Supporting Information

Lithium Dihydropyridine Dehydrogenation Catalysis: A Group 1 Approach to the Cyclization of Diamine Boranes

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General experimental considerations

All reactions and manipulations were conducted under a protective argon atmosphere using either standard Schlenk techniques or an MBraun glove box fitted with a gas purification and recirculation unit. NMR experiments were conducted in J. Youngs tubes oven dried and flushed with Argon prior to use. Hexane and THF were dried by heating to reflux over sodium benzophenone ketyl and then distilled under nitrogen prior to use. All other reagents were purchased commercially from Sigma-Aldrich and used as received. $^{1t}$Li, $^1$I and $^V$V were prepared as previously described or by slight variations thereof.

NMR Spectroscopy NMR spectra were recorded on a Bruker AV3 or AV 400 MHz spectrometer operating at 400.13 MHz for $^1$H, 128.38 MHz for $^{11}$B, 155.47 MHz for $^7$Li and 100.62 MHz for $^{13}$C. All $^{13}$C spectra were proton decoupled. $^1$H and $^{13}$C NMR spectra were referenced against the appropriate solvent signal. $^7$Li NMR spectra were referenced against LiCl in D$_2$O at 0.00 ppm and $^{11}$B spectra were reference against BF$_3$·OEt$_2$ in CDCl$_3$ at 0.00 ppm.

X-ray Crystallography Crystallographic data were collected on Oxford Diffraction instruments with Mo Kα radiation ($\lambda = 0.71073$ Å). Structures were solved using SHELXS-97$^3$ or OLEX2,$^4$ while refinement was carried out on F2 against all independent reflections by the full matrix least-squares method using the SHELXL-97 program or by the GaussNewton algorithm using OLEX2. All non-hydrogen atoms were refined using anisotropic thermal parameters. Selected crystallographic details and refinement details are provided in table S1. CCDC 1476810-1476813, 1513975 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Catalytic dehydrogenative cyclisation of I with 5 mol% $^{1t}$Li

$^1$Ia (93 mg, 0.5 mmol) and ferrocene (9.3 mg, 0.05 mmol) were placed in a J. Youngs NMR tube and dissolved in either d$_8$-THF or d$_6$-benzene and NMR data were recorded. $^{1t}$Li (3.6 mg, 5 mol%) was then added (in the case of d$_5$-pyridine $^{1t}$Li was added prior to NMR solvent due to an unwanted side reaction). The NMR tube was then heated for the prescribed period and the reaction monitored via $^1$H, and $^{11}$B spectroscopy.

Catalytic dehydrogenative cyclisation reactions of Ib-ID were conducted using the same procedure.
Figure S1: $^1$H and $^{11}$B NMR spectra of catalytic cyclisation of 1a in $d_8$-THF at 70 °C for 24 h.

A) $^1$H NMR spectra

B) $^{11}$B NMR spectra
Figure S2: $^1$H and $^{11}$B NMR spectra of catalytic cyclisation in $d_6$-benzene at 70 °C for 6 h.

A) $^1$H NMR spectra

- $\text{Ia + 1tLi 6 h. 70 °C}$
- $\text{Ia + 1tLi 10 min. 22 °C}$
- $\text{Ia}$

B) $^{11}$B NMR spectra

- $\text{Ia + 1tLi 6 h. 70 °C}$
- $\text{Ia + 1tLi 10 min. 22 °C}$
- $\text{Ia}$
Isolation of IVa

Ia (93 mg, 0.5 mmol) and 1tLi (3.6 mg, 5mol%) were stirred in benzene (1 mL) in a Schlenk flask at 70 °C for 6 h. Benzene was removed by distillation at atmospheric pressure (oil bath temp – 90 °C). A second colourless oil was collected via distillation (oil bath temp 105 °C) and was confirmed by NMR studies as IVa. Yield 86 mg, 94%.

$^1$H NMR (400.1 MHz, C$_6$D$_6$ 300K): δ 3.13 (4H, s, CH$_2$), 1.18 ppm (18H, s, tBu)

$^{11}$B NMR (128.4 MHz, C$_6$D$_6$ 300K): δ 25.5 ppm (d, $^{1}J_{B-H}$ 138.2 Hz, BH) and -18.8 ppm (q, $^{1}J_{B-H}$ 94.8 Hz, BH$_3$) corresponding to a small amount of starting diamine borane.

**Figure S3** NMR characterisation of IVa

A) $^1$H NMR spectrum
B) $^{11}$B NMR spectrum

C) $^7$Li NMR spectrum
Figure S4: $^1$H and $^{11}$B NMR spectra of catalytic cyclisation in $d_5$-pyridine at 70 °C for 45 min. Reaction affords a mixture of products due to the transfer of BH$_3$ from the diamine borane to pyridine, and consequently liberates the parent diamine.

