

## Electronic Supplementary Information

### ***N–H Deprotonation of a Diaminodialkoxido Diborane(4) – A Structural Study on Bifunctional Lewis Acids/Bases and their Dimerisation to $B(sp^2)_2B(sp^3)_2N_2$ Six Membered Rings***

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#### CONTENTS

##### 1. ADDITIONAL NMR DATA

1.a. $[(18\text{-crown-}6)\text{K}][(\text{tBuO})\text{pinB-Bdab}]$ ( <b>3</b> ) .....	S2
1.b. Deprotonation of <b>1</b> with Na(hmde): $\{\{\text{Na}(\text{thf})_{1/2}\}\}_2$ .....	S3
1.c. Reaction of <b>1</b> with $\text{tBuLi}$ : $\{\{\text{Li}(\text{thf})_{2.5}\}\}_2$ , $\{\{\text{Li}_3(\text{thf})_5\}\}_2$ ( <b>4</b> ) ( <b>5</b> ) and $\{\{\text{Li}_3(\text{thf})_3\}(\text{tBu})\}$ ( <b>5</b> ) .....	S5
1.d. Reaction of <b>1</b> with Li(tmp): $\{\{\text{Li}_2(\text{thf})(\text{Li}(\text{tmp}))\}\}_2$ .....	S7

##### 2. CRYSTALLOGRAPHIC DATA .....

S10

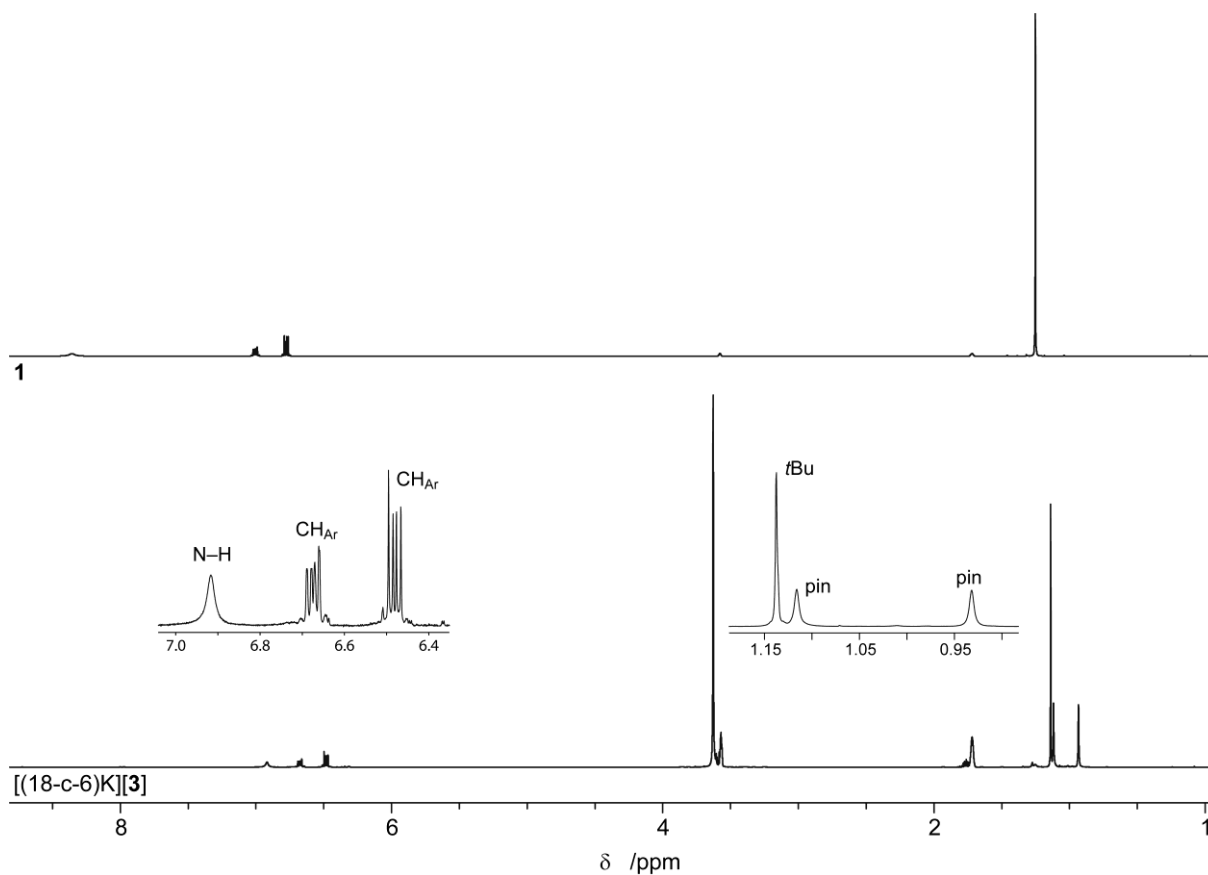
2.a. $\{\{\text{Li}(\text{tmeda})(\text{Li}(\text{thf})_2)\}\}_2$ .....	S13
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##### 4. REFERENCES .....

