Electronic Supplementary Data (ESI)

Synthesis of **1**;.Al(NMe$_2$)$_3$ in *n*-hexane (1.70 cm^3, 1 mol dm^{-3}, 1.7 mmol) was added to Me$_2$NHBH$_3$ (100 mg, 1.7 mmol) in thf (15 cm^3) and left to stir under Ar for *ca.* 16 h. The solvent was removed to produce a *ca.* 1cm^3 concentrated solution and the product was left to crystallise at -20 °C. Yield 0.13 g (67 % based on Me$_2$NHBH$_3$). ^{1}H NMR (+25 ^{o}C, 500.1 MHz, d$_8$-toluene), δ = 2.65 ppm (s., Me$_2$N) (also present minor doublet due to **B**, δ = 4.0 ppm (q., BH$_2$, $^1J_{BH}$ = 106 Hz), 2.64 (s., Me$_2$N). ^{11}B NMR (+25^{o}C, 160.5 MHz, d$_8$-toluene, rel. to BF$_3$-Et$_2$O), 1.87 ppm (t., $^1J_{B\text{-}H}$ = 107 Hz) (this appears as two overlapping triplets in d$_8$-thf). ^{27}Al {^{1}H-coupled} NMR (+25^{o}C, 130.3 MHz, d$_8$-toluene, rel. to Al(NO$_3$)$_3$/D$_2$O), δ = 82.8 ppm (d., $^1J_{Al\text{-}H}$ = 288 Hz). Satisfactory elemental analysis could not be obtained due to contamination of crystals of **1** with small amounts of **B** (observed in the ^{1}H and ^{11}B NMR spectra).
Crystal data for **1**: C$_8$H$_{29}$AlB$_2$N$_4$, M= 229.95, Orthorhombic, space group *Pnn2*, Z = 2, a= 10.1260(5), b= 11.6705(6), c = 6.4209(3) Å, V = 758.79(8) Å^3, μ(Mo–Kα) = 0.114 mm^{-1}, ρ_{calc} = 1.006 Mg m^{-3}, T = 180(2) K. Total reflections 3182, unique 1490 (R_{int}= 0.033). $R1$ = 0.057 [I>2σ(I)] and $wR2$ = 0.171 (all data): The major component of the disorder is shown in Fig. 2. Data were collected on a Nonius KappaCCD diffractometer, solved by direct methods and refined by full-matrix least squares on F^2 (G. M. Sheldrick, SHELX-97, Göttingen, **1997**). CCDC 803522 contains the supplementary crystallographic data for **1**. Data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax 441223 316033.

