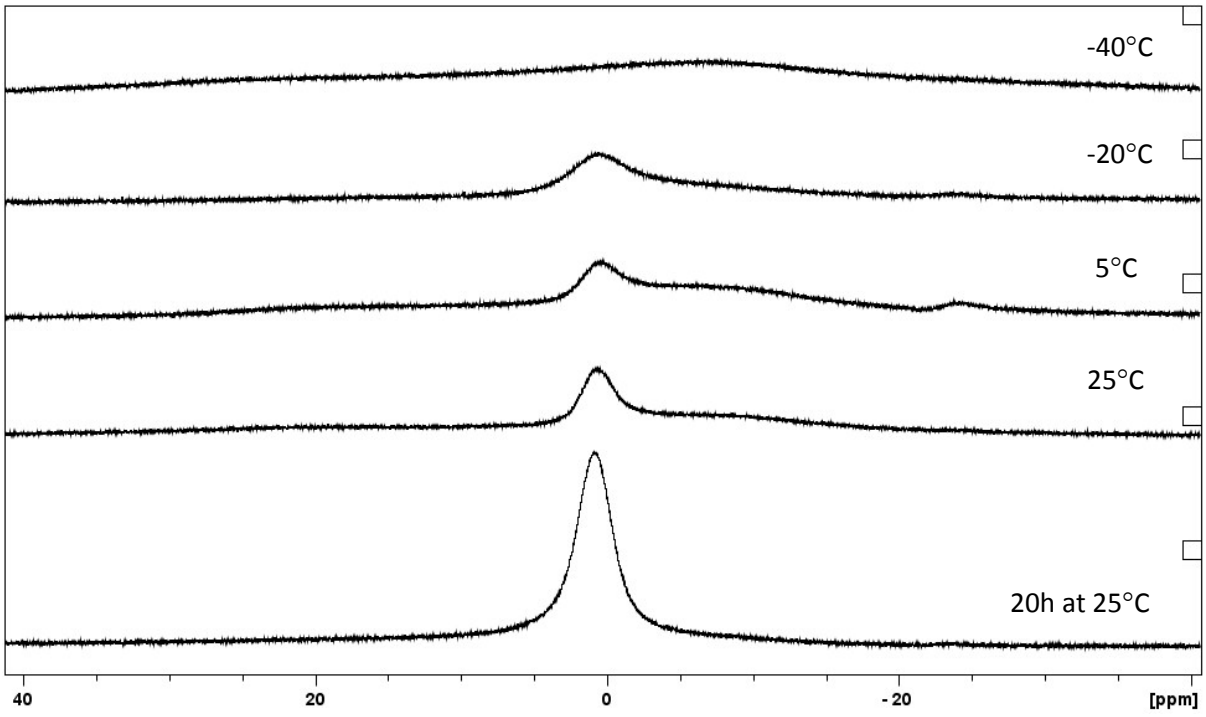

Figure S12 *In situ* variable-temperature ^{11}B NMR spectra of reaction of AB + 18-C-6 (1 eq.) with $AlCl_3$ (4 eq.) in d_8-THF.