A) $^1$H NMR spectra

B) $^{11}$B NMR spectra
Figure S5 Control reaction of la in d₅-pyridine demonstrating removal of BH₃ from the diamine borane.

A) $^1$H NMR spectra

1a in d₅-py 2 h at 70 °C

1a in d₅-py 10 min at 22 °C

B) $^{11}$B NMR spectra

1a in d₅-py 2 h at 70 °C

1a in d₅-py 10 min at 22 °C
Figure S6 DOSY NMR study of major catalytic cyclisation product in $d_5$-pyridine after 45 min at 70 °C

A molecular weight of 204.2 g mol$^{-1}$ was found, higher than that of the cyclised product (182.1 g mol$^{-1}$, 12% error).
Figure S7 $^1$H and $^{11}$B NMR spectra of catalytic cyclisation of 1b in $d_6$-benzene at 70 °C for 24 h.

$^1$H NMR Spectra

$^{11}$B NMR spectra
Figure S8 $^1$H and $^{11}$B NMR spectra of catalytic cyclisation of 1c in $d_6$-benzene at 70 °C for 48 h.

$^1$H NMR spectra

$\text{lc + 1tLi 24 h. 70 °C}$

$\text{lc + 1tLi 6 h. 70 °C}$

$\text{lc + 1tLi 10 min 22 °C}$

$^{11}$B NMR spectra

$\text{IVc}$

$\text{lc + 1tLi 24 h. 70 °C}$

$\text{IVc}$

$\text{lc + 1tLi 6 h. 70 °C}$

$\text{lc + 1tLi 10 min 22 °C}$
Figure S9 $^1$H and $^{11}$B NMR spectra of catalytic cyclisation of 1d in $d_6$-benzene at 70 °C for 48 h.

$^1$H NMR spectra

| Spectrum Type          | Condition                  |
|------------------------|----------------------------|
| ld + 1tLi 48 h. 70 °C  |                            |
| ld + 1tLi 6 h. 70 °C   |                            |
| ld + 1tLi 10 min 22 °C |                            |

$^{11}$B NMR spectra

| Spectrum Type          | Condition                  |
|------------------------|----------------------------|
| ld + 1tLi 24 h. 70 °C  |                            |
| ld + 1tLi 6 h. 70 °C   |                            |
| ld + 1tLi 10 min 22 °C |                            |
Figure S10 Identity of resonance at δ-13.4 ppm in catalytic cyclisation of 1a in benzene.

Reaction of 2-tert-butylpyridine with BH$_3$·SMe$_2$ in $d_6$-benzene shows conversion to 2-tert-butylpyridine-BH$_3$. The aromatic region in the $^1$H NMR spectrum confirms this displaying two sets of aromatic proton resonances. The $^{11}$B NMR confirms that the quartet at δ-13.4 ppm in the catalytic reaction does not belong to 2-t-butylpyridine-BH$_3$.

A) $^1$H NMR spectrum 10 min at 22 °C – Aromatic region.

B) $^{11}$B NMR spectrum 10 min at 22 °C

2-t-Bupyridine·BH$_3$
Reaction of 2-tert-butylpyridine with Ia in $d_6$-benzene results in formation of two products – 2-t-Bupyridine-BH$_3$ and an unknown BH$_3$ containing compound resonating at $\delta$-13.5 ppm, in agreement with the unknown catalytic intermediate. Although the identity of this species is unknown it is clear that it only occurs in reactions involving Ia.

C) $^{11}$B NMR spectrum 10 min at 22 °C
Figure S11 Control reaction between 1tLi and THF·BH$_3$ in $d_8$-THF.

Here reaction of 1tLi with a borane adduct containing no acidic protons results in formation of LiBH$_4$, in agreement with observations from our catalytic studies.

$^{11}$B NMR spectrum 16 h at 70 °C
Figure S12 Catalytic dehydrogenative cyclisation of Ia with 5 mol% LiBH₄ in d₆-benzene.

¹¹B NMR spectra

24 h at 70 °C

6 h at 70 °C

Co-product

IVa

Ia

LiBH₄
**Figure S13** Structural characterisation of IIa-THF, IIa-py, [VI-THF]₂, and [VI-py]₂, and selected bond parameters.

