Supplementary Information for

Bespoke Synthesis of Unsymmetrical Diaminoboranes by Alkaline Earth Catalysis

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General experimental procedures

All reactions were carried out using standard Schlenk line and glovebox techniques under an inert nitrogen 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). 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. $Me_2NH.BH_3$, and $(CH_3)_3CNH_2.BH_3$ were purchased from Sigma-Aldrich Ltd. and used without further purification. Pyrrolidine borane, $C_4H_8NH.BH_3$,[1] and the magnesium and calcium diamides $[M\{N(SiMe_3)_2\}_2(THF)_2]$ were synthesised by literature procedures.[2] Pyrrolidine and t-butylamine were purchased from Sigma-Aldrich Ltd. and dried over sodium and calcium hydride respectively. GCMS data was obtained on an Agilent Technologies 5975C GCMS using 0.5 mg/ml samples in toluene. CHN microanalysis was conducted by Mr. Stephen Boyer of London Metropolitan University.

Catalytic NMR-Scale Synthesis of $[\{Me_2N\}BH\{NMe_2\}]$ and $[\{Me_2N\}BH\{NC_4H_8\}]$, 1

(i) Using $[Ca\{N(SiMe_3)_2\}_2]_2$

C_6D_6 (ca. 0.5 ml) was added to a solid mixture of $Me_2NH.BH_3$ (59 mg, 1 mmol), one molar equivalent of C_4H_8NH (71 mg, 1 mmol) and $[Ca\{N(SiMe_3)_2\}_2]_2$ (18 mg, 2.5 mol%) and the solution sealed in a Youngs tap NMR tube before heating to 70°C for 24 hours. Approx. yields using ^{11}B NMR: $[\{Me_2N\}BH\{NMe_2\}]$ 44%, **1** 54%.

(ii) Using $[Mg\{N(SiMe_3)_2\}_2]_2$

C_6D_6 (ca. 0.5 ml) was added to a solid mixture of $Me_2NH.BH_3$ (59 mg, 1 mmol), one molar equivalent of C_4H_8NH (71 mg, 1 mmol) and $[Mg\{N(SiMe_3)_2\}_2]_2$ (17 mg, 2.5 mol%) and the solution sealed in a Youngs tap NMR tube before heating to 70°C for 24 hours. Approx. yields using ^{11}B NMR: [$\{Me_2N\}BH\{NMe_2\}$] 40%, **1** 40%.

(iii) Data

[$\{Me_2N\}BH\{NMe_2\}$] and **1** proved unstable to concentration under vacuum or by evaporation in a glovebox. Complete molecular ions of could not observed by GCMS for either compound. ^{1}H NMR (C_6D_6, 298 K) δ = ca. 1.48 (m, ($N(CH_2)_2(CH_2)_2$)), ca. 1.52 (m, ($N(CH_2)_2(CH_2)_2$)), 2.54 (s, N-CH_3), 2.57 (s, N-CH_3), 2.62 (s, N-CH_3), 2.70 (s, N-CH_3), 3.04 (t, ($N(CH_2)_2(CH_2)_2$), J_{HH} = 6.78 Hz), 3.08 (t, ($N(CH_2)_2(CH_2)_2$), J_{HH} = 6.78 Hz), 3.20 (t, ($N(CH_2)_2(CH_2)_2$), J_{HH} = 6.60 Hz), 3.28 (t, ($N(CH_2)_2(CH_2)_2$), J_{HH} = 6.60 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 298 K) δ = 26.60 ($N(CH_2)_2(CH_2)_2$), 26.90 ($N(CH_2)_2(CH_2)_2$), 39.91 (N-CH_3), 40.01 (N-CH_3), 40.18 (N-CH_3), 41.33 (N-CH_3), 48.18 ($N(CH_2)_2(CH_2)_2$), 49.99 (br, $N(CH_2)_2(CH_2)_2$). ^{11}B NMR (C_6D_6, 298 K) δ = 29.9 (d, [$\{Me_2N\}BH\{NMe_2\}$], *B*H, $^1J_{BH}$ = 128 Hz), 32.2 (d, **1**, *B*H, $^1J_{BH}$ = 106 Hz).

Catalytic NMR-Scale Synthesis of [$\{Me_2N\}BH\{NH^tBu\}$], 2

(i) Using [$Ca\{N(SiMe_3)_2\}_2]_2$

C_6D_6 (ca. 0.5 ml) was added to a solid mixture of $Me_2NH.BH_3$ (59 mg, 1 mmol), one molar equivalent of $(CH_3)_3CNH_2$ (73 mg, 1 mmol) and $[Ca\{N(SiMe_3)_2\}_2]_2$ (18 mg, 2.5 mol%) and the solution sealed in a Youngs tap NMR tube before heating to 70°C for 48 hours. Approx. yields using ^{11}B NMR: [$\{Me_2N\}BH\{NMe_2\}$] 8% , **2** 75%.