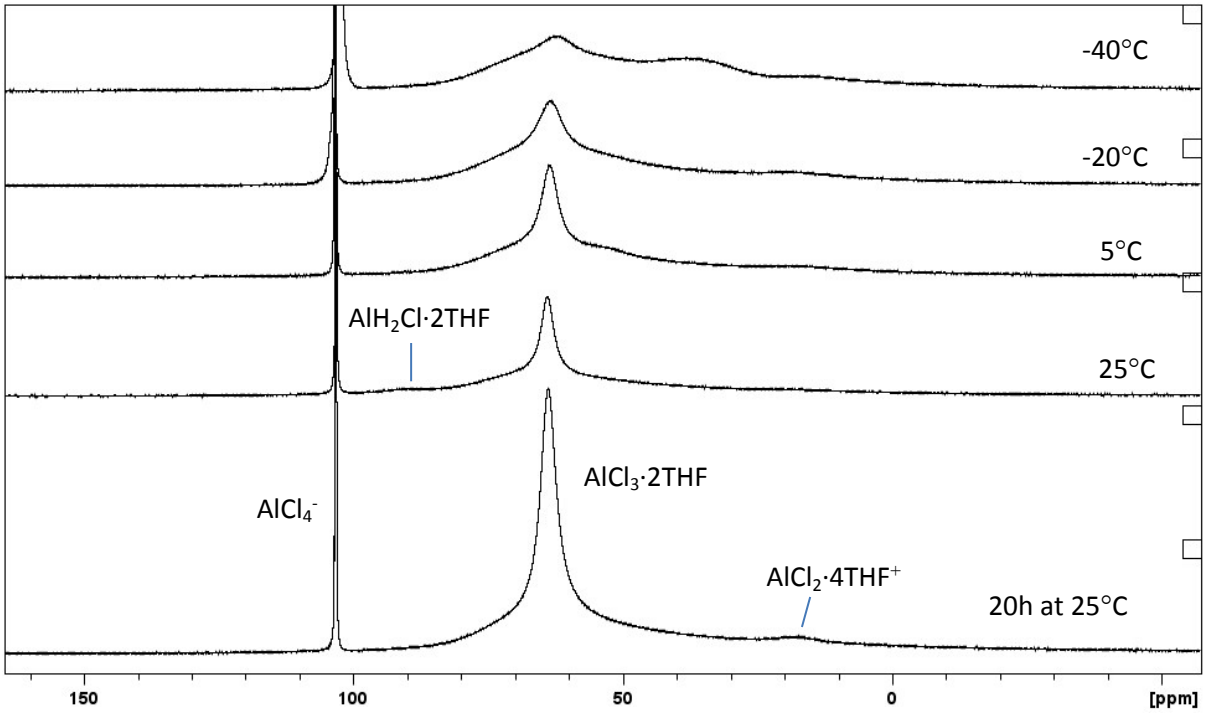

Figure S13 *In situ* variable-temperature ^{27}Al NMR spectra of reaction of AB + 18-C-6 (1 eq.) with $AlCl_3$ (4 eq.) in d_8-THF.