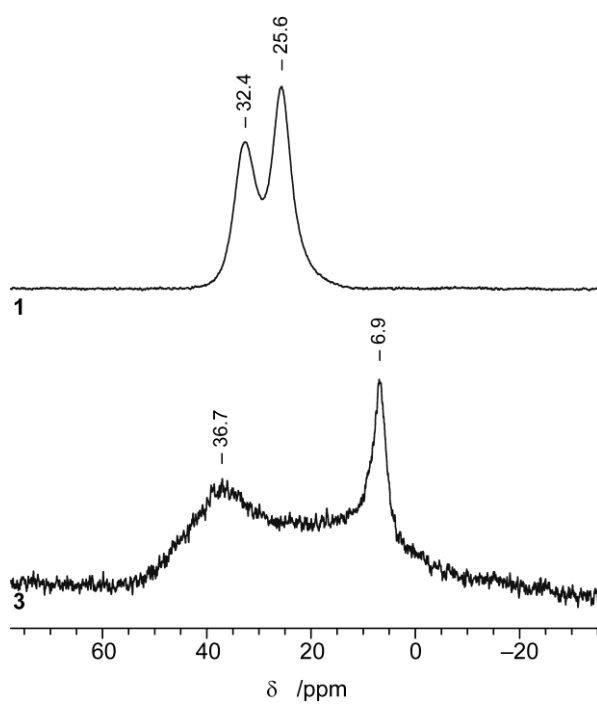
S14

# 1. ADDITIONAL NMR DATA

## 1.a. [(18-crown-6)K][[(tBuO)pinB-Bdab] (**3**)



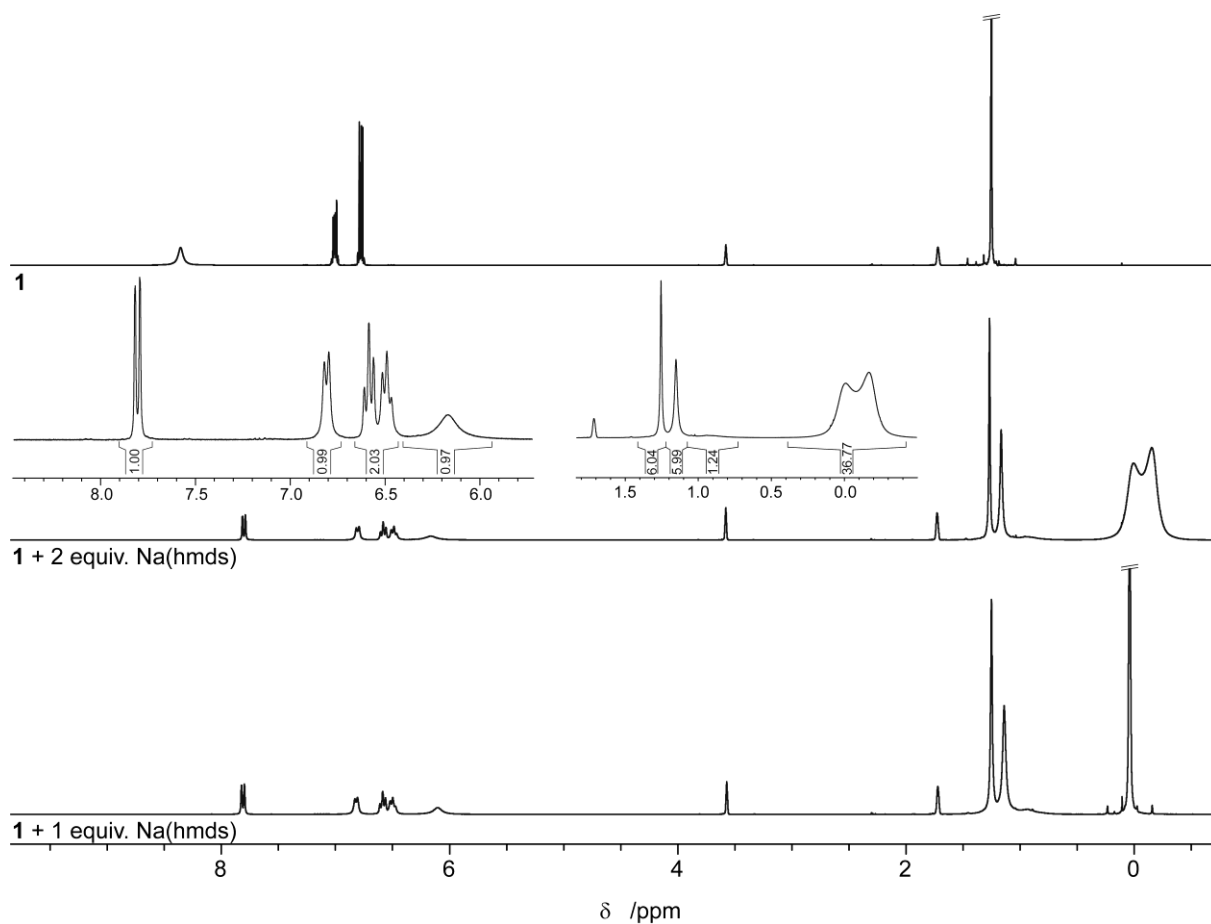
**Figure S1.**  $^1\text{H}$  NMR spectra of **3** and **1** (300 MHz, thf- $d_8$ , rt).



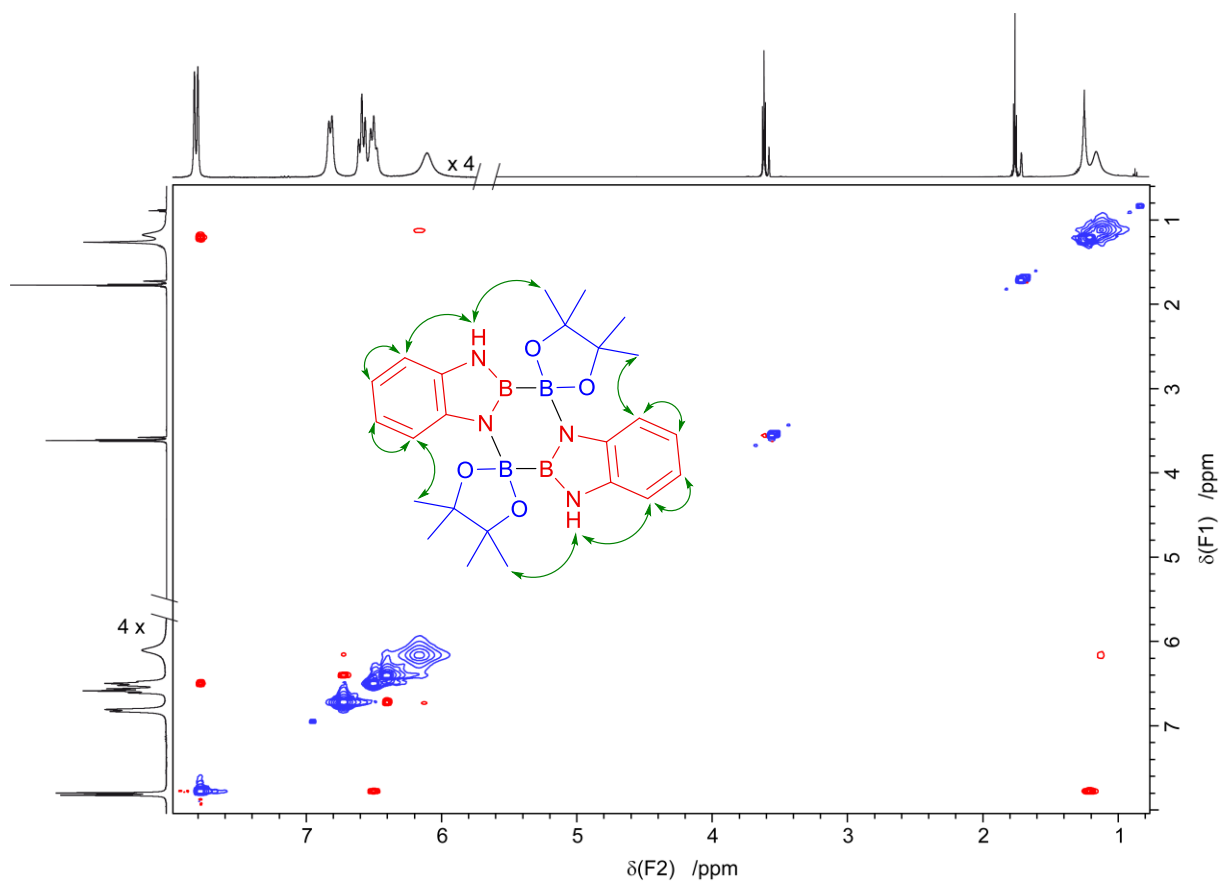
**Figure S2.**  $^{11}\text{B}\{^1\text{H}\}$  NMR spectra of **3** and **1** (96 MHz, thf- $d_8$ , rt).