(ii) Using $[Mg\{N(SiMe_3)_2\}_2]_2$

C_6D_6 (ca. 0.5 ml) was added to a solid mixture of $Me_2NH.BH_3$ (59 mg, 1 mmol), one molar equivalent of $(CH_3)_3CNH_2$ (73 mg, 1 mmol) and $[Mg\{N(SiMe_3)_2\}_2]_2$ (17 mg, 2.5 mol%) and the solution sealed in a Youngs tap NMR tube before allowing to react at RT for 92 hours. Approx. yields using ^{11}B NMR: [$\{Me_2N\}BH\{NMe_2\}$] 0%, **2** 79%.

(iii) Data

2 proved unstable to concentration under vacuum or by evaporation in a glovebox. Although the complete molecular ion could not be observed by GCMS analysis, an ion with *m*/*z* 113.0 corresponding to $M^+ - CH_3$ was clearly identified. ^{1}H NMR (C_6D_6, 298 K) δ = 1.16 (s, $C(CH_3)_3$), 2.48 (broad s, N-CH_3), 2.53 (s, N-CH_3), 2.62 (s, N-CH_3). ^{13}C{^{1}H} NMR (C_6D_6, 298 K) δ = 33.88 ($C(CH_3)_3$), 39.93 (N-CH_3), 41.34 (N-CH_3), 48.84 ($C(CH_3)_3$). ^{11}B NMR (C_6D_6, 298 K) δ = 30.2 (d, [$\{Me_2N\}BH\{NMe_2\}$], *B*H, $^1J_{BH}$ = 128 Hz), ca. 32.2 (d, **2**, *B*H, $^1J_{BH}$ = 120 Hz).

Catalytic NMR-Scale Synthesis of [{Me_2N}BH{N^iPr_2}], 3

(i) Using [Ca{$N(SiMe_3)_2$}$_2$]$_2$

D_8-toluene (ca. 0.5 ml) was added to a solid mixture of $Me_2NH.BH_3$ (29 mg, 0.5 mmol), one molar equivalent of $^iPr_2NH$ (51 mg, 0.5 mmol) and [Ca{$N(SiMe_3)_2$}$_2$]$_2$ (9 mg, 2.5 mol%) and the solution sealed in a Youngs tap NMR tube before heating to 90°C for ca. 101 hours. Approx. yield of **3** using ^{11}B NMR: 67%.

(ii) Using [Mg{$N(SiMe_3)_2$}$_2$]$_2$

C_6D_6 (ca. 0.5 ml) was added to a solid mixture of $Me_2NH.BH_3$ (29 mg, 0.5 mmol), one molar equivalent of $^iPr_2NH$ (51 mg, 0.5 mmol) and [Mg{$N(SiMe_3)_2$}$_2$]$_2$ (9 mg, 2.5 mol%) and the solution sealed in a Youngs tap NMR tube before heating to 60°C for ca. 44 hours. Approx. yield of **3** using ^{11}B NMR: 69%.

(iii) Data

3 proved unstable to concentration under vacuum or by evaporation in a glovebox. Although the complete molecular ion could not be observed by GCMS analysis, an ion with *m*/*z* 139.0 corresponding to **3** with the loss of 2H and CH_3 was observed. ^1H NMR (d_8-tol, 298 K) δ = 0.92 (d, ^iPr CH_3, J_{HH} = 6.0 Hz), 1.11 (d, ^iPr CH_3, J_{HH} = 6.8 Hz), 2.67 (s, N-CH_3), 2.74 (spt, ^iPr CH, J_{HH} = 6.0 Hz), 3.42 (spt, ^iPr CH, J_{HH} = 6.8 Hz). $^{13}C\{^1H\}$ NMR (d_8-tol, 298 K) δ = 23.91 (^iPr CH_3), 25.33 (^iPr CH_3), 42.44 (N-CH_3), 45.69 (^iPr CH), 46.04 (^iPr CH). ^{11}B NMR (d_8-tol, 298 K) δ = 29.7 (d, BH, $^1J_{BH}$ = 118.6 Hz).

Catalytic NMR-Scale Synthesis of [{Me_2N}BH{NPh_2}], 4

(i) Using [Ca{$N(SiMe_3)_2$}$_2$]$_2$

D_8-toluene (ca. 0.5 ml) was added to a solid mixture of $Me_2NH.BH_3$ (29 mg, 0.5 mmol), one molar equivalent of Ph_2NH (84 mg, 0.5 mmol) and [Ca{$N(SiMe_3)_2$}$_2$]$_2$ (9 mg, 2.5 mol%) and the solution sealed in a Youngs tap NMR tube before heating to 90°C for ca. 101 hours. Approx yield of **4** using ^{11}B NMR: 83%.