NMR Studies

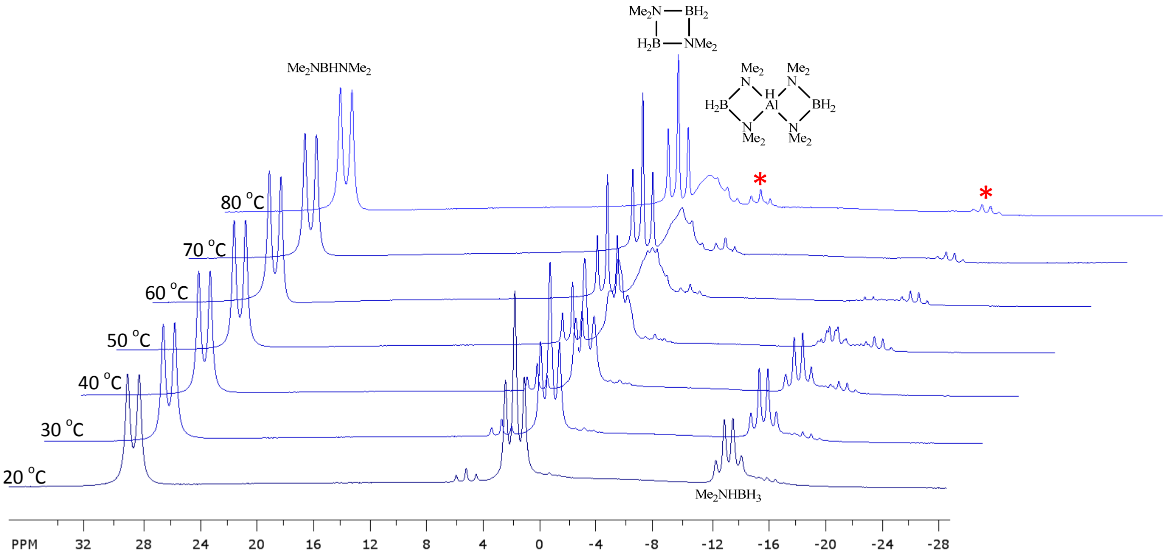

Fig. 1S ^{11}B NMR spectra of a 3 : 1 mixture of Me$_2$NHBH$_3$ with Al(NMe$_2$)$_3$ (* the NMe$_2$BH$_2$NMe$_2$BH$_3$]$^-$ anion).

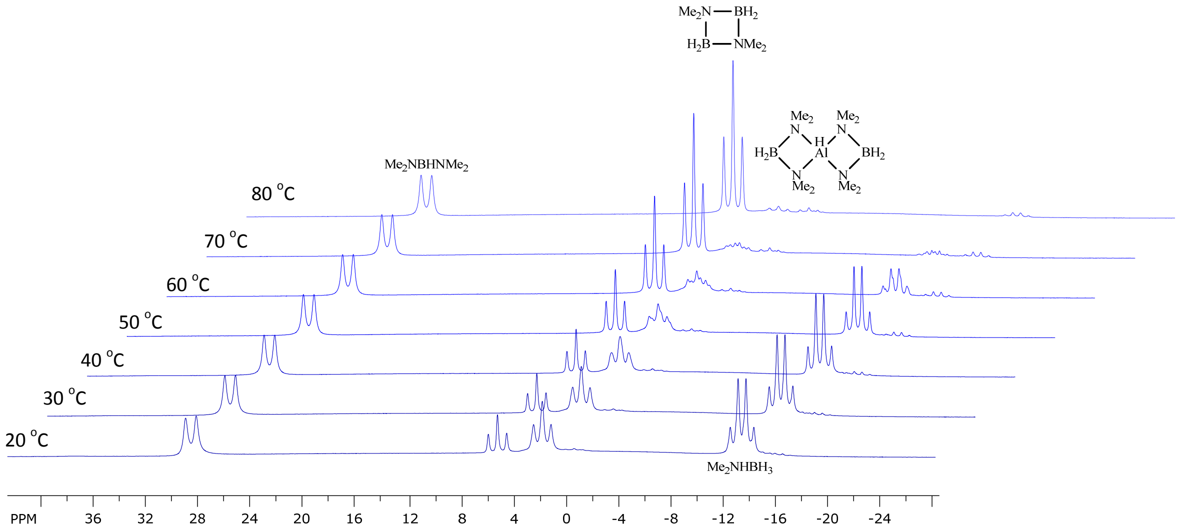

Fig. 2S ^{11}B NMR spectra of a 4 : 1 mixture of Me_2NHBH_3 with $Al(NMe_2)_3$.