Molecular structures of A) IIa-THF, Selected bond lengths (Å) and angles (°): Li1-N1, 2.031(3); Li1-N2, 1.969(3); B1-N2, 1.568(2); Li1-O1, 1.907(3); Li1-H1, 1.894(18); N1-Li1-N2, 92.67(13); N1-Li1-O1, 120.15(15); N2-Li1-O1, 136.30(17); O1-Li1-H1, 125.1(6); N1-Li1-H1, 99.0(6); N2-Li1-H1, 70.0(6); B) IIa-py, Selected bond lengths (Å) and angles: (°): Li1-N1, 2.025(11); Li1-N2, 1.985(12); B1-N2, 1.581(9); Li1-N3, 2.040(11); Li1-N1, 93.4(5); N1-Li1-N3, 126.4(6); N2-Li1-N3, 131.2(6); N3-Li1-H3, 122(2); N1-Li1-H3, 99(2); N2-Li1-H3, 69(2); C) [VI-THF]₂, Selected bond lengths (Å) and angles: (°): Li1-N1, 2.156(2); Li1-N2, 2.039(2); B1-N2, 1.555(1); Li1-O1, 1.984(2); H2-Li1’, 2.074(10); H3-Li1’, 1.962(13); N1-Li1-N2, 89.24(6); N1-Li1-O1, 105.92(6); N2-Li1-O1, 111.24(7); N1-Li1-H2’, 149.4(4); N1-Li1-H3’, 96.0(4); N2-Li1-H2’, 108.7(4); N2-Li1-H3’, 139.0(3); H2’-Li1-O1, 90.8(3); H3’-Li1-O1, 106.3(3). Transformations used to generate symmetry equivalent atoms -X,1-Y,-Z; and D) [VI-py]₂, Selected bond lengths (Å) and angles: (°): Li1-N1, 2.163(2); Li1-N2, 2.055(2); B1-N2, 1.558(1); Li1-N3, 2.098(2); H1-Li1’, 1.960(13); H2-Li1’, 2.107(11); N1-Li1-N2, 87.79(7); N1-Li1-N3, 102.75(7); N2-Li1-N3, 117.92(8); N1-Li1-H1’, 99.4(3); N1-Li1-H2’, 152.9(4); N2-Li1-H1’, 136.7(4); N2-Li1-H2’, 105.5(4); H1’-Li1-N3, 102.1(4); H2’-Li1-N3, 91.9(4). Transformations used to generate symmetry equivalent atoms -X,1-Y,-Z. All hydrogen atoms except those attached to boron and nitrogen are omitted for clarity.
Figure S14 Stoichiometric reaction of V and 1tLi in $d_6$-benzene

$^1$H NMR spectrum – dihydropyridyl hydrogen region

2.5 h at 70 °C

10 min at 22 °C

$^{11}$B NMR spectrum

2.5 h at 70 °C

10 min at 22 °C

2-t-Bupyrindine-BH$_3$
Figure S15 DOSY NMR study of IIa·THF in d₈-THF

The estimated molecular weight of IIa·THF in d₈-THF is 297 g mol⁻¹, 12% higher than the anticipated value for a monomeric unit (264 g mol⁻¹). While this difference is reasonably large the value is still much closer to that of a monomeric unit than to a dimeric species. In addition we cannot rule out a solvation-desolvation event between a second molecule of THF and the lithium atom in IIa·THF. This would also lead to an increased estimated value.
### ECC-MW-Determination of Small Molecules

**V1.7**

**Solvent:**

THF-d8

| Internal Reference | logDref,fix | Comment |
|--------------------|------------|---------|
| TMS                | -8.7018    |         |

**Diffusion Coefficient Internal Reference [m²/s]**

| Dref | 2.270E-09 |
|------|-----------|

**Diffusion Coefficient Analyte [m²/s]**

| Dx   | 1.208E-09 |
|------|-----------|

**normalized Diffusion Coefficient Analyte**

| logDx,norm | -8.9758 |
|------------|---------|

**MW Analyte [g/mol]**

| 264.19 |

**Calibration Curve**

Dissipated Spheres + Ellipsoids (in THF)

| Predicted MW [g/mol] | ΔMW [%] | Comment |
|----------------------|---------|---------|
| 297                  | -12     | error ±9% |
The estimated molecular weight of [VI·THF]₂ in d₈-THF is 265 g mol⁻¹, 4% higher than the anticipated value for the dimeric species observed in the crystal structure (228 g mol⁻¹, minus the solvating THF ligands from the crystal structure which were removed under application of vacuum during isolation). This small difference supports the view that a dimeric species is present in solution.
### ECC-MW-Determination of Small Molecules

#### V1.7

**Solvent:**

THF-d8

### Internal Reference

| Internal Reference | logDref,fix |
|--------------------|-------------|
| TMS                | -8.7018     | comment |