(ii) Using [Mg{$N(SiMe_3)_2$}$_2$]$_2$

C_6D_6 (ca. 0.5 ml) was added to a solid mixture of $Me_2NH.BH_3$ (29 mg, 0.5 mmol), one molar equivalent of Ph_2NH (84 mg, 0.5 mmol) and [Mg{$N(SiMe_3)_2$}$_2$]$_2$ (9 mg, 2.5 mol%) and the solution sealed in a Youngs tap NMR tube before heating to 50°C for ca. 26 hours. Approx yield of **4** using ^{11}B NMR: 95%.

(iii) Data

4 proved unstable to concentration under vacuum or by evaporation in a glovebox. Although the complete molecular ion could not be observed by GCMS analysis, an ion with *m*/*z* 207.00

corresponding to **4** with the loss of 2H and CH_3 was observed. ^1H NMR (d_8-tol, 298 K) δ = 1.95 (s, N-C*H*$_3$), 2.61 (s, N-C*H*$_3$), 6.67-7.01 (Ar). $^{13}C\{^1H\}$ NMR (d_8-tol, 298 K) δ = 38.81 (N-*C*H$_3$), 43.99 (N-*C*H$_3$), 118.52 (Ar), 121.46 (Ar), 123.74 (Ar). 126.04 (Ar), 129.27 (Ar), 129.84 (Ar), 143.98 (Ar), 149.87 (Ar). ^{11}B NMR (d_8-tol, 298 K) δ = 32.1 (d, *B*H, $^1J_{BH}$ = 122 Hz).

Catalytic NMR-Scale Synthesis of [{C_4H_8N}BH{NH^{t}Bu}], 5

D_8-toluene (ca. 0.5 ml) was added to a solid mixture of $C_4H_8NH.BH_3$ (85 mg, 1 mmol), one molar equivalent of $(CH_3)_3CNH_2$ (73 mg, 1 mmol) and $[Ca\{N(SiMe_3)_2\}_2]_2$ (18 mg, 2.5 mol%) and the solution sealed in a Youngs tap NMR tube before heating to 90°C for ca. 44 hours. Approx. yield of **5** using ^{11}B NMR: 87%. **5** proved unstable to concentration under vacuum or by evaporation in a glovebox. Although the complete molecular ion could not be observed by GCMS analysis, an ion with *m*/*z* 152.0 corresponding to **5** with the loss of 2H was observed. ^1H NMR (d_8-tol, 298 K) δ = 1.18 (s, C(C*H*$_3$)$_3$), 1.54 (s br., (N(CH$_2$)$_2$(C*H*$_2$)$_2$)), 2.61 (s broad, 1H, (N(C*H*$_2$)$_2$(CH$_2$)$_2$)), 2.80 (s broad, 1H, (N(C*H*$_2$)$_2$(CH$_2$)$_2$)), ca. 3.14 (s broad, 1H, (N(C*H*$_2$)$_2$(CH$_2$)$_2$)), 3.25 (t, (N(C*H*$_2$)$_2$(CH$_2$)$_2$), J_{HH} = 6.6 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K) δ = 26.90 (br., (N(CH$_2$)$_2$(*C*H$_2$)$_2$)), 33.86 (C(*C*H$_3$)$_3$), 44.84 (br. N(CH$_2$)$_2$(C*H*$_2$)$_2$)), 48.87 (*C*(CH$_3$)$_3$), 50.89 (br. (N(*C*H$_2$)$_2$(CH$_2$)$_2$)). ^{11}B NMR (d_8-tol, 298 K) δ = 28.9 (d, *B*H, $^1J_{BH}$ = 126 Hz).

