Supporting Information for

Group 3-centred Dehydrocoupling of Me₂NH.BH₃

Michael S. Hill,* Gabriele Kociok-Köhn and Thomas P. Robinson
Department of Chemistry, University of Bath
Claverton Down, Bath, BA2 7AY (UK)
E-mail: m.s.hill@bath.ac.uk

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 (¹³C), 96.3 MHz (¹¹B). Variable temperature ¹H NMR data were recorded on a Bruker AV400 spectrometer. The spectra were referenced relative to residual solvent resonances or an external BF₃.OEt₂ standard (¹¹B). 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. C₆D₆ and d₈-toluene were purchased from Goss Scientific Instruments Ltd. and dried over molten potassium before distilling under nitrogen and storing over molecular sieves. [Y{N(SiMe₃)₂}₃] and [Sc{N(SiHMMe₂)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$_2$NH.BH$_3$ after (a) 15 minutes at 25 °C; (b) 12 hours at 60 °C.

Synthesis of compound 1, [Sc{NMe$_2$BH$_2$NMe$_2$BH$_3$}]$_2$[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$_2$NHBH$_3$ (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$_4$N$_5$ScSi$_2$: C, 35.41; H, 11.91; N, 17.21. Found: C, 35.60; H, 11.74; N, 17.03. $^1$H{$_{^{11}}$B} NMR (C$_6$D$_6$, 298 K) $\delta$ = 0.25 (br. S., 12H, SiMe), 2.10 (s, 12H, CH$_3$), 2.43 (s, 12H, CH$_3$). $^{13}$C{$_{^1}$H} NMR (C$_6$D$_6$, 298 K) $\delta$ = 0.9 (SiMe), 43.9 (NCH$_3$), 49.8 (NCH$_3$). $^{11}$B NMR (C$_6$D$_6$, 298 K) $\delta$ = 4.0 (t, $^1$J$_{HB}$ = 104 Hz, BH$_2$), −2.9 (q, $^1$J$_{HB}$ = 90 Hz, BH$_3$).