1.b. Deprotonation of **1** with Na(hmnds):  $\{[\text{Na}(\text{thf})_{1/2}]\mathbf{4}\}_2$

*NMR experiment:* **1** (23 mg, 93  $\mu\text{mol}$ , 1.0 equiv.) was dissolved in  $\text{thf-}d_6$  (0.7 mL) and Na(hmnds) (17 mg, 93  $\mu\text{mol}$ , 1.0 equiv.) was added. After approx. 1 h NMR spectra were recorded. Subsequently a second equivalent of Na(hmnds) was added and NMR spectra were recorded.



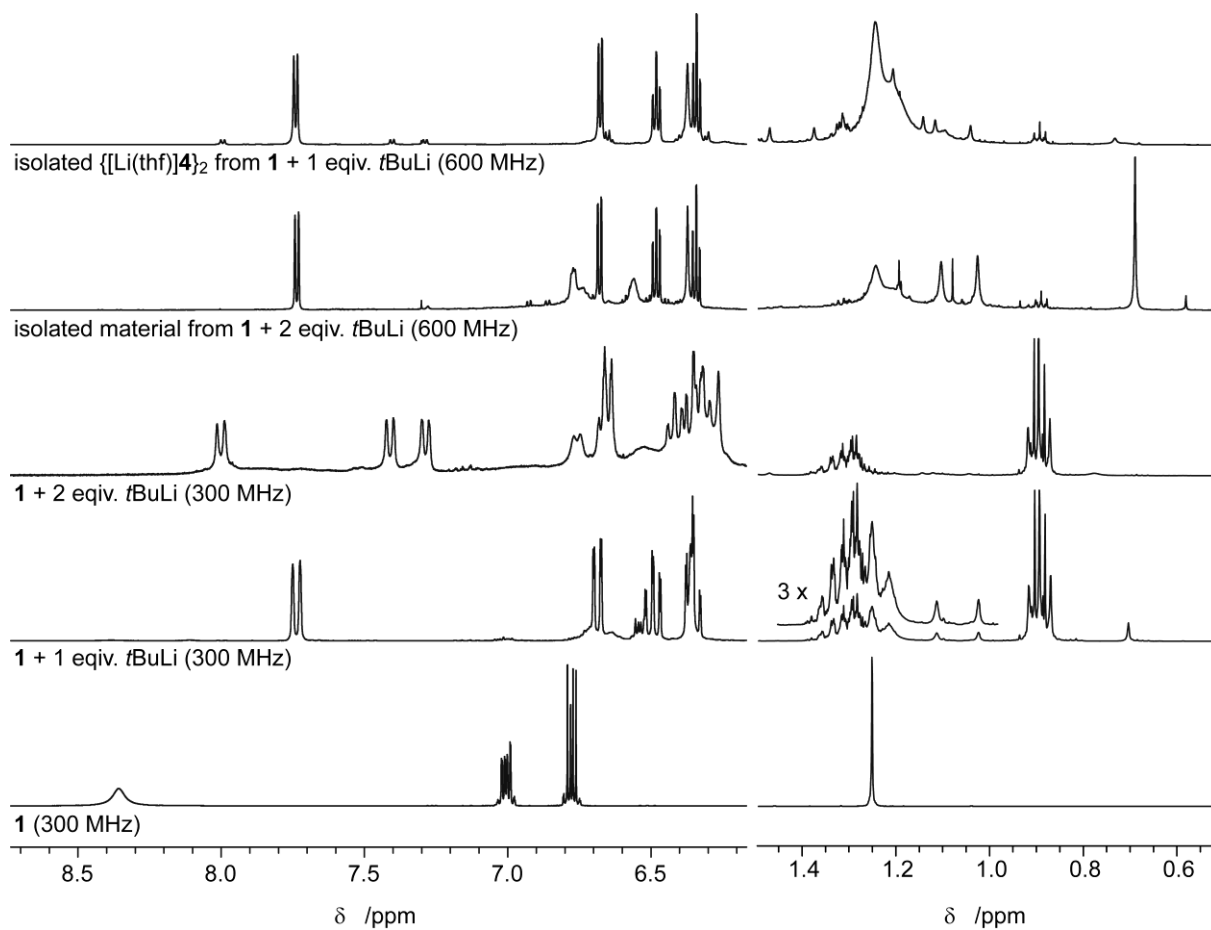
**Figure S3.**  $^1\text{H}$  NMR spectra of the reaction of **1** with Na(hmnds) (300 MHz,  $\text{thf-}d_6$ ).



