

Supplementary Information

The hafnium mediated NH activation of an amido-borane

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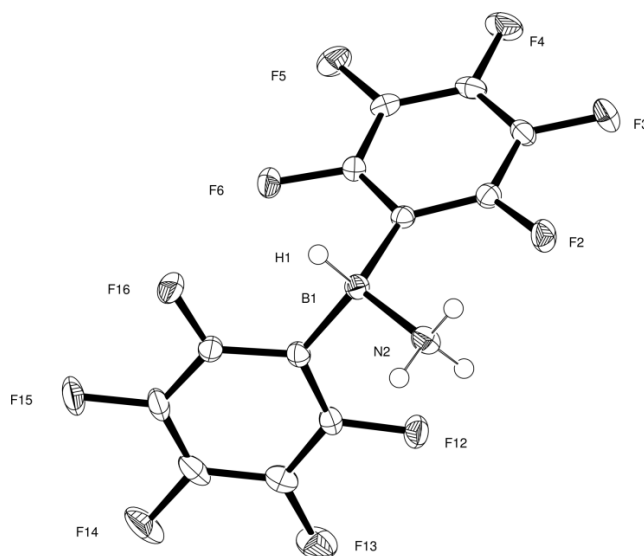


Figure S1. ORTEP representation of the structure of **1**.C₆D₆ showing 50% probability ellipsoids; the C₆D₆ solvent molecule has been omitted for clarity. Selected bond lengths [Å] and angles [°] B(1)—N(2) 1.603(2), B(1)—C(1) 1.6309(18), B(1)—C(11) 1.6324(19); N(2)—B(1)—C(1) 111.02(10), N(2)—B(1)—C(11) 107.97(10), C(1)—B(1)—C(11) 112.70(10).

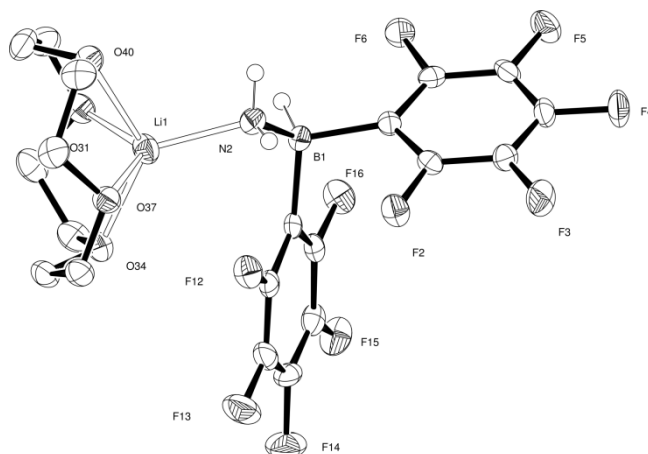


Figure S2. ORTEP representation of the structure of **2**·12-crown-4 showing 50% probability ellipsoids; hydrogen atoms have been omitted for clarity. Selected bond lengths [\AA] and angles [$^\circ$] B(1)—N(2) 1.544(2), B(1)—C(1) 1.661(2), B(1)—C(11) 1.648(3); N(2)—B(1)—C(1) 114.38(13), N(2)—B(1)—C(11) 111.78(14), C(11)—B(1)—C(1) 105.21(13), B(1)—N(2)—Li(1) 114.32(13).

Table S1. Hydrogen bonds present within the solid state structure of **3**.

D-H \cdots A	d(D-H)	d(H \cdots A)	d(D \cdots A)	\angle (DHA)
N(11)-H(11A) \cdots O(71)	0.79(4)	2.30(4)	3.053(3)	158(4)
N(11)-H(11B) \cdots F(26)	0.84(3)	2.19(3)	2.874(3)	139(3)
N(41)-H(41A) \cdots O(76)	0.86(3)	2.14(3)	2.995(3)	173(3)
N(41)-H(41B) \cdots F(62)	0.78(3)	2.34(3)	2.894(3)	129(3)

