Supporting Information for

Group 3-centred Dehydrocoupling of $Me_2NH.BH_3$

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General Experimental Procedures

All manipulations were carried out using standard Schlenk line and glovebox techniques under an inert atmosphere of either nitrogen or argon. NMR experiments were conducted in Youngs tap NMR tubes made up and sealed in a Glovebox. NMR were collected on a Bruker AV300 spectrometer operating at 75.5 MHz (^{13}C), 96.3 MHz (^{11}B). Variable temperature ^1H NMR data were recorded on a Bruker AV400 spectrometer. The spectra were referenced relative to residual solvent resonances or an external $BF_3.OEt_2$ standard (^{11}B). Solvents (Toluene, THF, Hexane) were dried by passage through a commercially available (Innovative Technologies) solvent purification system, under nitrogen and stored in ampoules over molecular sieves. C_6D_6 and d_8-toluene were purchased from Goss Scientific Instruments Ltd. and dried over molten potassium before distilling under nitrogen and storing over molecular sieves. $[Y\{N(SiMe_3)_2\}_3]$ and $[Sc\{N(SiHMe_2)_2\}_3(THF)_2]$ were prepared by literature procedures.[1,2]

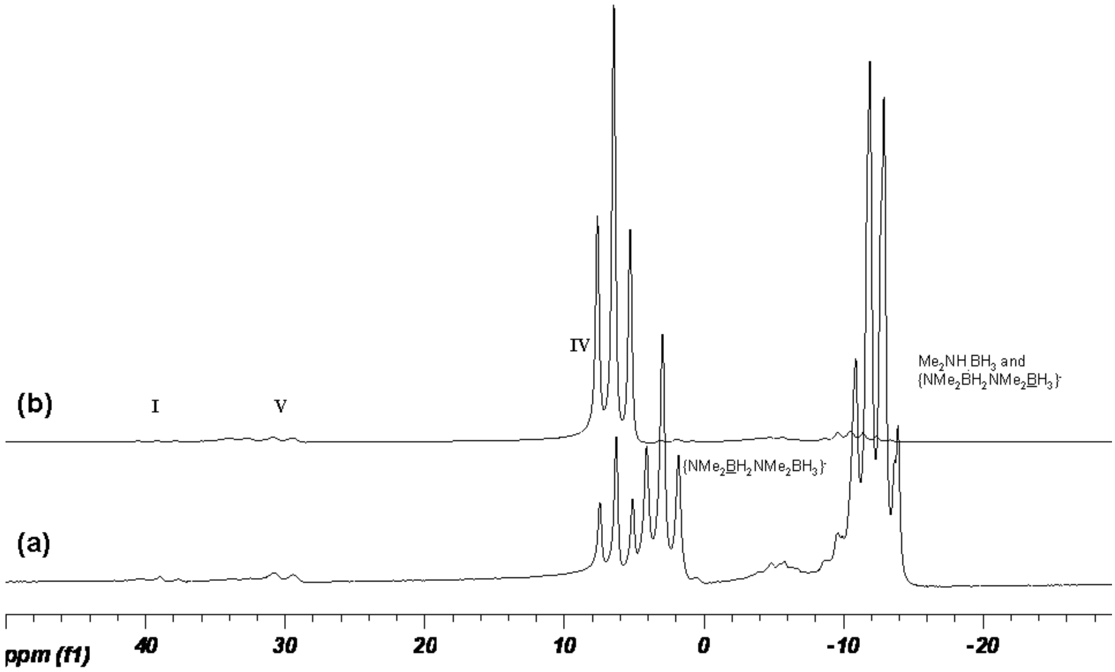

Figure S1: ^{11}B NMR spectrum, with tentative assignments, of the Y-catalysed dehydrocoupling of $Me_2NH.BH_3$ after (a) 15 minutes at 25 °C; (b) 12 hours at 60 °C

Synthesis of compound 1, $[Sc\{NMe_2BH_2NMe_2BH_3\}_2\{N(SiHMe_2)_2\}]$

A solution of $[Sc\{N(SiHMe_2)_2\}_3(THF)_2]$ (0.15 g, 0.28 mmol) in toluene (10 mL) was added at room temperature to a solution of Me_2NHBH_3 (0.07 g, 1.1 mmol) in toluene (5 mL). After gas evolution had ceased, the solution was stirred overnight before *in vacuo* removal of volatiles. Crystallisation of the resultant colourless solid from the minimum amount of toluene (ca. 0.5 mL) at –30 °C resulted in the isolation of compound **1** as colourless crystals suitable for an X-ray diffraction analysis (0.08 g, 70 %). %). Anal. Calc. for $C_{12}H_{48}B_4N_5ScSi_2$: C, 35.41; H, 11.91; N, 17.21. Found: C, 35.60; H, 11.74; N, 1703. $^1H\{^{11}B\}$ NMR (C_6D_6, 298 K) $\delta = 0.25$ (br. S,, 12H, Si*Me*), 2.10 (s, 12H, C*H*$_3$), 2.43 (s, 12H, C*H*$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K) $\delta = 0.9$ (Si*Me*), 43.9 (N*C*H$_3$), 49.8 (N*C*H$_3$). ^{11}B NMR (C_6D_6, 298 K) $\delta = 4.0$ (t, $^1J_{HB} = 104$ Hz, *B*H$_2$), –2.9 (q, $^1J_{HB} = 90$ Hz, *B*H$_3$).

1 D C. Bradley, J. S. Ghotra and J. Hart, *J. Chem. Soc., Dalton Trans.*, 1973, 1021.

2 R. Anwander, O. Runte, J. Eppinger, G. Gerstberger, E. Herdtweck and M. Spiegler, *J. Chem. Soc., Dalton Trans.*, 1998, 847.