### Diffusion Coefficient

#### Internal Reference [m2/s]

| logDref | 2.178E-09 Dref |
|---------|---------------|

#### Analyte [m2/s]

| logDx | 1.322E-09 Dx |
|-------|--------------|

### Normalized Diffusion Coefficient

| logDx, norm | -8.9186   |
|-------------|-----------|

### Calibration Curve

Dissipated Spheres + Ellipsoids (in THF)

### Predicted MW

| MW Predicted | THF [g/mol] | ΔMW [%] |
|--------------|-------------|---------|
|              | 237         | -4      | ±9%     |
| error        |             |         |         |
Synthesis and NMR characterisation of IIa·THF

IIa (186 mg, 1 mmol) was dissolved in hexane (3 mL) and nBuLi (0.63 mL, 1 mmol 1.6M in hexane) was added, resulting in precipitation of a white solid after several minutes. After 30 min. stirring THF was added dropwise until a colourless solution was obtained. Crystals suitable for single crystal X-ray diffraction studies were grown after standing the solution at -20 °C for 24 h. Yield 193 mg, 73%.

Elemental analysis (%) calculated for C_{14}H_{34}N_{2}B_{1}Li_{1}O_{1}: C 63.65, H 12.97, N 10.60; found: C 63.61, H 13.01, N 10.42.

$^1$H NMR (400.1 MHz, C$_6$D$_6$ 300K): δ 3.57 (4H, br t, OCH$_2$-THF), 2.67 (4H, br s, CH$_2$CH$_2$-diamine), 1.41 (4H, br t, (CH$_2$)$_2$-THF), 1.40 (9H, s, tBu), 1.06 (9H, s, tBu), 0.56 ppm (1H, t, $^3$J$_{H-H}$ 7.05 Hz, NH).

$^{11}$B NMR (128.4 MHz, C$_6$D$_6$ 300K): δ -21.7 ppm (q, $^1$J$_{B-H}$ 86.7 Hz, BH$_3$).

$^7$Li NMR (155.5 MHz, C$_6$D$_6$ 300K): δ 0.13 ppm.

$^{13}$C NMR (100.6 MHz, C$_6$D$_6$ 300K): δ 67.8 (THF), 53.5 (tBu quaternary), 51.6 (CH$_3$), 50.7 (CH$_2$), 42.8 (tBu quaternary), 29.2 (CH$_3$-tBu), 28.4 ppm (CH$_3$-tBu).

Figure S17 NMR characterisation of IIa-THF

A) $^1$H NMR spectrum
B) $^7\text{Li}$ NMR spectrum

![B) $^7\text{Li}$ NMR spectrum](image)

C) $^{11}\text{B}$ NMR spectrum

![C) $^{11}\text{B}$ NMR spectrum](image)
D) $^{13}$C NMR spectrum

![NMR spectrum of IIa-THF](image)

E) Infrared spectrum of IIa-THF

![Infrared spectrum of tBu THF](image)
Figure S18 IIa-THF in $d_6$-benzene at 70 °C for 70 h.

A) $^1$H NMR spectrum

B) $^{11}$B NMR spectrum
Figure S19 IIa-THF in $d_5$-pyridine at 70 °C for 25 h.

A) $^1$H NMR spectrum

B) $^{11}$B NMR spectrum
Synthesis and NMR characterisation of IIa·py

IIa (186 mg, 1 mmol) was dissolved in hexane (3 mL) and nBuLi (0.63 mL, 1 mmol 1.6M in hexane) was added, resulting in precipitation of a white solid after several minutes. After 30 min. stirring pyridine was added dropwise until a colourless solution was obtained. Crystals suitable for single crystal X-ray diffraction studies were grown after standing the solution at -20 °C for 24 h. Yield 169 mg, 62%.

Elemental analysis (%) calculated for C_{15}H_{31}N_{3}B_{1}Li_{1}: C 66.44, H 11.52, N 15.49; found: C 66.26, H 11.19, N 15.30.

$^1$H NMR (400.1 MHz, C$_6$D$_6$ 300K): $\delta$ 8.52 (2H, m, CH-Pyr), 6.95 (1H, tt, $^3$J$_{H-H}$ 7.68 Hz; $^4$J$_{H-H}$ 1.93 Hz, CH-pyr), 6.64 (2H, m, CH-Pyr), 2.75 (4H, br s, CH$_2$CH$_2$-diamine), 1.41 (9H, s, tBu), 1.01 (9H, s, tBu), 0.54 ppm (1H, t, $^3$J$_{H-H}$ 8.27 Hz, NH).