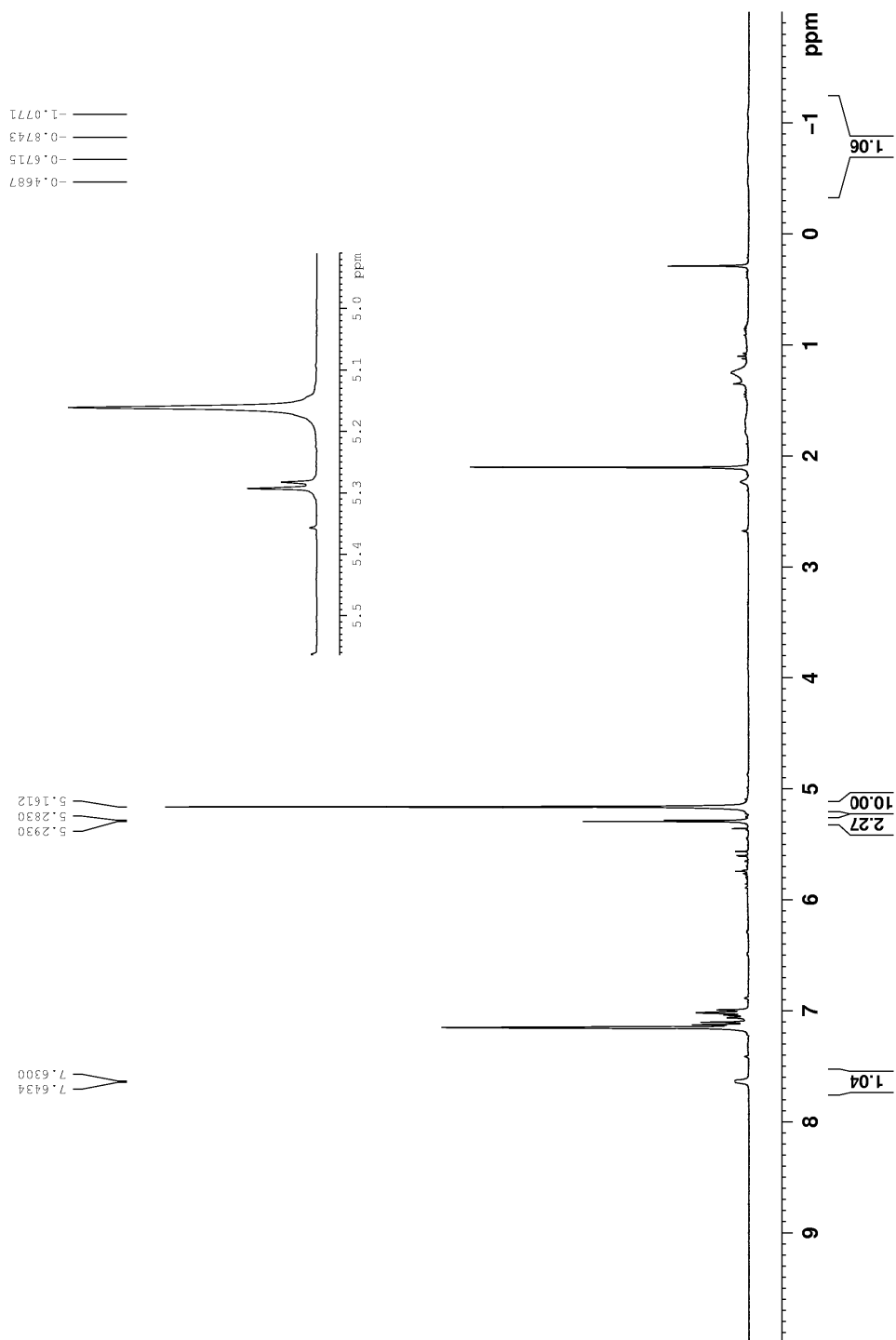


Figure S3. ^1H NMR spectrum of crude reaction mixture (toluene solution) from the preparation of **4** illustrating the three different peaks observed in the Cp region. The major peak corresponds to product **4**.

Experimental

All reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques in pre-dried glassware. Solvents were dried using an appropriate drying agent and distilled under nitrogen prior to use, dichloromethane (CaH₂), light petroleum (Na/dyglyme/benzophenone), tetrahydrofuran (sodium/benzophenone) and toluene (sodium); 12-crown-4 was degassed and dried over activated 4 Å molecular sieves prior to use.

NMR samples were prepared using degassed deuterated solvents dried over activated 4 Å molecular sieves. NMR spectra were obtained using a Bruker Avance DPX300 spectrometer at 23 °C, *J* values are given in Hz. Chemical shifts are reported in ppm and referenced to residual solvent resonances (¹H, ¹³C); ¹⁹F is relative to CFCl₃; ¹¹B is relative to Et₂O·BF₃. Elemental analyses were carried out at the Department of Health and Human Sciences, London Metropolitan University.