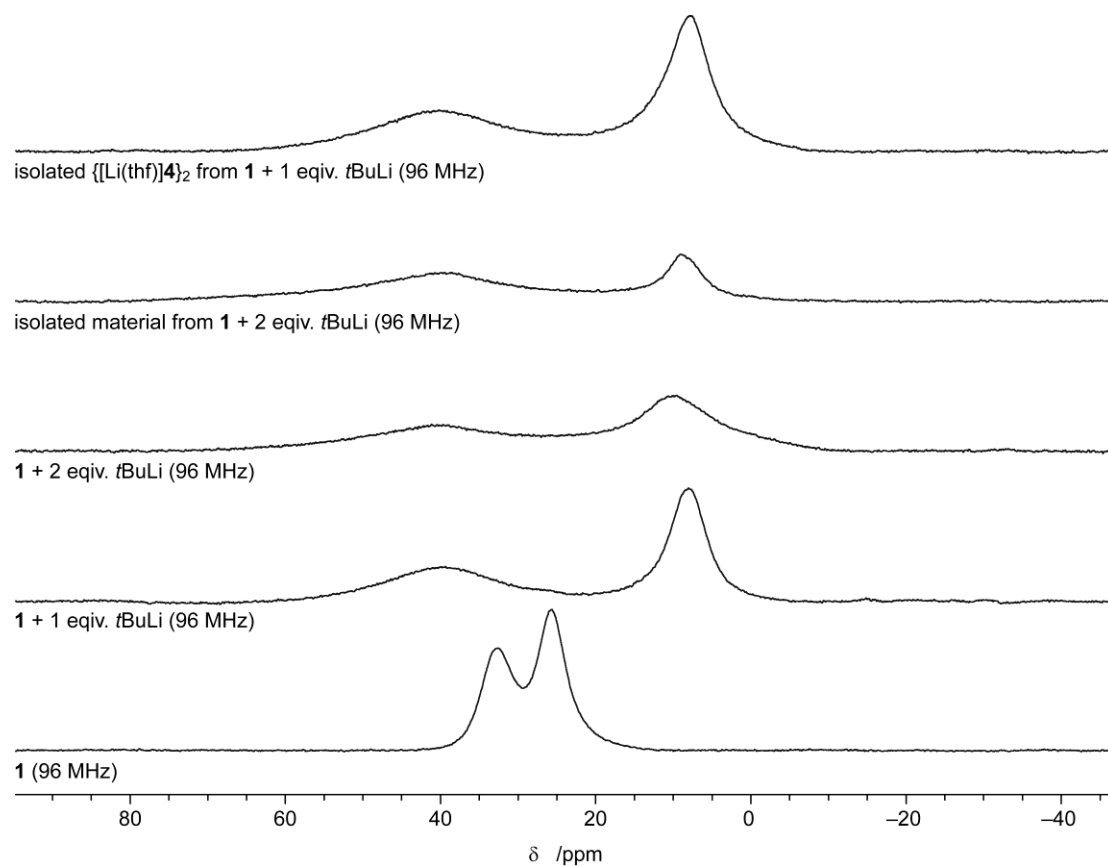
**Figure S4.**  $^1\text{H}$ - $^1\text{H}$  NOESY NMR spectra of  $\{[\text{Na}(\text{thf})_{1.2}]_2\}$  (600 MHz,  $\text{thf}-d_6$ , rt).

1.c. Reaction of **1** with *t*BuLi:  $\{[\text{Li}(\text{thf})_{2.5}]\mathbf{4}\}_2$ ,  $\{[\text{Li}_3(\text{thf})_5]\mathbf{4}(\mathbf{5})\}$  and  $\{[\text{Li}_3(\text{thf})_3](\mathbf{tBu})\mathbf{5}\}$

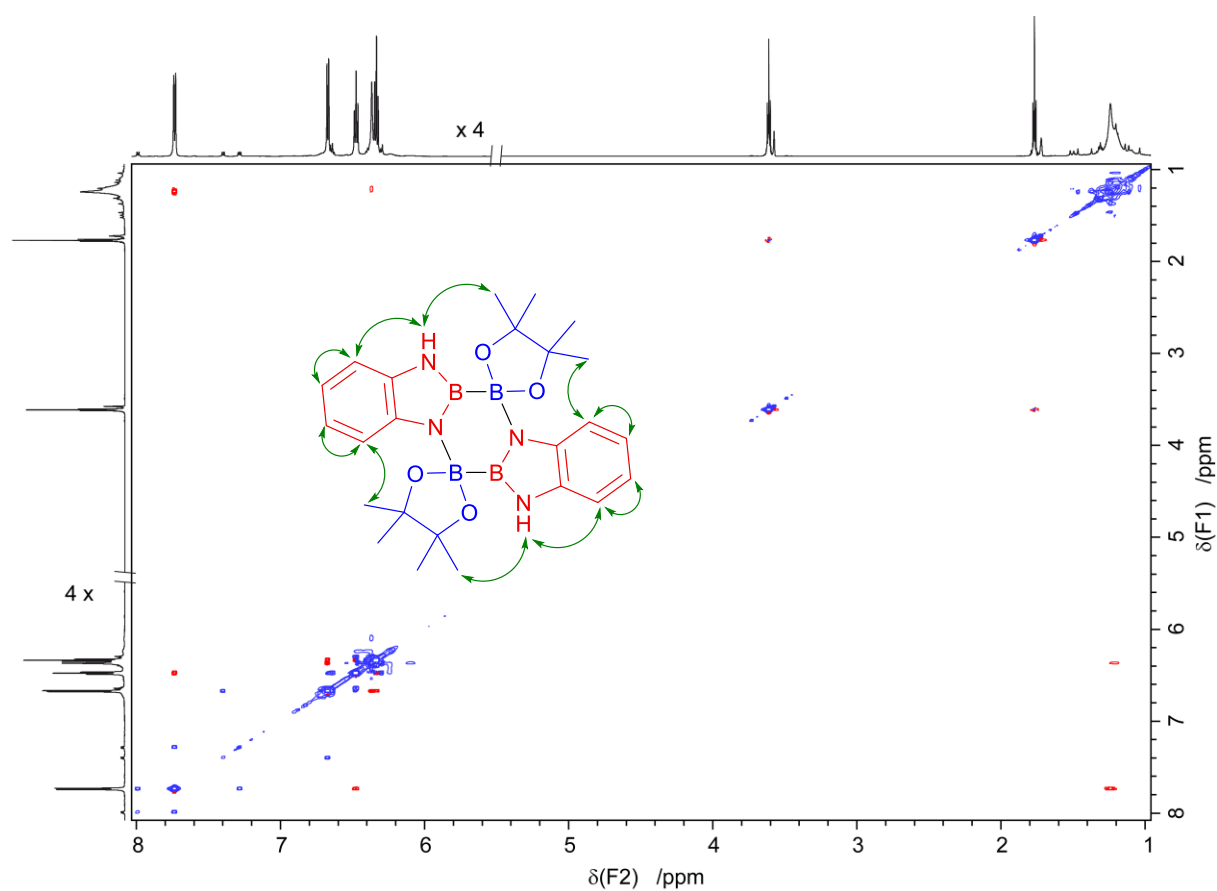
*NMR experiment:* **1** (30 mg, 123  $\mu\text{mol}$ , 1.0 equiv.) was dissolved in  $\text{thf-}d_8$  (0.7 mL) and *t*BuLi as 1.9 molar solution in pentane (65  $\mu\text{L}$ , 124  $\mu\text{mol}$ , 1.0 equiv.) was added. After approx. 1 h NMR spectra were recorded. Subsequently a second equivalent of *t*BuLi was added and NMR spectra were recorded.



**Figure S5.**  $^1\text{H}$  NMR spectra of the reaction of **1** with *t*BuLi and isolated materials; see main text for details ( $\text{thf-}d_8$ , rt).