C_6D_6 (ca. 0.5 ml) was added to a solid mixture of $^tBuNH_2.BH_3$ (87 mg, 1 mmol), one molar equivalent of C_4H_8NH (71 mg, 1 mmol) and $[Ca\{N(SiMe_3)_2\}_2]_2$ (18 mg, 2.5 mol%) and the solution sealed in a Youngs tap NMR tube before heating to 70°C for ca. 24 hours. Approx. yield using ^{11}B NMR: 100%. Compound **5** proved unstable to concentration under vacuum or by evaporation in a glovebox. GCMS results identified ion with *m*/*z* of 154.2 corresponding to the complete molecule. ^1H NMR (C_6D_6, 298 K) δ = 1.20 (s, 9H, C(C*H*$_3$)$_3$), 1.51 (s broad, 4H, (N(CH$_2$)$_2$(C*H*$_2$)$_2$)), 2.65 (s broad, 1H, (N(C*H*$_2$)$_2$(CH$_2$)$_2$)), 2.80 (s broad, 1H, (N(C*H*$_2$)$_2$(CH$_2$)$_2$)), ca. 3.09 (s broad, 1H, (N(C*H*$_2$)$_2$(CH$_2$)$_2$)), 3.27 (t, 1H, (N(C*H*$_2$)$_2$(CH$_2$)$_2$), J_{HH} = 6.8 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K) δ = 26.92 (br., N(CH$_2$)$_2$(C*H*$_2$)$_2$)), 33.94 (C(*C*H$_3$)$_3$), 44.80 (br. N(CH$_2$)$_2$(C*H*$_2$)$_2$)), 48.94 (*C*(CH$_3$)$_3$), 51.08 (br., N(CH$_2$)$_2$(C*H*$_2$)$_2$)). ^{11}B NMR (C_6D_6, 298 K) δ = 29.0 (d, *B*H, $^1J_{BH}$ = 127 Hz).

Catalytic NMR-Scale Synthesis of [{C_4H_8N}BH{N^iPr_2}], 6

D_8-toluene (ca. 0.5 ml) was added to a solid mixture of $C_4H_8NH.BH_3$ (43 mg, 0.5 mmol), one molar equivalent of $^iPr_2NH$ (51 mg, 0.5 mmol) and [Ca{N($SiMe_3$)$_2$}$_2$]$_2$ (9 mg, 2.5 mol%) and the solution sealed in a Youngs tap NMR tube before heating to 90°C for ca. 96 hours. Approx yield using ^{11}B NMR: 79%. 20 proved unstable to concentration under vacuum or by evaporation in a glovebox. GCMS results identified a M^+ ion with *m*/*z* of 182.1, corresponding to **6**. ^{1}H NMR (d_8-tol, 298 K) δ = 0.93 (d, ^{i}Pr C*H*$_3$, J_{HH} = 6.4 Hz), 1.14 (d, ^{i}Pr C*H*$_3$, J_{HH} = 6.8 Hz), ca. 1.53 (quint., (N(CH_2)$_2$(C*H*$_2$)$_2$), J_{HH} = 6.6 Hz), ca. 1.54 (quint., (N(CH_2)$_2$(C*H*$_2$)$_2$), J_{HH} = 6.6 Hz), 2.76 (spt, ^{i}Pr C*H*, J_{HH} = 6.0 Hz), 3.22 (t, (N(C*H*$_2$)$_2$(CH_2)$_2$), J_{HH} = 6.8 Hz), 3.26 (t, (N(C*H*$_2$)$_2$(CH_2)$_2$), J_{HH} = 6.8 Hz), 3.53 (spt, ^{i}Pr C*H*, J_{HH} = 6.3 Hz). ^{13}C{^{1}H} NMR (d_8-tol, 298 K) δ = 24.04 (^{i}Pr *C*H$_3$), 25.51 (^{i}Pr *C*H$_3$), 25.56 (N(CH_2)$_2$(*C*H$_2$)$_2$), 27.08 (N(CH_2)$_2$(*C*H$_2$)$_2$), 45.78 (^{i}Pr *C*H), 45.94 (^{i}Pr *C*H), 50.92 (br, N(*C*H$_2$)$_2$(CH_2)$_2$). ^{11}B NMR (d_8-tol, 298 K) δ = 29.8 (d, *B*H, $^1J_{BH}$ = 123 Hz).