H₃N·BH(C₆F₅)₂ (1)

Ammonia was passed over a solution of Me₂S·BH(C₆F₅)₂ (4.60 g, 11.3 mmol) in toluene (45 cm³) for approximately 5 minutes. The solvent was then removed under reduced pressure and the crude product recrystallized from dichloromethane–light petroleum mixture at –25 °C, (3.40 g, 83%). Crystals suitable for X-ray analysis were grown at room temperature from the NMR sample. Elemental analysis found: C 39.9, H 1.0, N 4.0. Calculated for C₁₂H₄BF₁₀N: C 39.7, H 1.1, N 3.9. δ_H/ppm (300.1 MHz, C₆D₆) 3.18 (1H, br, BH), 1.73 (3H, br, NH₃). δ_B/ppm (96.3 MHz, C₆D₆) –15.8 (d, *J*_{BH} 102). δ_F/ppm (C₆D₆) –134.9 (4F, d, *J*_{FF} 23, *o*-F), –157.5 (2F, t, *J*_{FF} 20, *p*-F), –163.4 (4F, m, *m*-F).

[Li][NH₂BH(C₆F₅)₂] (2)

A solution of **1** (0.30 g, 0.8 mmol) in thf (10 cm³) was cooled to -78 °C and n-BuLi (0.8 mmol) added before warming to room temperature to yield [Li(thf)_x][H₂NBH(C₆F₅)₂] (**2**). 12-crown-4 (0.1 cm³, 0.8 mmol) was added before removal of the volatiles under reduced pressure to yield a colourless solid. Recrystallization from dichloromethane–light petroleum solution yielded X-ray quality crystals of [Li(12-crown-4)][NH₂BH(C₆F₅)₂], (0.31 g, 72%). Elemental analysis found: C 43.9, H 3.4, N 2.5. Calculated for C₂₀H₁₉BF₁₀LiNO₄: C 44.0, H 5.3, N 2.6. δ_H/ppm (300.1 MHz, CDCl₃) 3.71 (16H, s, CH₂), 3.22 (2H, br NH₂) δ_C/ppm (75.5 MHz {¹H}, CDCl₃) 66.9 (CH₂). δ_B/ppm (96.3 MHz, CDCl₃) -15.5 (d, *J*_{BH} 96). δ_F/ppm (282.4 MHz, CDCl₃) -135.5 (4F, d, *J*_{FF} 23, *o*-F), -163.2 (2F, br, *p*-F), -166.2 (4F, m, *m*-F).

Cp₂Hf{NH₂BH(C₆F₅)₂}₂ (3)

To a freshly prepared solution of **2** (1.1 mmol) in toluene (15 cm³) at -78 °C was added Cp₂HfCl₂ (0.44 g, 1.1 mmol) before returning to room temperature. The pale brown solution was stirred over night to yield a colourless precipitate of LiCl, which was separated by filtration. Removal of the volatiles from the filtrate yielded a sticky colourless solid, which was recrystallized from a thf–light petroleum solvent mixture to yield few X-ray quality crystals of Cp₂Hf{NH₂BH(C₆F₅)₂}₂. NMR analysis displayed a mixture of products and isolation of a crystalline compound could not be repeated despite numerous attempts.

Crystallography

Data were processed using the CrysAlisPro program,^{S1} while solving the structure was carried out within the WinGX suite.^{S2} The structures were determined by the direct methods routines in SHELXS (**1**, **2** and **3**)^{S3} or SIR-92 (**4**),^{S4} and refined by full-matrix least-squares methods on *F*² in SHELXL.^{S3} The non-hydrogen atoms were refined with anisotropic

thermal parameters. Hydrogen atoms on cyclopentadienyl rings and on the nitrogen atom in **4** were included in idealised positions and their U_{iso} values were set to ride on the U_{eq} values of the parent carbon atoms; all other hydrogen atoms were located in the Fourier difference map and freely refined.

- S1. *CrysAlisPro*, Oxford Diffraction Ltd., Abingdon, UK, 2009.
- S2. L. J. Farrugia, *J. Appl. Cryst.*, **1999**, 32, 837–838.
- S3. G. M. Sheldrick, *Acta Cryst. A*, **2008**, 64, 112–122.
- S4. A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Cryst.*, **1993**, 26, 343–350.