$^{11}$B NMR (128.4 MHz, C$_6$D$_6$ 300K): $\delta$ -21.3 ppm $^1$J$_{B-H}$ 84.9 Hz

$^7$Li NMR (155.5 MHz, C$_6$D$_6$ 300K): $\delta$ 0.52 ppm

$^{13}$C NMR (100.6 MHz, C$_6$D$_6$ 300K): $\delta$ 150.1 (pyr), 135.8 (pyr), 123.7 (pyr), 53.5 (tBu quaternary), 51.6 (CH$_2$), 50.7 (CH$_3$), 43.0 (tBu quaternary), 29.3 (CH$_3$-tBu), 28.8 ppm (CH$_3$-tBu).

Figure S21 NMR characterisation of IIa·py

A) $^1$H NMR spectrum
B) $^7\text{Li}$ NMR spectrum

\[ \text{IIa-} \text{py} \]

C) $^{11}\text{B}$ NMR spectrum

\[ \text{IIa-} \text{py} \]
D) $^{13}$C NMR spectrum

E) Infrared spectrum of IIa·py
Figure S22 Ila-py in $d_6$-benzene at 70 °C for 22 h.

A) $^1$H NMR spectrum

B) Expansion of $^1$H NMR showing resonances attributable to DHP species.
C) $^{11}$B NMR spectrum
Synthesis and NMR characterisation of [VI-THF]₂

V (116 mg, 1 mmol) was dissolved in hexane (3 mL) and nBuLi (0.63 mL, 1 mmol 1.6M in hexane) was added, resulting in precipitation of a white solid after several minutes. After 30 min. stirring THF was added dropwise until a colourless solution was obtained. Crystals suitable for single crystal X-ray diffraction studies were grown after standing the solution at -20 °C for 24 h. Yield 112 mg, 81%.

Elemental analysis (%) calculated for C₁₀H₃₂N₄B₂Li₂: C 49.25, H 13.23, N 22.97; found: C 49.51, H 12.28, N 22.92. Consistent with loss of 2 x THF upon drying in vacuo.

¹H NMR (400.1 MHz, C₆D₆ 300K): δ 2.64 (3H, br s, CH₃-diamine), 2.45 (2H, br s,CH₂-diamine), 2.34 (2H, br s,CH₂-diamine), 2.01 ppm (1H, s, 2xCH₃-diamine).

¹¹B NMR (128.4 MHz, C₆D₆ 300K): δ -17.9 ppm ¹J_B-H 83.3 Hz

⁷Li NMR (155.5 MHz, C₆D₆ 300K): δ 0.56 ppm

¹³C NMR (100.6 MHz, C₆D₆ 300K): δ 68.0 (THF), 58.6 (CH₂), 57.1 (CH₂), 48.0 (CH₃), 45.0 (2xCH₃), 25.6 ppm (THF).

Figure S23 NMR characterisation of [VI-THF]₂

A) ¹H NMR spectrum

[VI-THF]₂
B) $^7$Li NMR spectrum

![Li NMR spectrum]

C) $^{11}$B NMR spectrum

![B NMR spectrum]
D) $^{13}$C NMR spectrum

E) Infrared spectrum of $[VI\cdot\text{THF}]_2$
Figure S24 $[\text{VI-THF}]_2$ in $d_6$-benzene at 70 °C for 90 h.

A) $^1\text{H}$ NMR spectrum

B) $^{11}\text{B}$ NMR spectrum
Figure S25 [VI-THF]₂ in d₅-pyridine at 70 °C for 90 h.

A) ¹H NMR spectrum

B) ¹¹B NMR spectrum
C) \textsuperscript{13}C NMR spectrum

\begin{center}
\includegraphics[width=\textwidth]{C13_NMR_spectrum.png}
\end{center}

D) HSQC spectrum

\begin{center}
\includegraphics[width=\textwidth]{HSQC_spectrum.png}
\end{center}

The \textsuperscript{1}H NMR spectrum indicates the presence of two similar products, in an approximate 3:2 ratio. A heteronuclear \textsuperscript{1}H-\textsuperscript{13}C HSQC experiment supports this view since there are no cross-peaks between the two components.
A DOSY experiment reveals the two components possess a similar diffusion coefficient and near identical MWs (258.8 and 258.5 g mol\(^{-1}\)). The MW of [VI·THF]\(_2\) without any solvating THF is 243 g mol\(^{-1}\), thus it is reasonable to assume that the two molecules may be isomers of each other and are potentially the result of an intermolecular coupling between two monomers. At this point the identity of the mixture is unclear but the result does again illustrate the profound impact that the reaction solvent has on the process.
Synthesis and NMR characterisation of \([\text{VI-py}]_2\)

\(\text{V} (116 \text{ mg}, 1 \text{ mmol})\) was dissolved in hexane (3 mL) and \(n\text{BuLi} (0.63 \text{ mL}, 1 \text{ mmol} 1.6\text{M in hexane})\) was added, resulting in precipitation of a white solid after several minutes. After 30 min. stirring, pyridine was added dropwise until a colourless solution was obtained. Crystals suitable for single crystal X-ray diffraction studies were grown after standing the solution at -20 °C for 24 h. Yield 96 mg, 48%.