Catalytic NMR-Scale Synthesis of [{C_4H_8N}BH{NPh_2}], 7

D_8-toluene (ca. 0.5 ml) was added to a solid mixture of $C_4H_8NH.BH_3$ (43 mg, 0.5 mmol), one molar equivalent of Ph_2NH (84 mg, 0.5 mmol) and [Ca{N($SiMe_3$)$_2$}$_2$]$_2$ (9 mg, 2.5 mol%) and the solution sealed in a Youngs tap NMR tube before heating to 90°C for ca. 96 hours. Approx yield using ^{11}B NMR: 97%. The product proved unstable to concentration under vacuum or by evaporation in a glovebox. GCMS results did not identify the complete molecule, but did show pyrrolidine and NPh_2 fragments, consistent with compound **7**. ^{1}H NMR (d_8-tol, 298 K) δ = 1.28 (quint., (N(CH_2)$_2$(C*H*$_2$)$_2$), J_{HH} = 6.4 Hz), 1.41 (quint., (N(CH_2)$_2$(C*H*$_2$)$_2$), J_{HH} = 6.8 Hz), 2.40 (t, (N(C*H*$_2$)$_2$(CH_2)$_2$), J_{HH} = 6.8 Hz), 3.31 (t, (N(C*H*$_2$)$_2$(CH_2)$_2$), J_{HH} = 6.0 Hz), 6.76 (d, Ar, J_{HH} = 6.8 Hz), 6.81 (d, Ar, J_{HH} = 7.5 Hz), 6.88 (t, Ar, J_{HH} = 6.8 Hz), 7.02 (t, Ar, J_{HH} = 7.5 Hz), 7.07 (t, Ar, J_{HH} = 7.2 Hz). ^{13}C{^{1}H} NMR (d_8-tol, 298 K) δ = 26.11 (N(CH_2)$_2$(*C*H$_2$)$_2$), 26.79 (N(CH_2)$_2$(*C*H$_2$)$_2$), 47.69 (N(*C*H$_2$)$_2$(CH_2)$_2$), 52.52 (N(*C*H$_2$)$_2$(CH_2)$_2$), 118.53 (Ar), 121.47 (Ar), 123.76 (Ar), 126.27 (Ar), 129.38 (Ar), 143.98 (Ar), 150.03 (Ar). ^{11}B NMR (d_8-tol, 298 K) δ = 30.5 (br. s, *B*H).

Catalytic NMR-Scale Synthesis of [{^{t}BuHN}BH{N^iPr_2}], 8

C_6D_6 (ca. 0.5 ml) was added to a solid mixture of $^tBuNH_2.BH_3$ (43 mg, 0.5 mmol), one molar equivalent of $^iPr_2NH$ (51 mg, 0.5 mmol) and [Ca{N($SiMe_3$)$_2$}$_2$]$_2$ (9 mg, 2.5 mol%) and the solution sealed in a Youngs tap NMR tube before heating to 70°C for ca. 96 hours. Compound **8** proved unstable to concentration under vacuum. Approx. yield using ^{11}B NMR:

81%. Although the complete molecular ion of **8** was not observed by GCMS analysis, ions with *m*/*z* of 167.1 (**8** - CH_3 - 2H), 140.9 (**8** - 2(CH_3) - 2H) and 128.0 (**8** - iPr) could be be identified. ^{1}H NMR (C_6D_6, 298 K) δ = 0.95 (d, ^{i}Pr CH_3, J_{HH} = 6.4 Hz), 1.09 (d, ^{i}Pr CH_3, J_{HH} = 6.8 Hz), 1.20 (s, C(CH_3)$_3$), 2.78 (spt, ^{i}Pr C*H*, J_{HH} = 6.4 Hz), 3.20 (spt, ^{i}Pr C*H*, J_{HH} = 6.7 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 298 K) δ = 24.15 (^{i}Pr *C*H_3), 24.72 (^{i}Pr *C*H_3), 33.87 C(*C*H_3)$_3$, 45.72 (s, ^{i}Pr *C*H), 46.08 (s, ^{i}Pr C*H*), 49.12 (s, *C*(CH_3)$_3$). ^{11}B NMR (C_6D_6, 298 K) δ = 29.2 (d, *B*H, $^1J_{BH}$ = 124 Hz).

Catalytic NMR-Scale Synthesis of [{^{t}BuHN}BH{NPh_2}], 9

(i) Using [Ca{N($SiMe_3$)$_2$}$_2$]$_2$

C_6D_6 (ca. 0.5 ml) was added to a solid mixture of ^{t}BuNH_2.BH_3 (43 mg, 0.5 mmol), one molar equivalent of Ph_2NH (84 mg, 0.5 mmol) and [Ca{N($SiMe_3$)$_2$}$_2$]$_2$ (9 mg, 2.5 mol%) and the solution sealed in a Youngs tap NMR tube before heating to 70°C for ca. 72 hours. Approx yield using ^{11}B NMR: 100%.

(ii) Using [Mg{N($SiMe_3$)$_2$}$_2$]$_2$

C_6D_6 (ca. 0.5 ml) was added to a solid mixture of ^{t}BuNH_2.BH_3 (87 mg, 1 mmol), one molar equivalent of Ph_2NH (169 mg, 1 mmol) and [Mg{N($SiMe_3$)$_2$}$_2$]$_2$ (17 mg, 2.5 mol%) and the solution sealed in a Youngs tap NMR tube before allowing the contents to react at room temperature for ca. 24 hours. Approx yield using ^{11}B NMR: 100%.