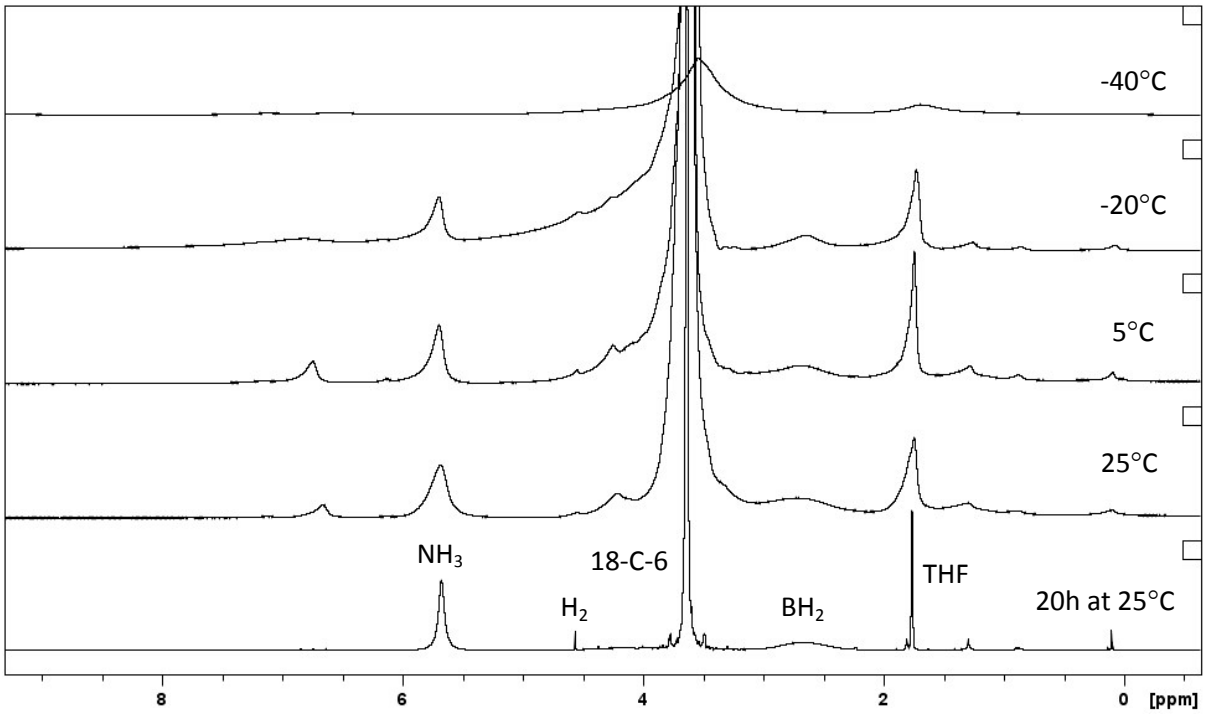

Figure S14 *In situ* variable-temperature ^1H NMR spectra of reaction of AB + 18-C-6 (1 eq.) with $AlCl_3$ (4 eq.) in d_8-THF.

***In situ* variable-temperature ^{11}B NMR study of reaction of [(THF)BH_2NH_3(18-C-6)][$AlCl_4$] with diisopropylethylamine**

$^{i}Pr_2EtN$ (33 μl, 24 mg, 0.19 mmol) was injected directly into an NMR tube containing [(THF)BH_2NH_3(18-C-6)][$AlCl_4$] (50 mg, 0.09 mmol) in 0.5 ml CD_2Cl_2 held at -78°C and shaken before transferring to the spectrometer. ^{11}B and ^{1}H spectra were collected at -40°C and at further 10°C intervals until room temperature.