Elemental analysis (%) calculated for \(\text{C}_{20}\text{H}_{42}\text{N}_6\text{B}_2\text{Li}_2\): C 59.74, H 10.53, N 20.90; found: C 59.31, H 11.04, N 20.96.

\(^1\text{H NMR} (400.1 \text{ MHz, } \text{C}_6\text{D}_6 300K): \delta \) 8.53 (2H, m, \(\text{CH-Pyr}\)), 6.95 (1H, tt, \(^3\text{J}_{\text{HH}}\) 7.60 Hz; \(^4\text{J}_{\text{HH}}\) 1.80 Hz, \(\text{CH-pyr}\)), 6.64 (2H, m, \(\text{CH-Pyr}\)), 2.71 (3H, br s, \(\text{CH}_2\)-diamine), 2.56 (2H, br s,\(\text{CH}_2\)-diamine), 2.43 (2H, br s,\(\text{CH}_2\)-diamine), 1.98 ppm (1H, s, \(2\times\text{CH}_2\)-diamine).

\(^{11}\text{B NMR} (128.4 \text{ MHz, } \text{C}_6\text{D}_6 300K): \delta \) -17.0 ppm \(^{1}\text{J}_{\text{BH}}\) 77.6 Hz

\(^7\text{Li NMR} (155.5 \text{ MHz, } \text{C}_6\text{D}_6 300K): \delta \) 0.96 ppm

\(^{13}\text{C NMR} (100.6 \text{ MHz, } \text{C}_6\text{D}_6 300K): \delta \) 150.1 (pyr), 135.7 (pyr), 123.6 (pyr), 58.9 (\(\text{CH}_2\)), 57.6 (\(\text{CH}_2\)), 48.3 (\(\text{CH}_3\)), 45.2 ppm (\(2\times\text{CH}_3\)).

Figure S26 NMR characterisation of \([\text{VI-py}]_2\)

A) \(^1\text{H NMR spectrum}\)
B) $^7\text{Li}$ NMR spectrum

\[
[\text{VI-\text{py}}]_2
\]

C) $^{11}\text{B}$ NMR spectrum

\[
[\text{VI-\text{py}}]_2
\]
D) $^{13}$C NMR spectrum

E) Infrared spectrum of $[\text{VI-py}]_2$
Figure S27 [VI-py]$_2$ in $d_6$-benzene at 70 °C for 10 min and 72 h.

A) $^1$H NMR spectra

[VI-py]$_2$ in $d_6$-benzene for 72 h at 70 °C

[VI-py]$_2$ in $d_6$-benzene for 10 min at 70 °C

1,4-dihydropyridine formation

B) $^{11}$B NMR spectra

[VI-py]$_2$ in $d_6$-benzene for 72 h at 70 °C

[VI-py]$_2$

[VI-py]$_2$ in $d_6$-benzene for 10 min at 70 °C

BH$_2$ formation
Figure S28 Reaction of IVa with PhLi – Formation of IVaPh

A) $^1$H NMR spectrum in $d_6$-benzene after reacting PhLi and IVa (prepared in situ) for 2 hours at room temperature. Indicating formation of IVaPh

B) $^{11}$B NMR spectrum in $d_6$-benzene after reacting PhLi and IVa (prepared in situ) for 2 hours at room temperature.
Synthesis and NMR characterisation of IVaPh

1a (372 mg, 2 mmol) and 1tLi (14 mg, 5 mol%) were dissolved in toluene (2 mL) and heated at 80 °C for 7h to ensure in situ conversion to IVa. Phenyllithium (168 mg, 2 mmol) was added and the reaction stirred overnight. Hexane (5 mL) was added and the reaction placed at −70 °C. After 24 hours, colourless crystals suitable for X-ray diffraction studies formed. Yield 361 mg, 70%.