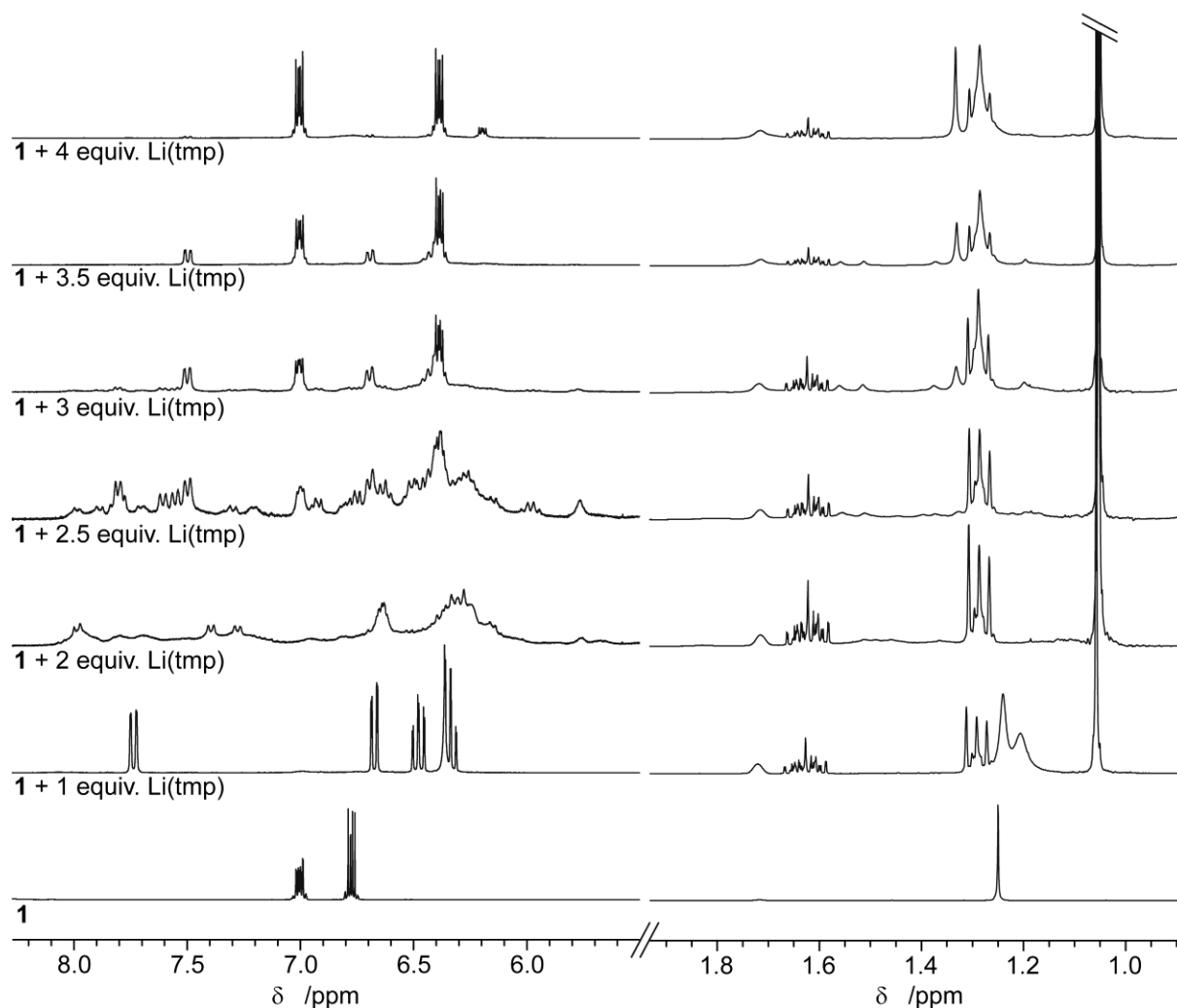
**Figure S6.**  $^{11}\text{B}\{^1\text{H}\}$  NMR spectra of the reaction of **1** with *t*BuLi and isolated materials; see main text for details (thf- $d_6$ , rt).



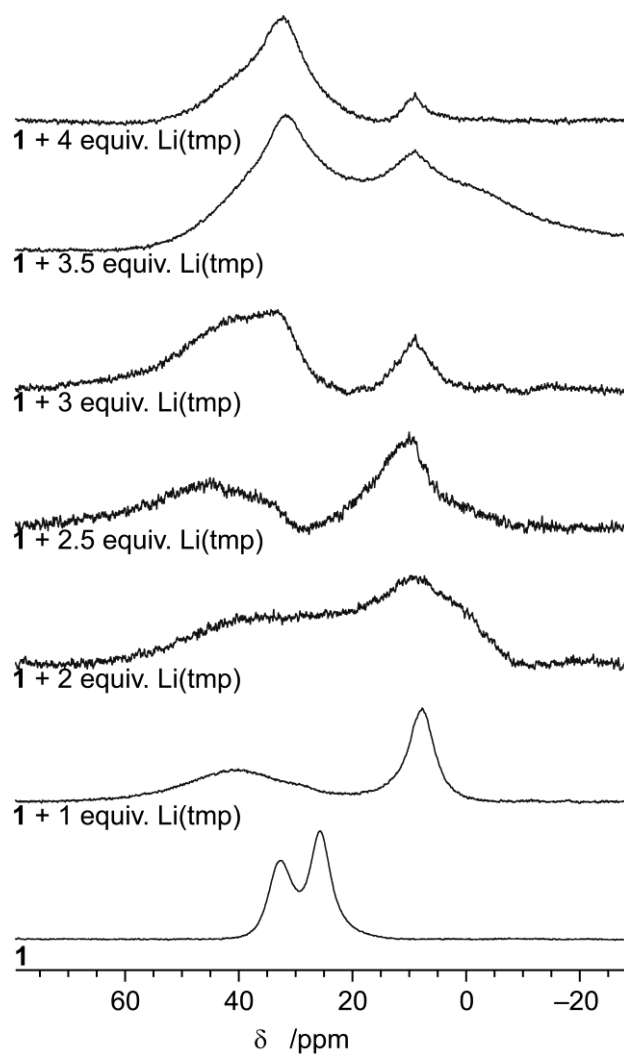
**Figure S7.**  $^1\text{H}$ - $^1\text{H}$  NOESY NMR spectra of  $\{[\text{Li}(\text{thf})_4]_2\}$  (600 MHz, thf- $d_6$ , rt).

1.d. Reaction of **1** with Li(tmp):  $\{[Li_2(thf)(Li(tmp))][5]\}_2$

*NMR experiment:* **1** (20 mg, 82  $\mu$ mol, 1.0 equiv.) was dissolved in thf- $d_8$  (0.7 mL) and Li(tmp) (12 mg, 82  $\mu$ mol, 1.0 equiv.) was added and NMR spectra recorded. Additional amounts of Li(tmp) were added NMR spectra were recorded.