(iii) Data

GCMS results identified an ion with *m*/*z* of 207.1, corresponding to **9** - 3(CH_3). ^{1}H NMR (C_6D_6, 298 K) δ = 0.97 (s, 9H, C(CH_3)$_3$), 3.19 (d, 1H, N*H*, J_{HH} = 9.0 Hz), 6.70 (d, Ar, J_{HH} = 7.2 Hz), 6.72 (d, Ar, J_{HH} = 6.8 Hz), 6.82 (t, Ar, J_{HH} = 6.4 Hz), 6.99 (t, Ar, J_{HH} = 6.9 Hz), 7.01 (t, Ar, J_{HH} = 8.3 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 298 K) δ = 33.69 (C(*C*H_3)$_3$), 49.44 (*C*(CH_3)$_3$), 118.54 (Ar), 121.50 (Ar), 124.10 (Ar), 125.90 (Ar), 129.80 (Ar), 129.88 (Ar), 143.93 (Ar), 149.13 (Ar). ^{11}B NMR (C_6D_6, 298 K) δ = 29.8 (br. s, *B*H).

Catalytic Synthesis of [{^{t}BuHN}BH{NPh_2}], 9

Toluene (ca. 10ml) was added to a solid mixture of ^{t}BuNH_2.BH_3 (173 mg, 2 mmol), one molar equivalent of Ph_2NH (338 mg, 2 mmol) and [Ca{N($SiMe_3$)$_2$}$_2$]$_2$ (36 mg, 2.5 mol%) and the solution sealed in a Youngs tap ampoule before heating to 80°C for ca. 96 hours. A single crystal suitable for X-ray diffraction analysis was isolated from concentrated toluene. Compound **9** was isolated as a white powder in effectively stoichiometric yield after complete removal of solvent. Anal. Calc. for $C_{16}H_{21}BN_2$: C, 76.21; H, 8.39; N, 11.11 %. Found: C, 76.08; H, 8.29; N, 11.02 %.

Uncatalysed NMR-Scale Reaction of $Me_2NH.BH_3$ and C_4H_8NH to Synthesise [{Me_2N}BH{NMe_2}] and [{Me_2N}BH{NC_4H_8}], 1

C_6D_6 (ca. 0.5 ml) was added to a solid mixture of $Me_2NH.BH_3$ (59 mg, 1 mmol) and one molar equivalent of C_4H_8NH (71 mg, 1 mmol) and the solution sealed in a Youngs tap NMR tube before heating to 70°C for 207 hours. Approx. yields using ^{11}B NMR: 12% [{Me_2N}BH{NMe_2}], 15% **1**.

^1H NMR (C_6D_6, 298 K) δ = ca. 1.48 (m, ($N(CH_2)_2(CH_2)_2$)), ca. 1.52 (m, ($N(CH_2)_2(CH_2)_2$)), ca. 2.54 (s, N-CH_3), 2.56 (s, N-CH_3), ca. 2.65 (s, N-CH_3), ca. 3.14 (t, ($N(CH_2)_2(CH_2)_2$), J_{HH} = 6.40 Hz), ca. 3.15 (t, ($N(CH_2)_2(CH_2)_2$), J_{HH} = 6.40 Hz). ^{11}B NMR (C_6D_6, 298 K) δ = 29.82 (d, [{Me_2N}BH{NMe_2}], *B*H, $^1J_{BH}$ = 112.7 Hz), 32.1 (d, **1**, *B*H, $^1J_{BH}$ = 103 Hz).

Uncatalysed NMR-Scale Reaction of $Me_2NH.BH_3$ and $(CH_3)_3CNH_2$ to Synthesise [{Me_2N}BH{NH^tBu}], 2

C_6D_6 (ca. 0.5 ml) was added to a solid mixture of $Me_2NH.BH_3$ (59 mg, 1 mmol) and one molar equivalent of $(CH_3)_3CNH_2$ (73 mg, 1 mmol) and the solution sealed in a Youngs tap NMR tube before heating to 70°C for 207 hours. Approx. yields using ^{11}B NMR: 3%, **2**. ^1H NMR (C_6D_6, 298 K) δ = 1.16 (s, C(CH_3)$_3$), 2.46 (broad s, N-CH_3), 2.57 (s, N-CH_3). ^{11}B NMR (C_6D_6, 298 K) δ = 30.3 (d, *B*H, $^1J_{BH}$ = 130 Hz).

Uncatalysed NMR-Scale Reaction of $Me_2NH.BH_3$ and $^iPr_2NH$ to Synthesise [{Me_2N}BH{NMe_2}] and [{Me_2N}BH{N^iPr_2}], 3

C_6D_6 (ca. 0.5 ml) was added to a solid mixture of $Me_2NH.BH_3$ (29 mg, 0.5 mmol) and one molar equivalent of $^iPr_2NH$ (51 mg, 0.5 mmol) and the solution sealed in a Youngs tap NMR tube before heating to 70°C for ca. 119hours and 80°C for ca. 115 hours. Approx. yields using ^{11}B NMR: 7% [{Me_2N}BH{NMe_2}], 0% **3**.