\[ ^1\text{H NMR (400.1 MHz, C}_6\text{D}_6\text{ 300K):} \delta \text{ 7.42 (2H, m, CH-phenyl), 7.20-7.10 (3H, m, CH-phenyl), 3.19 (4H, s,CH}_2\text{), 1.03 ppm (18H, s, CH}_3\text{).} \]

\[ ^{11}\text{B NMR (128.4 MHz, C}_6\text{D}_6\text{ 300K):} \delta \text{ 31.8 ppm (s, BPh).} \]

\[ ^{13}\text{C NMR (100.6 MHz, C}_6\text{D}_6\text{ 300K):} \delta \text{ 132.7 (C-Ph), 127.4 (C-Ph), 126.9 (C-Ph), 51.8 (quaternary C-tBu), 45.2 (CH}_2\text{), 30.9 ppm (CH}_3\text{-tBu).} \]

**Figure S29** NMR characterisation of IVaPh

A) \(^1\text{H NMR spectrum}\)
B) $^{11}$B NMR spectrum

C) $^{13}$C NMR spectrum
Figure S30 Structural characterisation of IVaPh and selected bond parameters.

Molecular structure of IVaPh, transformations used to generate symmetry equivalent atoms $-x+y,1/2-z$. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): B1-N1, 1.4285(12); B1-C6, 1.578(2); N1-B1-N1', 109.68(12); N1-B1-C6, 125.16(6).
Figure S31 Reaction of IVb with PhLi – Formation of IVbPh

A) $^1$H NMR in $d_6$-benzene after reacting PhLi and IVb (prepared in situ) for 2 hours at room temperature. Indicating formation of IVbPh

B) $^{11}$B NMR in $d_6$-benzene after reacting PhLi and IVb (prepared in situ) for 2 hours at room temperature.
Synthesis and NMR characterisation of IVbPh

Ib (1.640 g, 4 mmol) and 1tLi (29 mg, 5 mol%) were dissolved in toluene (4 mL) and heated at 80 °C for 24 h to ensure in situ conversion to IVb. Phenyllithium (336 mg, 4 mmol) was added and the reaction stirred overnight. Hexane (5 mL) was added and the reaction placed at −70 °C. After 24 hours, colourless crystals formed and were isolated by filtration. Yield 1.052 g, 81%.

$^1$H NMR (400.1 MHz, C$_6$D$_6$ 300K): $\delta$ 7.68 (2H, m, CH-phenyl), 7.21 (11H, m, CH-phenyl), 7.10 (2H, m, CH-phenyl), 4.14 (4H, s,CH$_2$), 3.03 ppm (4H, s, CH$_2$).

$^{11}$B NMR (128.4 MHz, C$_6$D$_6$ 300K): $\delta$ 32.7 ppm (s, BPh).

$^{13}$C NMR (100.6 MHz, C$_6$D$_6$ 300K): $\delta$ 141.1 (C-Ph), 133.2 (C-Ph), 128.8 (C-Ph), 128.7 (C-Ph), 128.4 (C-Ph), 127.6 (C-Ph), 126.9 (C-Ph), 51.4 (benzyl CH$_2$), 48.4 ppm (CH$_2$).

Figure S32 NMR characterisation of IVbPh

A) $^1$H NMR spectrum
B) $^{11}$B NMR spectrum

C) $^{13}$C NMR spectrum
Figure S33 Reaction of IVc with PhLi – Formation of IVcPh

A) $^1$H NMR in $d_6$-benzene after reacting PhLi and IVc (prepared in situ) for 2 hours at room temperature. Indicating formation of IVcPh

B) $^{11}$B NMR in $d_6$-benzene after reacting PhLi and IVc (prepared in situ) for 2 hours at room temperature. Indicating formation of IVcPh
Synthesis and NMR characterisation of IVcPh

Ic (462 mg, 3 mmol) and 1tLi (21 mg, 5 mol%) were dissolved in toluene (4 mL) and heated at 80 °C for 48 h to ensure in situ conversion to IVc. Phenyllithium (252 mg, 4 mmol) was added and the reaction stirred overnight. Hexane (5 mL) was added and the reaction placed at –70 °C. After 24 hours, colourless crystals formed. These were isolated at low temperature by decanting the solution from the solid. IVcPh exists as a colourless oil at room temperature. Yield 421 mg, 61%.

$^1$H NMR (400.1 MHz, C$_6$D$_6$ 300K): δ 7.54 (2H, d, CH-phenyl), 7.32 (2H, m, CH-phenyl), 7.25 (1H, t, CH-phenyl), 3.60 (2H, septet, CH(CH$_3$)$_2$), 3.16 (4H, s,CH$_2$), 0.98 ppm (12H, d, CH(CH$_3$)$_2$).

$^{11}$B NMR (128.4 MHz, C$_6$D$_6$ 300K): δ 31.6 ppm (s, BPh).