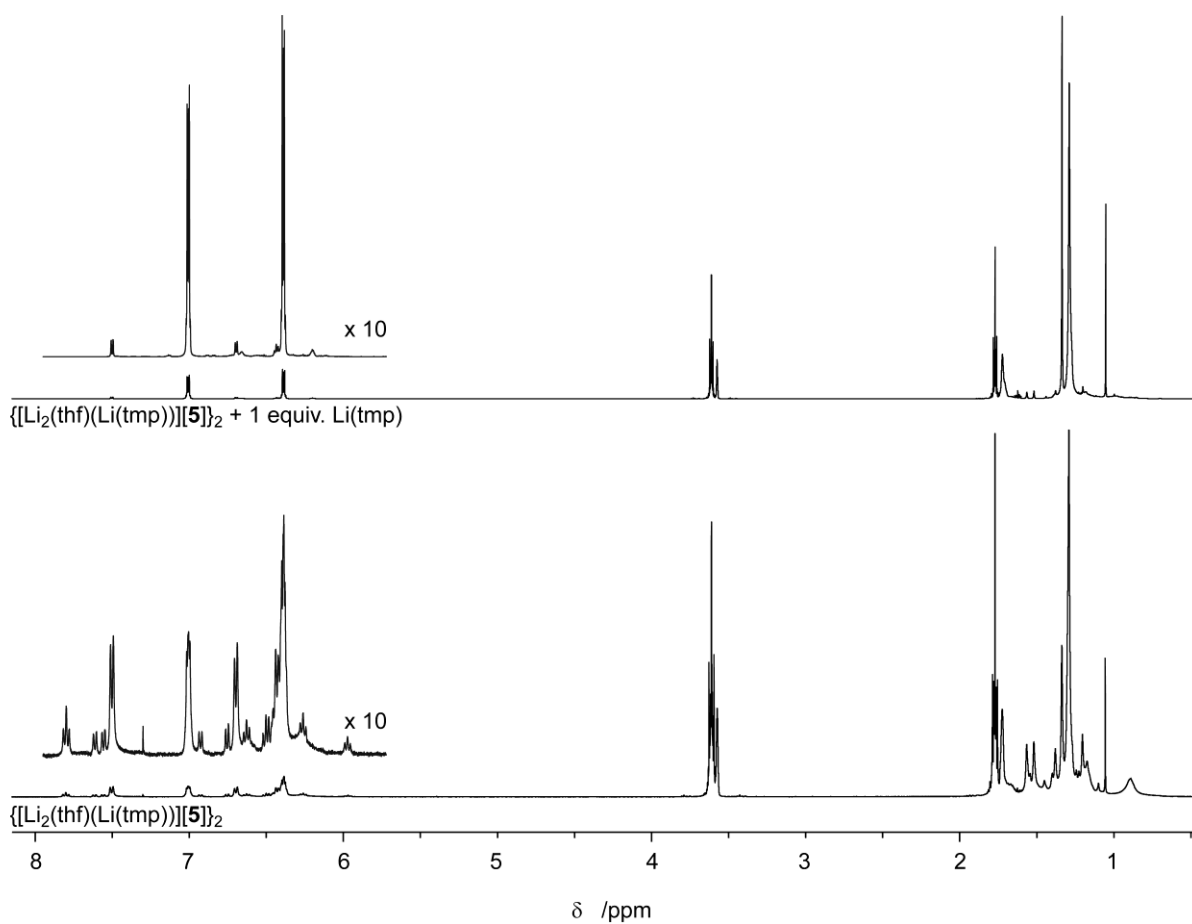


**Figure S8.** *In situ*  $^1H$  NMR spectra of the deprotonation of **1** by Li(tmp) (300 MHz, thf- $d_8$ , rt).



**Figure S9.** *In situ*  $^{11}\text{B}\{^1\text{H}\}$  NMR spectra of the deprotonation of **1** by  $\text{Li}(\text{tmp})$  (96 MHz,  $\text{thf-d}_8$ , rt). It is noted that for the spectra with 4, 3.5 and 3 equiv.





**Figure S10.**  $^1\text{H}$  NMR spectra of  $\{[\text{Li}_2(\text{thf})(\text{Li}(\text{tmp}))][\mathbf{5}]\}_2$  as isolated (bottom) and after addition of one additional equivalent of  $\text{Li}(\text{tmp})$  (400 MHz,  $\text{thf-d}_8$ , rt).

## 2. CRYSTALLOGRAPHIC DATA

The single crystals were transferred into inert perfluoroether oil inside a nitrogen-filled glovebox and, outside the glovebox, rapidly mounted on top of a human hair and placed in the cold nitrogen gas stream on the diffractometer.<sup>S1</sup> The data were either collected on an Oxford Diffraction Nova A instrument, using mirror-focused CuK $\alpha$  radiation. The reflections were indexed, integrated and appropriate absorption corrections were applied as implemented in the CrysAlisPro software package.<sup>S2</sup> The structures were solved employing the program SHELXT and refined anisotropically for all non-hydrogen atoms by full-matrix least squares on all F<sup>2</sup> using SHELXL software.<sup>S3,S4</sup> Unless noted otherwise hydrogen atoms were refined employing a riding model; methyl groups were treated as rigid bodies and were allowed to rotate about the E-CH<sub>3</sub> bond. During refinement and analysis of the crystallographic data the programs WinGX, OLEX2, PLATON/SQUEEZE, Mercury and Diamond were used.<sup>S5-S9</sup> Unless noted otherwise the shown ellipsoids represent the 50% probability level and only selected hydrogen atoms are shown with arbitrary radii. Adapted numbering schemes may be used to improve the readability.

**Table S1.** Crystallographic data collection parameter of  $[(\text{thf})_{1.5}\text{K}][\mathbf{3}]$ ,  $\{[\text{Na}(\text{thf})_{1.2}]\mathbf{4}\}_2$  and  $\{[\text{Li}(\text{tmeda})](\text{Li}(\text{thf})_2)[\mathbf{4}]\}_2$