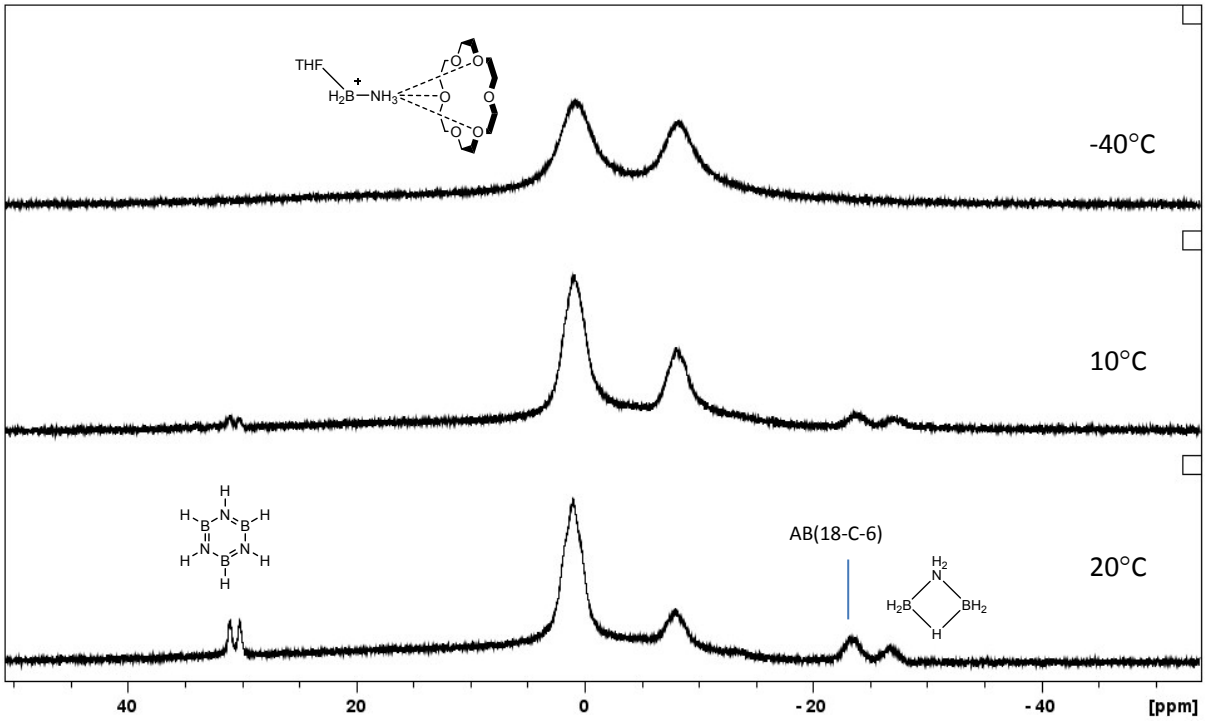

Figure S15 *In situ* variable temperature ^{11}B NMR spectra of [(Et_3N)BH_2NH_3(18-C-6)][$AlCl_4$] + $^{i}Pr_2EtN$ (2 eq.) in CD_2Cl_2.