^1H NMR (C_6D_6, 298 K) δ = 2.60 (s, N-CH_3). ^{11}B NMR (C_6D_6, 298 K) δ = 32.1 (d, *B*H, $^1J_{BH}$ = 130 Hz).

Uncatalysed NMR-Scale Reaction of $Me_2NH.BH_3$ and Ph_2NH to Synthesise [{Me_2N}BH{NPh_2}], 4

C_6D_6 (ca. 0.5 ml) was added to a solid mixture of $Me_2NH.BH_3$ (29 mg, 0.5 mmol), one molar equivalent of Ph_2NH (84 mg, 0.5 mmol) and the solution sealed in a Youngs tap NMR tube before heating to 70°C for ca. 119 hours and 80°C for ca. 115 hours. Approx. yield using ^{11}B NMR: 34%.

^1H NMR (C_6D_6, 298 K) δ = 1.91 (s, N-C*H*$_3$), 2.77 (s, N-C*H*$_3$), 6.95-7.06 (Ar). ^{11}B NMR (C_6D_6, 298 K) δ = 32.1 (d, *B*H, $^1J_{BH}$ = 110 Hz).

Uncatalysed NMR-Scale Reaction of $C_4H_8NH.BH_3$ and $(CH_3)_3CNH_2$ to Synthesise [{C_4H_8N}BH{NH^tBu}], 5

D_8-toluene (ca. 0.5 ml) was added to a solid mixture of $C_4H_8NH.BH_3$ (85 mg, 1 mmol and one molar equivalent of $(CH_3)_3CNH_2$ (73 mg, 1 mmol) and the solution sealed in a Youngs tap NMR tube before heating to 90°C for ca. 144 hours. Approx. yield using ^{11}B NMR: 64%. ^1H NMR (d_8-tol, 298 K) δ = 1.18 (s, C(C*H*$_3$)$_3$), 1.53 (s br., (N(CH$_2$)$_2$(C*H*$_2$)$_2$)), 2.63 (s broad, (N(C*H*$_2$)$_2$(CH$_2$)$_2$)), 2.81 (s broad, (N(C*H*$_2$)$_2$(CH$_2$)$_2$)), ca. 3.14 (s broad, (N(C*H*$_2$)$_2$(CH$_2$)$_2$)), 3.22 (t, (N(C*H*$_2$)$_2$(CH$_2$)$_2$), J_{HH} = 6.4 Hz). ^{11}B NMR (d_8-tol, 298 K) δ = 28.9 (d, *B*H, $^1J_{BH}$ = 126 Hz).

Uncatalysed NMR-Scale Reaction of $^tBuNH_2.BH_3$ and C_4H_8NH to Synthesise [{^tBuHN}BH{NC_4H_8}], 5

C_6D_6 (ca. 0.5 ml) was added to a solid mixture of $^tBuNH_2.BH_3$ (87 mg, 1 mmol) and one molar equivalent of C_4H_8NH (71 mg, 1 mmol) and the solution sealed in a Youngs tap NMR tube before heating to 70°C for ca. 142 hours. Approx. yield using ^{11}B NMR: 19%. ^1H NMR (C_6D_6, 298 K) δ = 1.17 (s, C(C*H*$_3$)$_3$), ca. 1.49 (m, (N(CH$_2$)$_2$(C*H*$_2$)$_2$)), ca. 2.51 (m, (N(C*H*$_2$)$_2$(CH$_2$)$_2$)), ca. 2.85 (m, (N(C*H*$_2$)$_2$(CH$_2$)$_2$)), ca. 2.89 (m, (N(C*H*$_2$)$_2$(CH$_2$)$_2$)). ^{11}B NMR (C_6D_6, 298 K) δ = 28.9 (d, *B*H, $^1J_{BH}$ = 126 Hz).

Uncatalysed NMR-Scale Reaction of $C_4H_8NH.BH_3$ and $^iPr_2NH$ to Synthesise [{C_4H_8N}BH{NC_4H_8}], 6

D_8-toluene (ca. 0.5 ml) was added to a solid mixture of $C_4H_8NH.BH_3$ (43 mg, 0.5 mmol) and one molar equivalent of $^iPr_2NH$ (51 mg, 0.5 mmol) and the solution sealed in a Youngs tap NMR tube before heating to 80°C for ca. 120 hours. Approx yield using ^{11}B NMR: 12%. ^1H NMR (d_8-tol, 298 K) δ = 0.95 (d, ^{i}Pr C*H*$_3$, J_{HH} = 5.8 Hz), 1.14 (d, ^{i}Pr C*H*$_3$, J_{HH} = 7.3 Hz), ca.