Compound	$[(\text{thf})_{1.5}\text{K}][\mathbf{3}]^b$	$\{[\text{Na}(\text{thf})_{1.2}]\mathbf{4}\}_2$	$\{[\text{Li}(\text{thf})_{2.5}]\mathbf{4}\}_2$	$\{[\text{Li}(\text{tmeda})](\text{Li}(\text{thf})_2)[\mathbf{4}]\}_2$
Formula	$\text{C}_{22}\text{H}_{39}\text{B}_2\text{KN}_2\text{O}_{4.5}$	$\text{C}_{66.9}\text{H}_{105.8}\text{B}_8\text{N}_8\text{Na}_4\text{O}_{12.7}$	$\text{C}_{44}\text{H}_{74}\text{B}_4\text{N}_4\text{Li}_2\text{O}_9$	$\text{C}_{38}\text{H}_{66}\text{B}_4\text{N}_6\text{Li}_2\text{O}_6$
$M_r/(\text{g mol}^{-1})$	464.27	1404.41	860.19	760.08
crystal shape	block	fragment of prism	fragment of prism	prism
crystal colour	colourless	clear colourless	colourless	colourless
cryst. dim. /mm <sup>3</sup>	$0.26 \times 0.19 \times 0.14$	$0.31 \times 0.25 \times 0.24$	$0.31 \times 0.20 \times 0.14$	$0.35 \times 0.20 \times 0.13$
crystal system	monoclinic	trigonal	monoclinic	monoclinic
space group (no.)	$C2 (5)$	$P3_221 (154)$	$P2_1/n (14)$	$P2_1/n (14)$
$a/\text{\AA}$	11.5005(5)	16.6556(2)	11.5646(5)	12.5438(4)
$b/\text{\AA}$	21.0732(9)	16.6556(2)	23.7208(10)	19.8952(6)
$c/\text{\AA}$	11.587(6)	27.4355(3)	18.0699(10)	17.7349(6)
$\alpha$	90°	90°	90°	90°
$\beta$	114.857(6)°	90°	99.697(4)°	106.128(3)°
$\gamma$	90°	120°	90°	90°
$V/\text{\AA}^3$	2607.6(2)	6591.19(17)	4886.1(4)	4251.8(2)
$Z, Z'$	4, 1	3, 1/2	4, 1	4, 1
$D_{\text{calcd.}}/(\text{g cm}^{-3})$	1.183	1.061	1.169	1.187
$\mu/\text{mm}^{-1} (\lambda/\text{\AA})$	2.025 (1.54184)	0.740 (1.54184)	0.623 (1.54184)	0.611 (1.54184)
Absorption corr.	multi-scan	multi-scan	multi-scan	multi-scan
$\theta$ range (compl.)	4.11 – 76.60° (99.3%)	3.46 – 76.06° (99.5%)	3.73 – 69.99° (99.0%)	3.42 – 76.01° (99.3%)
refl. measured	34751	59566	34055	68449
unique ( $R_{\text{int}}$ )	5235 (0.0501)	9108 (0.0426)	9161 (0.0505)	8841 (0.0735)
observed <sup>a</sup>	5013	8695	7136	6865
param. / restr.	323 / 16	535 / 60	584 / 0	525 / 0
$R_1$ (obs. rflns.) <sup>a</sup>	0.0339	0.0535	0.0435	0.0490
$wR_2$ (all rflns.)	0.0860	0.1469	0.1135	0.1366
Goof on $F^2$	1.061	1.069	1.026	1.027
max/min $\rho/(\text{e}\text{\AA}^{-3})$	0.187 / –0.446	0.293 / –0.304	0.261 / –0.238	0.343 / –0.291
CCDC No.	2089027	2089029	2089031	2089028

<sup>a</sup> Observation criterion:  $I > 2\sigma(I)$ . <sup>b</sup> Abs. Structure Parameter: 0.020(5), *Friedel* Coverage: 92% to 76.6°  $\theta$ .

$[(\text{thf})_{1.5}\text{K}][\mathbf{3}]$ : The NH hydrogen atoms were refined freely. Refinement as an inversion twin resulted in a BASF differing less than  $2\sigma$  from zero. A thf moiety located on a C2 axis was described using a split atom model; geometrical restraints were applied.

$\{[\text{Na}(\text{thf})_{1.2}]\mathbf{4}\}_2$ : The crystal was refined as 2-component inversion twin. The twin factor refined to 0.10(10). No appropriate model could be established for co-crystallised solvent molecules; the data were processed using the SQUEEZE/PLATON programme.<sup>S7</sup> Two disordered thf moieties (one including the coordinated Na atom) were refined using split atom model (0.51(2) and 0.769(7) SOF of main components). One of these moieties was refined applying similarity restraints (SAME) and restraining the ADP to approximate isotropic behaviour. The N–H hydrogen atoms were identified clearly in the difference *Fourier* map and were refined restraining the N–H distance to 0.87 Å (DFIX).

$\{[\text{Li}(\text{thf})_{2.5}]\mathbf{4}\}_2$ : The NH hydrogen atoms were refined freely.

$\{[\text{Li}(\text{tmeda})](\text{Li}(\text{thf})_2)[\mathbf{4}]\}_2$ : The NH hydrogen atoms were refined freely.

**Table S1 (contd)** Crystallographic data collection parameter of  $\{[Li_3(thf)_5](4)(5)\}_2$ ,  $\{[Li_3(thf)_3](tBu)5\}_2(thf)_{1.8}$  and  $\{[Li_2(thf)_2(Li(tmp))][5]\}_2$ .

Compound	$\{[Li_3(thf)_5](4)(5)\}_2$	$\{[Li_3(thf)_3](tBu)5\}_2(thf)_{1.8}$	$\{[Li_2(thf)_2(Li(tmp))][5]\}_2$
Formula	C <sub>88</sub> H <sub>146</sub> B <sub>8</sub> Li <sub>6</sub> N <sub>8</sub> O <sub>18</sub>	C <sub>63.2</sub> H <sub>112.5</sub> B <sub>4</sub> N <sub>4</sub> Li <sub>6</sub> O <sub>11.8</sub>	C <sub>58</sub> H <sub>100</sub> B <sub>4</sub> N <sub>6</sub> Li <sub>6</sub> O <sub>8</sub>
M <sub>r</sub> /(g mol <sup>-1</sup> )	1732.34	1202.73	1094.31
crystal shape	fragment of prism	irregular block	prism
crystal colour	clear colourless	clear colourless	clear colourless
cryst. dim. /mm <sup>3</sup>	0.35 × 0.19 × 0.16	0.446 × 0.363 × 0.243	0.298 × 0.128 × 0.110
crystal system	monoclinic	monoclinic	monoclinic
space group (no.)	C2/c (15)	I2/a (15)	C2/c (15)
a /Å	27.2197(8)	22.5108(4)	19.3963(10)
b /Å	12.9528(5)	12.8635(2)	16.7860(8)
c /Å	33.2002(12)	27.2387(5)	22.9634(14)
α	90°	90°	90°
β	103.948(3)°	111.665(2)°	101.073(6)°
γ	90°	90°	90°
V /Å <sup>3</sup>	11360.3(7)	7330.3(2)	7337.4(7)
Z, Z'	4, ½	4, ½	4, ½
D <sub>calcd.</sub> / (g cm <sup>-3</sup> )	1.013	1.061	0.991
μ /mm <sup>-1</sup> (λ /Å)	0.536 (1.54184)	0.559 (1.54184)	0.488 (1.54184)
Absorption corr.	multi-scan	gaussian	multi-scan
θ range (compl.)	3.35 – 67.0° (99.9%)	3.49 – 76.08° (99.5%)	3.51 – 76.21° (99.4%)
refl. measured	52148	84735	61863
unique (R <sub>int</sub> )	10115 (0.0467)	7627 (0.0492)	7623 (0.0827)
observed <sup>a</sup>	8512	6880	5796
param. / restr.	654 / 0	486 / 20	402 / 4
R <sub>1</sub> (obs. rflns.) <sup>a</sup>	0.0578	0.0540	0.0523
wR <sub>2</sub> (all rflns.)	0.1520	0.1655	0.1497
GooF on F <sup>2</sup>	1.054	1.025	1.058
max/min ρ / (eÅ <sup>-3</sup> )	0.377 / -0.415	0.450 / -0.363	0.548 / -0.289
CCDC No.	2089033	2089030	2089032