$^{13}$C NMR (100.6 MHz, C$_6$D$_6$ 300K): δ 132.9 (C-Ph), 128.1 (C-Ph), 126.9 (C-Ph), 45.2 (CH$_2$), 41.9 (CH-CH$_3$)$_2$, 22.0 ppm (CH(CH$_3$)$_2$).

**Figure S34 NMR characterisation of IVcPh**

A) $^1$H NMR spectrum
B) $^{11}$B NMR spectrum

C) $^{13}$C NMR spectrum
Figure S35 Reaction of IVd with PhLi – Formation of IVdPh

A) $^1$H NMR in $d_6$-benzene after reacting PhLi and IVd (prepared in situ) for 2 hours at room temperature. Indicating formation of IVdPh

B) $^{11}$B NMR in $d_6$-benzene after reacting PhLi and IVd (prepared in situ) for 2 hours at room temperature. Indicating formation of IVdPh
Synthesis and NMR characterisation of IVdPh

Id (420 mg, 2.5 mmol) and 1tLi (18 mg, 5 mol%) were dissolved in toluene (4 mL) and heated at 80 °C for 48 h to ensure in situ conversion to IVd. Phenyllithium (156 mg, 2.5 mmol) was added and the reaction stirred overnight. Hexane (5 mL) was added and the reaction placed at −70 °C. After 24 hours a white solid formed. These were isolated at low temperature by decanting the solution from the solid. The reaction product mixture exists as a waxy white solid in a 3:1 ratio of IVcPh:IVc. Combined yield 421 mg, 38%.

Figure S36 NMR characterisation of IVdPh/IVd product mixture

A) $^1$H NMR spectrum
B) $^{11}$B NMR spectrum
Table S1 Crystallographic data and refinement details for complexes IIa-THF, IIa-py, [VI-THF]₂, [VI-py]₂ and IVaPh

|                          | IIa-THF       | IIa-py        | [VI-THF]₂      | [VI-py]₂       | IVaPh         |
|--------------------------|---------------|---------------|----------------|----------------|---------------|
| **Empirical formula**    | LiON₂C₁₄BH₃₄  | LiN₂C₁₃BH₃₃  | Li₂O₂N₂C₁₈B₃H₴₈| Li₂B₂N₆C₂₀H₴₂| C₁₆H₂₂B₃N₂   |
| **Mol. Mass**            | 264.18        | 271.18        | 388.10         | 402.09         | 258.2         |
| **Crystal system**       | monoclinic    | Monoclinic    | Triclinic      | Monoclinic     | Monoclinic    |
| **a/ Å**                 | 6.1321(6)     | 8.4263(19)    | 8.4191(6)      | 8.4964(11)     | 14.5259(12)   |
| **b/ Å**                 | 15.8714(15)   | 6.2044(9)     | 8.8743(7)      | 9.8471(10)     | 10.3281(7)    |
| **c/ Å**                 | 18.017(2)     | 16.977(3)     | 9.7883(8)      | 15.8260(19)    | 11.2033(10)   |
| **α**                    | 90            | 90            | 67.501(8)      | 90             | 90            |
| **β**                    | 93.743(10)    | 100.745(19)   | 72.307(7)      | 104.836(12)    | 110.814(10)   |
| **γ**                    | 90            | 90            | 72.253(7)      | 90             | 90            |
| **V/ Å³**                | 1749.7(3)     | 872.0(3)      | 628.76(10)     | 1279.9(3)      | 1571.1(2)     |
| **Z**                    | 4             | 2             | 1              | 2              | 4             |
| **λ, Å**                 | 0.71073       | 0.71073       | 0.71073        | 0.71073        | 0.71073       |
| **Measured reflections** | 17408         | 6136          | 12110          | 12683          | 3789          |
| **Unique reflections**   | 4579          | 3083          | 3436           | 3477           | 1906          |
| **R_{int}**              | 0.0512        | 0.0704        | 0.0257         | 0.0248         | 0.0151        |
| **Observed rflns [I>2σ(I)]** | 3317     | 2109          | 2911           | 2965           | 1636          |
| **Goof**                 | 1.038         | 1.061         | 1.111          | 1.049          | 1.027         |
| **R [on F, obs rflns only]** | 0.0668     | 0.0753        | 0.0401         | 0.0419         | 0.0426        |
| **ωR [on F', all data]** | 0.1750        | 0.2117        | 0.1461         | 0.1150         | 0.1158        |
| **Largest diff. Peak/hole. e/ Å⁻³** | 0.37/-0.23 | 0.29/-0.21    | 0.31/-0.18     | 0.34/-0.24     | 0.41/-0.20    |
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