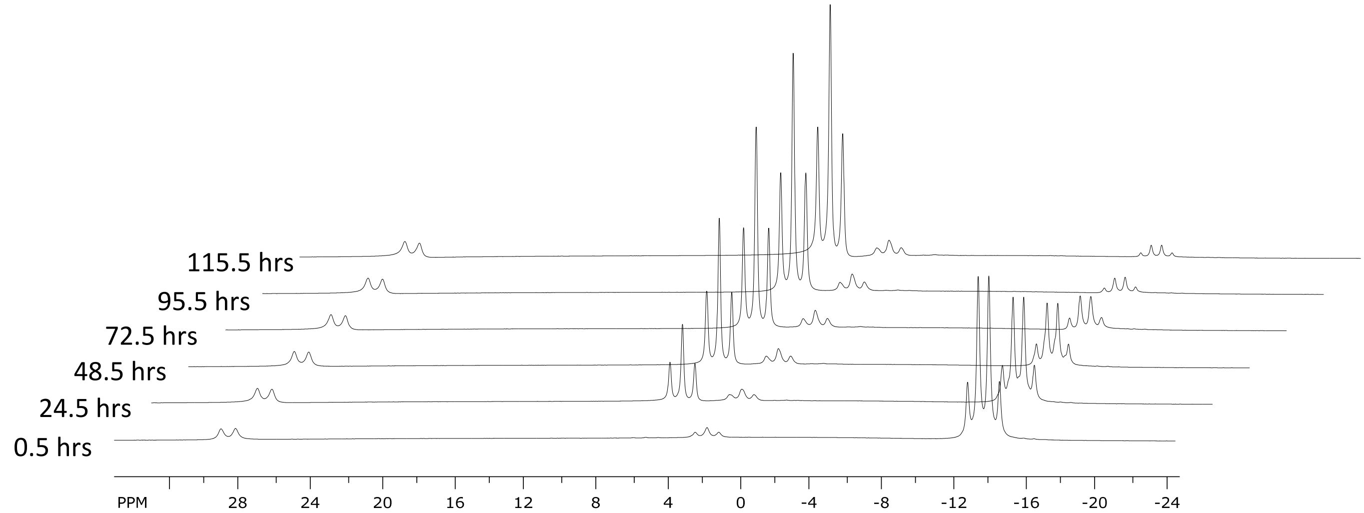

Fig. S3 ^{11}B NMR spectra of a 12 : 1 reaction mixture of Me_2NHBH_3 to $Al(NMe_2)_3$ at 25^{o}C.

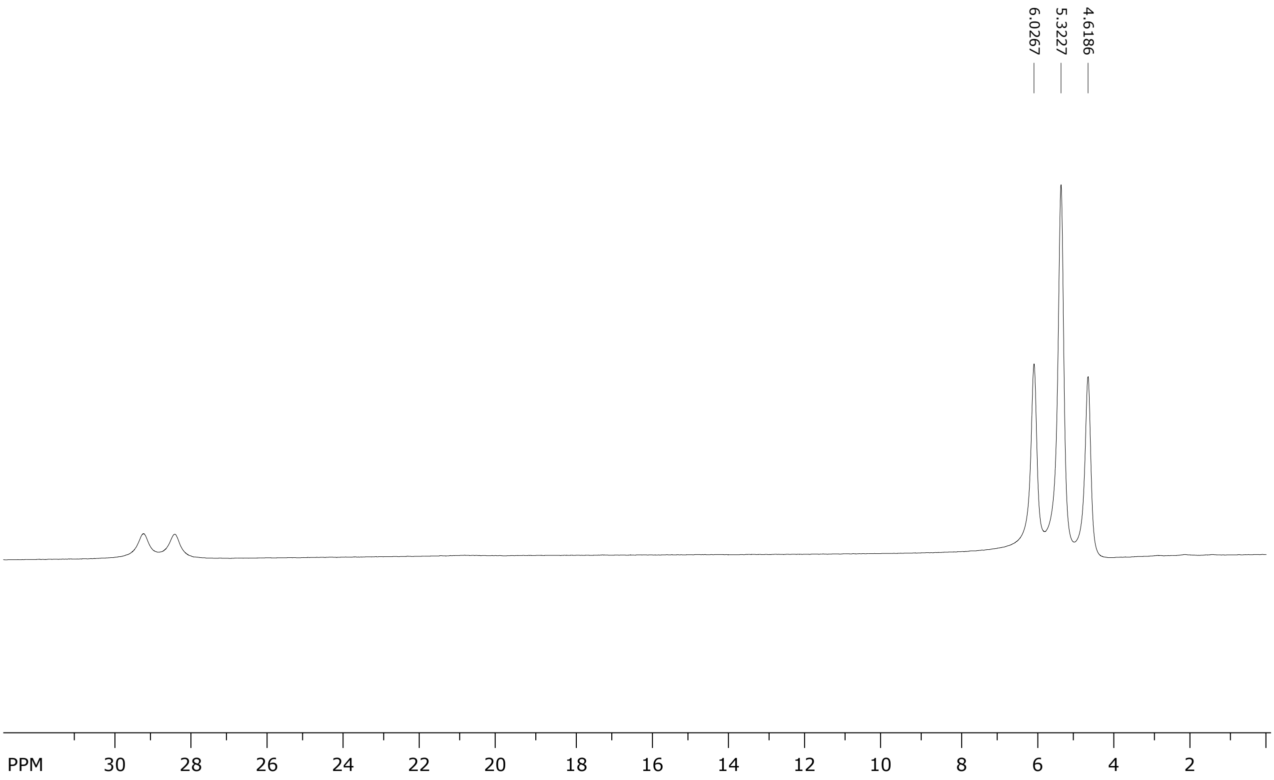

Fig. S5 ^{11}B NMR spectrum of a toluene solution of Me_2NHBH_3 (large excess) with a 5 mol% loading of $Al(NMe_2)_3$ after 48hrs at 50°C.