1.51 (s br., ($N(CH_2)_2(CH_2)_2$)), ca. 1.55 (s br., ($N(CH_2)_2(CH_2)_2$)), 2.77 (s br., ^{i}Pr C*H*), ca. 3.22 (s br., ($N(CH_2)_2(CH_2)_2$)), 3.27 (s br., ($N(CH_2)_2(CH_2)_2$)), 3.55 (s br., ^{i}Pr C*H*). ^{11}B NMR (d_8-tol, 298 K) δ = 29.6 (d, *B*H, $^1J_{BH}$ = 127 Hz).

Uncatalysed NMR-Scale Reaction of $C_4H_8NH.BH_3$ and Ph_2NH to Synthesise [{C_4H_8N}BH{NPh_2}], 7

D_8-toluene (ca. 0.5 ml) was added to a solid mixture of $C_4H_8NH.BH_3$ (43 mg, 0.5 mmol) and one molar equivalent of Ph_2NH (84 mg, 0.5 mmol) and the solution sealed in a Youngs tap NMR tube before heating to 80°C for ca. 120 hours. Using ^{11}B NMR: 31% yield. ^{1}H NMR (d_8-tol, 298 K) δ = ca. 1.29 (m, ($N(CH_2)_2(CH_2)_2$)), ca. 1.39 (m, ($N(CH_2)_2(CH_2)_2$)), ca. 2.39 (m, ($N(CH_2)_2(CH_2)_2$)), 3.31 (t, ($N(CH_2)_2(CH_2)_2$), J_{HH} = 6.8 Hz), 6.76 – 7.11 (Ar). ^{11}B NMR (d_8-tol, 298 K) δ = 30.72 (br. s, *B*H).

Uncatalysed NMR-Scale Reaction of ^{t}BuNH$_2$.BH$_3$ and ^{i}Pr$_2$NH to Synthesise [{^{t}BuHN}BH{N^{i}Pr$_2$}], 8

D_8-toluene (ca. 0.5 ml) was added to a solid mixture of ^{t}BuNH$_2$.BH$_3$ (43 mg, 0.5 mmol) and one molar equivalent of ^{i}Pr$_2$NH (51 mg, 0.5 mmol) and the solution sealed in a Youngs tap NMR tube before heating to 80°C for ca. 157 hours. Approx. yield using ^{11}B NMR: 58%. ^{1}H NMR (d_8-tol, 298 K) δ = 0.94 (d, ^{i}Pr C*H*$_3$, J_{HH} = 6.0 Hz), 1.07 (d, ^{i}Pr C*H*$_3$, J_{HH} = 6.8 Hz), 1.18 (s, C(C*H*$_3$)$_3$), 2.77 (spt, ^{i}Pr C*H*, J_{HH} = 6.8 Hz), 3.18 (spt, ^{i}Pr C*H*, J_{HH} = 6.8 Hz). ^{11}B NMR (d_8-tol, 298 K) δ = 29.0 (d, *B*H, $^1J_{BH}$ = 125 Hz).

Uncatalysed NMR-Scale Reaction of ^{t}BuNH$_2$.BH$_3$ and Ph$_2$NH to Synthesise [{^{t}BuHN}BH{NPh$_2$}], 9

D_8-toluene (ca. 0.5 ml) was added to a solid mixture of ^{t}BuNH$_2$.BH$_3$ (43 mg, 0.5 mmol) and one molar equivalent of Ph_2NH (84 mg, 0.5 mmol) and the solution sealed in a Youngs tap NMR tube before heating to 80°C for ca. 67 hours. Approx yield using ^{11}B NMR: 96%. ^{1}H NMR (d_8-tol, 298 K) δ = 0.97 (s, C(C*H*$_3$)$_3$), 3.19 (d, 1H, N*H*, J_{HH} = 9.4 Hz), 6.73 - 7.06 (Ar). ^{11}B NMR (d_8-tol, 298 K) δ = 30.5 (br. s, *B*H).

Crystallographic analysis

Data for compound **9** were collected at 150 K on a Nonius KappaCCD diffractometer equipped with an Oxford Cryostream, using graphite monochromated MoK$_{\alpha}$ radiation (λ= 0.71073 Å). Data were processed using the Nonius Software.[3] Structure solution, followed by full-matrix least squares refinement was performed using the WinGX-1.80 suite of programs throughout.[4]

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