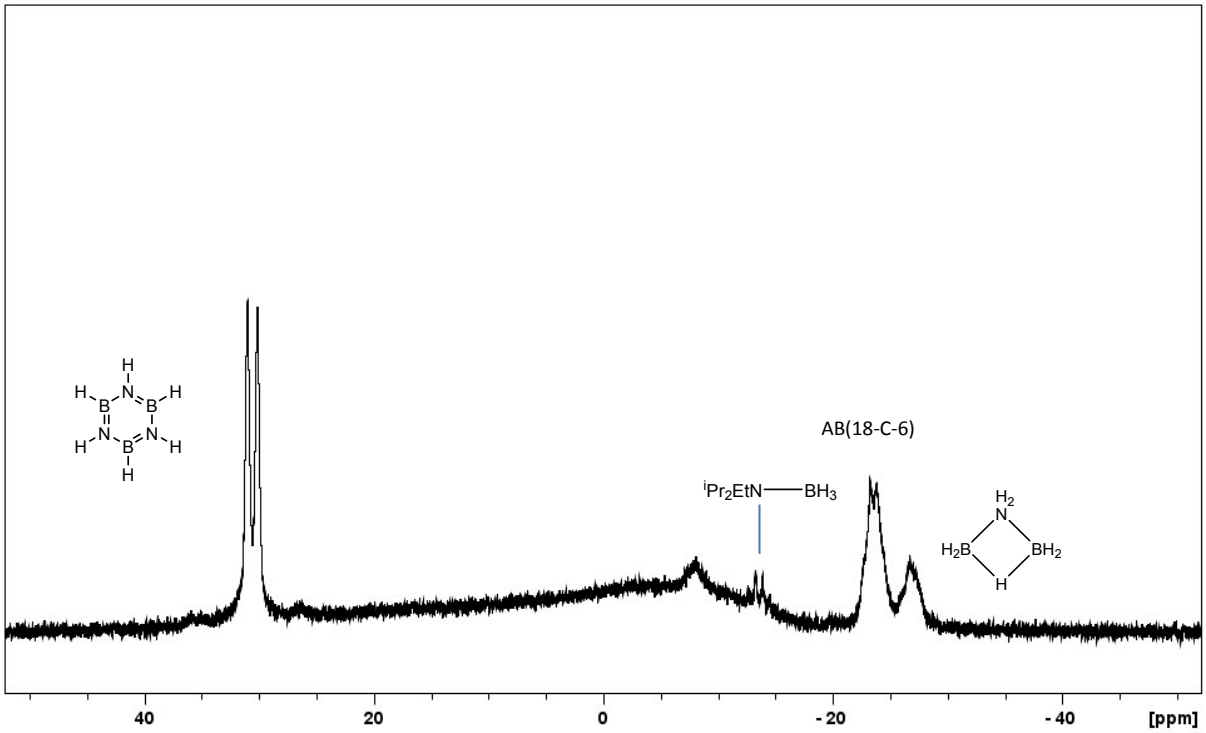

Figure S16 *In situ* variable temperature ^{11}B NMR spectrum of $[(Et_3N)BH_2NH_3(18\text{-}C\text{-}6)][AlCl_4]$ + $^{i}Pr_2EtN$ (2 eq.) in CD_2Cl_2 after shaking again at room temperature.

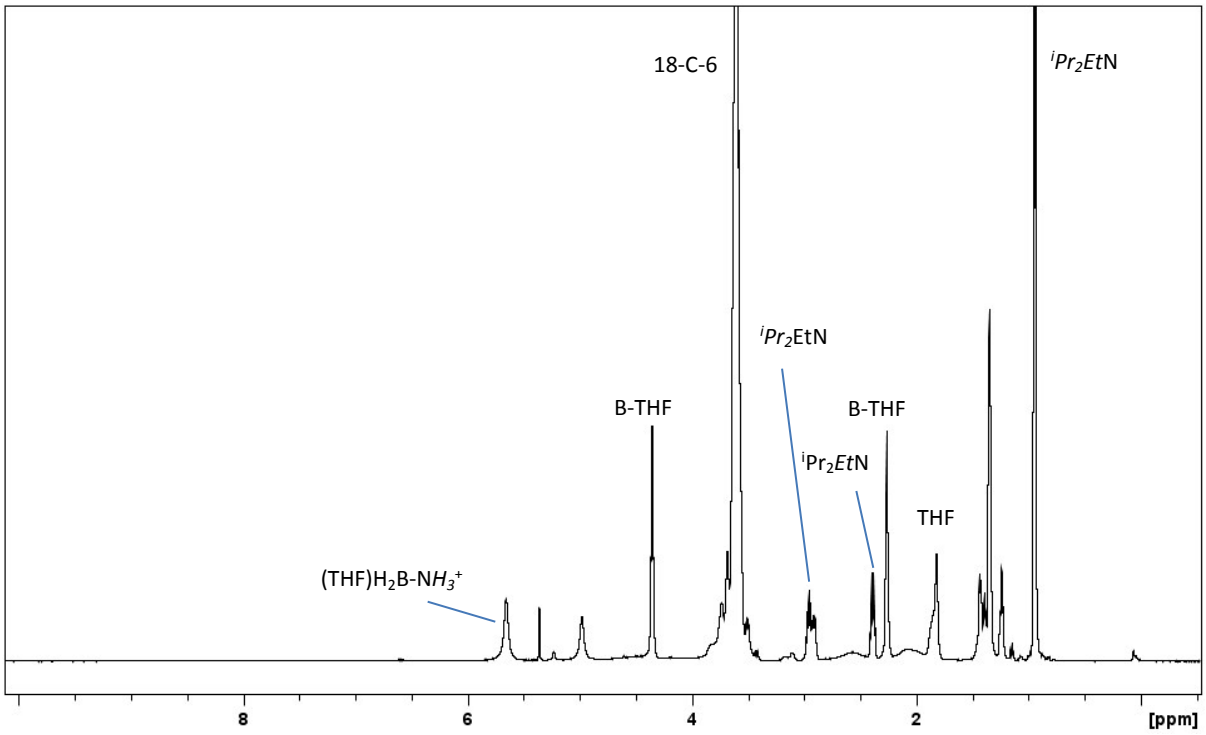

Figure S17 *In situ* variable temperature ^{1}H NMR spectrum of $[(Et_3N)BH_2NH_3(18\text{-}C\text{-}6)][AlCl_4]$ + $^{i}Pr_2EtN$ (2 eq.) in CD_2Cl_2 (-40°C).

