

Supplementary Information for

Alkali Metal-mediated Dehydrocoupling of $\text{Me}_2\text{NH}\cdot\text{BH}_3$

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General Experimental Procedures

All reactions were carried out using standard Schlenk line and glovebox techniques under an inert argon atmosphere. NMR experiments were conducted in Youngs tap NMR tubes prepared and sealed in a glovebox. NMR spectra were collected on a Bruker AV300 spectrometer operating at 75.5 MHz (^{13}C), 96.3 MHz (^{11}B). Variable-temperature ^1H NMR data, ^1H - ^{11}B HMQC, ^1H TOCSY and kinetic experiments were recorded on a Bruker AV400 spectrometer. Solvents (toluene, THF, hexane) were dried by a commercially available solvent purification system (Innovative Technologies) under nitrogen before storage in ampoules over molecular sieves. C_6D_6 and d_8 -toluene were purchased from Goss Scientific Instruments Ltd., dried over molten potassium before distillation under nitrogen and storage over molecular sieves. $\text{Me}_2\text{NH}\cdot\text{BH}_3$ and the group 1 bis(trimethylsilyl)amides were purchased from Sigma-Aldrich Ltd. and were either sublimed or recrystallized before use. GCMS data was obtained on an Agilent Technologies 5975C GCMS using 0.5 mg/ml samples in toluene. CHN microanalysis was attempted by Mr. Stephen Boyer of London Metropolitan University.

Synthesis of $[\text{K}(\text{NMe}_2\text{BH}_2\text{NMe}_2\text{BH}_3)]$, **5**

Toluene (ca. 10ml) was added to solid $[\text{K}\{\text{N}(\text{SiMe}_3)_2\}]$ (1.296 g, 6.5 mmol) and two molar equivalents of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ (0.764 g, 13 mmol) in a Schlenk tube and stirred at room temperature for ca. 3 hours, allowing dihydrogen gas to vent under an inert atmosphere. Solvent and volatile $[\text{HN}\{\text{Si}(\text{CH}_3)_2\}_2]$ byproduct were removed under vacuum to provide a white solid **29**. ^1H NMR (d_8 -tol, 298 K) δ = 2.31 (s, 6H, $\text{N}(\text{CH}_3)_2$), 2.76 (s, 6H, $\text{N}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (d_8 -tol, 298 K) δ = 47.2 ($\text{N}(\text{CH}_3)_2$), 49.4 ($\text{N}(\text{CH}_3)_2$). ^{11}B NMR (d_8 -tol, 298 K) δ = -12.3 (br. s, BH_3), 2.6 (br. s, BH_2). A single crystal of compound **5** suitable for X-ray diffraction analysis was isolated from a concentrated

toluene/THF solution at $-30\text{ }^{\circ}\text{C}$. Accurate CHN microanalysis could not be obtained for this highly air- and moisture-sensitive species.

NMR-Scale Synthesis of $[\text{Li}(\text{NMe}_2\text{BH}_2\text{NMe}_2\text{BH}_3)]$, 6

D₈-toluene (ca. 0.5 ml) was added to a solid mixture of $[\text{Li}\{\text{N}(\text{SiMe}_3)_2\}]$ (88 mg, 0.5 mmol) and two molar equivalents of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ (58.8 mg, 1.0 mmol). The solution was sealed in a Youngs tap NMR tube and allowed to react at room temperature for ca. 16 hours. ^1H NMR (d_8 -tol, 298 K) δ = 2.25 (s, 6H, $\text{N}(\text{CH}_3)_2$), 2.41 (s, 6H, $\text{N}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (d_8 -tol, 298 K) δ = 45.9 ($\text{N}(\text{CH}_3)_2$), 53.0 ($\text{N}(\text{CH}_3)_2$). ^{11}B NMR (d_8 -tol, 298 K) δ = -14.7 (q, BH_3 , $^1J_{\text{BH}} = 89\text{ Hz}$), 3.5 (t, BH_2 , $^1J_{\text{BH}} = 98\text{ Hz}$).