Ab Initio Calculations

Preliminary electronic structure calculations were carried out at MP2 level using Dunning's cc-pVTZ basis set ([1], [2]) within the GAUSSIAN 03 [3] quantum chemistry package in order to determine the equilibrium geometry of the molecule (see Fig. S6). Within the calculations a Natural Bond Orbital analysis [4] was performed in order to further examine the bonding within molecule and partial charges were derived based on the Merz-Singh-Kollman scheme ([5],[6]) (see Table S1).

The crystal structure and theoretical calculations both provide evidence of a "square-based pyramid" structure. This is backed-up by the NBO analysis which shows the hybridisation of the central Aluminium to be consistent with this geometry. The hydride attached to the Aluminium atom shows the greatest partial negative charge of all the hydrides consistent with the mechanism proposed in this paper.

Label	Atom	Charge	Comment
1	Al	1.150	
2	H	-0.460	Hydride attached to Al
3	N	-0.828	
4	N	-0.688	
5	H	0.266	
6	H	0.266	
7	H	0.319	
8	H	0.291	
9	B	0.580	
10	H	-0.261	Hydride attached to B(9)
11	H	-0.281	Hydride attached to B(9)
12	N	-0.867	
13	N	-0.734	
14	H	0.282	
15	H	0.279	
16	H	0.331	
17	H	0.303	
18	B	0.588	
19	H	-0.258	Hydride attached to B(18)
20	H	-0.277	Hydride attached to B(18)

Table S1 Partial Charges on the atoms of the model compound calculated using the Merz-Singh-Kollman scheme.

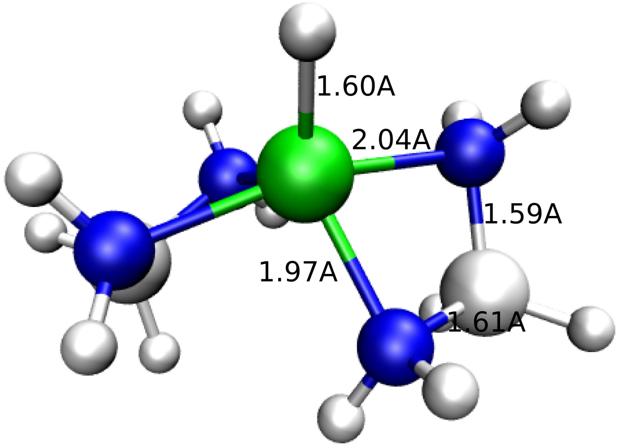

Fig. S6 Geometry-optimised structure of $[(NH_2)_2BH_2\}_2AlH]$.

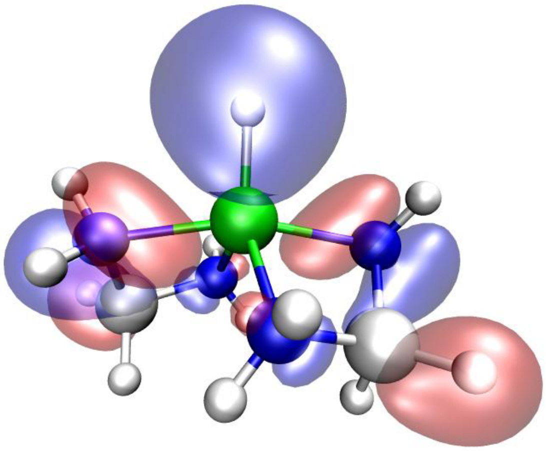

Fig. S7 The HOMO of $[(NH_2)_2BH_2\}_2AlH]$.

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