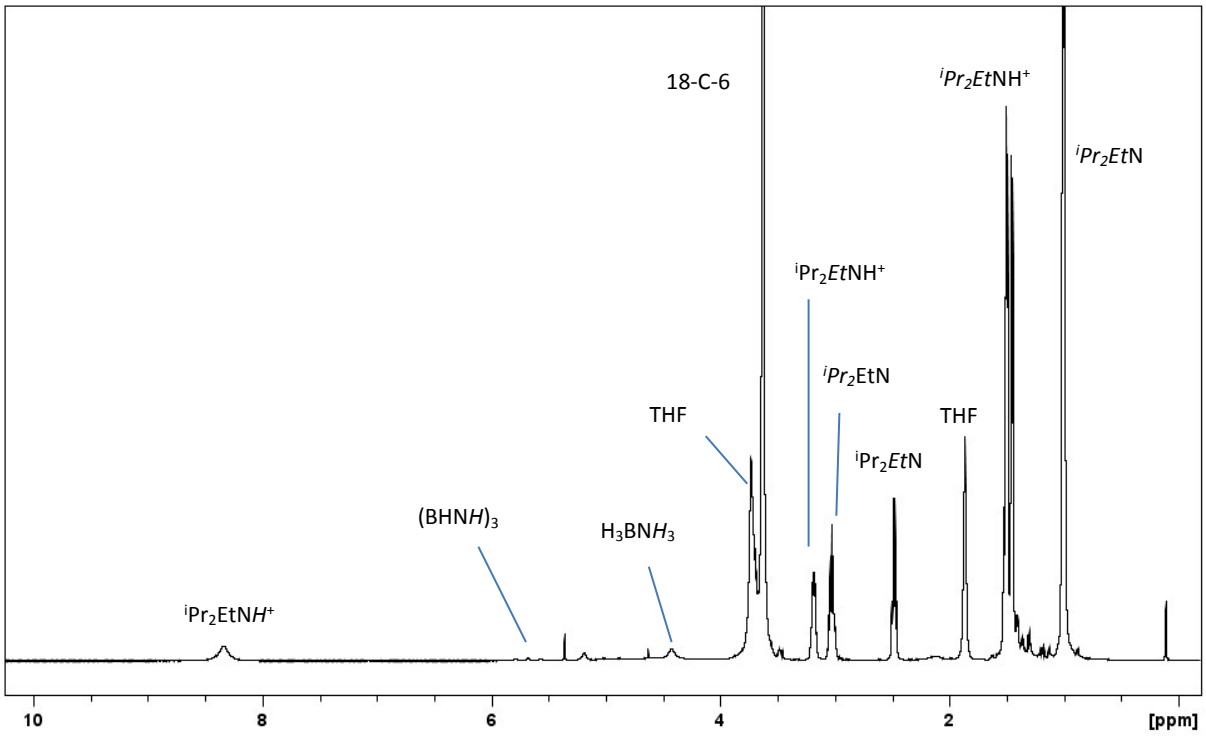

Figure S18 *In situ* variable temperature ^{1}H NMR spectrum of $[(Et_3N)BH_2NH_3(18\text{-}C\text{-}6)][AlCl_4]$ + $^{i}Pr_2EtN$ (2 eq.) in CD_2Cl_2 (room temperature after shaking sample).

Growth of crystals for X-ray diffraction

[(THF)BH_2NH_3(18-C-6)][$AlCl_4$] *[**1**·THF(18-C-6)][$AlCl_4$]*

$AlCl_3$ (258 mg, 1.93 mmol) was added to a solution of ammonia borane (20 mg, 0.65 mmol) and 18-crown-6 (172 mg, 0.65 mmol) in 3 ml THF and stirred at room temperature for 16h. Layering of 1 ml of the reaction mixture with hexane in a narrow (1cm diameter) tube produced crystals after standing for several days.