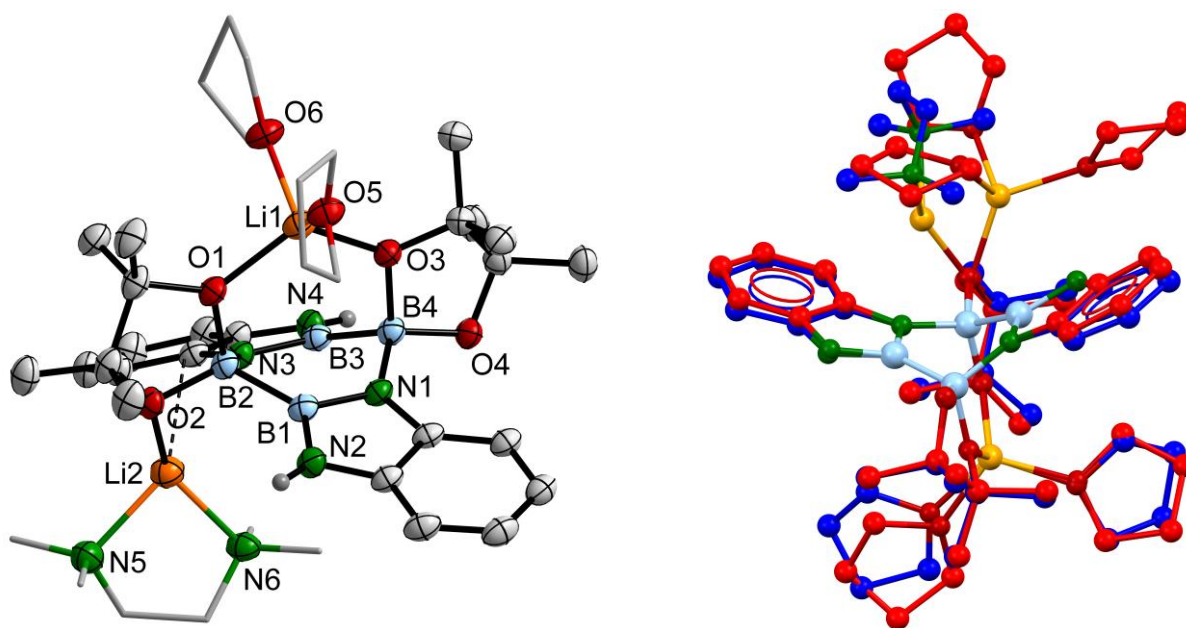
<sup>a</sup> Observation criterion:  $I > 2\sigma(I)$ .

$\{[Li_3(thf)_5](4)(5)\}_2$ : The N–H hydrogen atom was refined freely. Two disordered thf moieties were refined using split atom model (0.43(2) and 0.745(8) SOF of main component). No appropriate model could be established for co-crystallised solvent molecules; the data were processed using the SQUEEZE/PLATON program.<sup>S1</sup>

$\{[Li_3(thf)_3](tBu)5\}_2$ : Three disordered thf molecules were refined using split atom models. The SOF refined to 0.802(4) (O4), 0.78(1) (O5) and, only partly occupied, 0.137(3) (O6) and 0.768(4) (O6'). Similarity restraints (SAME) were employed for the fragments containing O4/O4' and O6/O6'. Common ADPs were refined for the thf molecules containing O6/O6' (EADP).

$\{[Li_2(thf)_2(Li(tmp))][5]\}_2$ : No appropriate model could be established for two sites of co-crystallised thf/Et<sub>2</sub>O molecules; the data were processed using the SQUEEZE/PLATON program.<sup>S7</sup> A disordered tmp moiety was refined using a split atom model (0.873(2) SOF of main component), applying similarity restraints on the C-CH<sub>3</sub> distances (SADI). A common ADP was refined for each disordered atom pair (EADP).

2.a.  $\{[(\text{Li}(\text{tmeda}))(\text{Li}(\text{thf})_2)](\mathbf{4})_2\}$



**Figure S11.** Selected view on the solid state structure of  $\{[(\text{Li}(\text{tmeda}))(\text{Li}(\text{thf})_2)](\mathbf{4})_2\}$  (left) and superimposed structures (right) of  $\{[(\text{Li}(\text{tmeda}))(\text{Li}(\text{thf})_2)](\mathbf{4})_2\}$  and  $\{[(\text{Li}(\text{thf})_{2.5})](\mathbf{4})_2\}$  (best fit of the Atoms B1–B4). Selected geometrical data [Å] for  $\{[(\text{Li}(\text{tmeda}))(\text{Li}(\text{thf})_2)](\mathbf{4})_2\}$ : B1–B2 1.738(3), B3–B4 1.737(3), N1–B1 1.445(2), N2–B1 1.450(2), N1–B4 1.558(2), N3–B3 1.460(2), N4–B3 1.450(2), N3–B2 1.570(2), O1–B2 1.505(2), O2–B2 1.507(2), O3–B4 1.543(2), O4–B4 1.481(2).

Specific to the structure of  $\{[(\text{Li}(\text{tmeda}))(\text{Li}(\text{thf})_2)](\mathbf{4})_2\}$  is the comparably short distance of the lithium ion Li2 to the centroid of the atoms N3, C13 and C14,  $\text{Li2}\cdots\text{Cp}[\text{N3},\text{C13},\text{C14}]$  of 2.317(3) Å, suggesting an appreciable ‘ $\eta^3$ -benzylic’ coordination of the Bdmab moiety to the lithium ion. The shortest respective distance in  $\{[(\text{Li}(\text{thf})_{2.5})](\mathbf{4})_2\}$  is with  $\text{Li2}\cdots\text{Cp}[\text{N1},\text{C1},\text{C2}]$  of 3.862(3) Å significantly longer.

## 4. REFERENCES

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