NMR-Scale Synthesis of $[\text{Na}(\text{NMe}_2\text{BH}_2\text{NMe}_2\text{BH}_3)]$, 7

D₈-toluene (ca. 0.5 ml) was added to a solid mixture of $[\text{Na}\{\text{N}(\text{SiMe}_3)_2\}]$ (49.9 mg, 0.25 mmol) and two molar equivalents of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ (14.7 mg, 0.25 mmol). The solution was sealed in a Youngs tap NMR tube and allowed to react at room temperature for ca. 2 hours. ^1H NMR (d_8 -tol, 298 K) δ = 2.20 (s, 6H, $\text{N}(\text{CH}_3)_2$), 2.33 (s, 6H, $\text{N}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (d_8 -tol, 298 K) δ = 47.4 ($\text{N}(\text{CH}_3)_2$), 50.1 ($\text{N}(\text{CH}_3)_2$). ^{11}B NMR (d_8 -tol, 298 K) δ = -14.7 (q, BH_3 , $^1J_{\text{BH}} = 87\text{ Hz}$, coincidental with BH_3 of $\text{Na}[\text{NMe}_2\text{BH}_3]$), 1.9 (t, BH_2 , $^1J_{\text{BH}} = 98\text{ Hz}$).

Catalytic NMR-Scale Reaction Between $[\text{LiN}(\text{SiMe}_3)_2]$ and $\text{Me}_2\text{NH}\cdot\text{BH}_3$

d_8 -toluene (ca. 0.5 ml) was added to a mixture of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ (58.8 mg, 1.0 mmol) and $[\text{LiN}(\text{SiMe}_3)_2]$ (8 mg, 0.05 mmol) and the solution sealed in a Youngs tap NMR tube before heating at $80\text{ }^{\circ}\text{C}$ for ca. 124 hours and monitored periodically by ^{11}B NMR spectroscopy. Comparison of chemical shifts in the NMR spectra to literature values identified conversion to ca. 72.0 % $[\text{Me}_2\text{NBH}_2]_2$, ca. 5.0 % $\text{HB}(\text{NMe}_2)_2$ and ca. 2.8 % $\text{Li}[\text{NMe}_2\text{BH}_2\text{NMe}_2\text{BH}_3]$, 6.

Catalytic NMR-Scale Reaction Between $[\text{NaN}(\text{SiMe}_3)_2]$ LIX-Na and $\text{Me}_2\text{NH}\cdot\text{BH}_3$

d_8 -toluene (ca. 0.5 ml) was added to a mixture of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ (58.8 mg, 1.0 mmol) and $[\text{NaN}(\text{SiMe}_3)_2]$ (9 mg, 0.05 mmol). The solution was sealed in a Youngs tap NMR tube, heated at $80\text{ }^{\circ}\text{C}$ for ca. 172 hours and monitored periodically by ^{11}B NMR spectroscopy. Comparison of chemical shifts in the NMR spectra to literature values identified

conversion to ca. 43.0 % $[\text{Me}_2\text{NBH}_2]_2$, ca. 2.8 % $\text{HB}(\text{NMe}_2)_2$ and ca 6.0 % $\text{Na}[\text{NMe}_2\text{BH}_2\text{NMe}_2\text{BH}_3]$, 7.

Catalytic NMR-Scale Reaction Between $[\text{KN}(\text{SiMe}_3)_2]$ and $\text{Me}_2\text{NH.BH}_3$

d_8 -toluene (ca. 0.5 ml) was added to a mixture of $\text{Me}_2\text{NH.BH}_3$ (58.8 mg, 1.0 mmol) and $[\text{KN}(\text{SiMe}_3)_2]$ (10 mg, 0.05 mmol) and the solution sealed in a Youngs tap NMR tube. The reaction was heated at 80 °C for ca. 172 hours and monitored periodically by ^{11}B NMR spectroscopy. Comparison of chemical shifts in the NMR spectra to literature values identified conversion to ca. 43.0 % $[\text{Me}_2\text{NBH}_2]_2$, ca. 6.0 % $\text{HB}(\text{NMe}_2)_2$ and ca 4.4 % $\text{Na}[\text{NMe}_2\text{BH}_2\text{NMe}_2\text{BH}_3]$, 5.