[$BH_2(NH_3)_2$(18-C-6)$_2$][$AlCl_4$] *[**2**(18-C-6)$_2$][$AlCl_4$]*

Method 1: from AB + $AlCl_3$ / THF reflux

$AlCl_3$ (87 mg, 0.65 mmol) was added to a solution of ammonia borane (20 mg, 0.65 mmol) and 18-crown-6 (172 mg, 0.65 mmol) in 2 ml THF and the mixture heated to reflux for 16h. Layering of 1 ml of the reaction mixture with hexane in a narrow (10 mm diameter) tube produced crystals after standing for several days.

Method 2: from [**1**·THF(18-C-6)][$AlCl_4$] + Et_3N / THF

Triethylamine (50 μl, 37 mg, 0.36 mmol) was added to a solution of [(THF)BH_2NH_3(18-C-6)][$AlCl_4$] (100 mg, 0.23 mmol) in 2 ml THF at room temperature and was stirred for 16h. Layering of 1 ml of the reaction mixture with hexane in a narrow (10 mm diameter) tube produced crystals after standing for several days.

Both methods gave crystals of identical unit cell parameters. The data presented are those obtained from method 2.

[(Et_3N)BH_2NH_3(18-C-6)][$AlCl_4$] *[**1**·Et_3N(18-C-6)][$AlCl_4$]*

Triethylamine (50 μl, 37 mg, 0.36 mmol) was added to a solution of [(THF)BH_2NH_3(18-C-6)][$AlCl_4$] (100 mg, 0.23 mmol) in 3 ml DCM at room temperature and was stirred for 16h. The solution was filtered and layered with hexane in a 20 mm diameter tube, which produced crystals after standing for several days.

X-Ray Crystallography

Data for all complexes were collected at 180(2) K on a Bruker D8-QUEST diffractometer using an Incoatec IμS Cu microsource (λ = 1.5418 Å). Crystals were mounted directly from solution using perfuorohydrocarbon oil to prevent atmospheric oxidation, hydrolysis, and solvent loss. Structures were solved using SHELXT (Sheldrick, 2015) and refined using SHELXL-2014 (Sheldrick, 2015).

CCDC No.	**1443249**	**1443250**	**1443248**
Compound	**[(THF)BH_2NH_3(18-C-6)] [$AlCl_4$]** [**1**·THF(18-C-6)][$AlCl_4$]	**[$BH_2(NH_3)_2$(18-C-6)$_2$] [$AlCl_4$]** [**2**(18-C-6)$_2$][$AlCl_4$]	**[(Et_3N)BH_2NH_3(18-C-6)] [$AlCl_4$]** [**1**·Et_3N(18-C-6)][$AlCl_4$]
Chemical formula	$C_{16}H_{37}AlBCl_4NO_7$	$C_{24}H_{56}AlBCl_4N_2O_{12}$	$C_{18}H_{44}AlBCl_4N_2O_6$
FW / g·mol^{-1}	535.05	744.29	564.14
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	$Pna2_1$	Pn	$Pna2_1$
a / Å	19.0847(7)	13.6132(5)	12.7434(3)
b / Å	16.0369(6)	16.0212(6)	13.7696(3)
c / Å	8.8244(3)	17.7762(7)	16.4706(4)
β / °		94.329(2)	
V / Å^3	2700.79(17)	3865.9(3)	2890.12(12)
Z	4	4	4
ρ_{calcd} / g·cm^{-3}	1.316	1.279	1.187
μ / mm^{-1}	4.589	3.457	4.296
Reflections collected	16779	53146	17536
Independent reflections	4023	14383	4838
R_{int}	0.060	0.058	0.038
*R*1 [$I > 2\sigma(I)$]	0.099	0.075	0.032
w*R*2 (all data)	0.219	0.194	0.072

Flack parameter	0.02(2)	0.25(2)*	0.15(2)*

* Refined as an inversion twin.