

# Syntheses and structures of new alkali-metal boraamidates and ferrocenyl aminoboranes†‡§

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The ferrocenyl bis(amino)boranes  $\text{FcB}[\text{N}(\text{H})\text{R}]_2$  ( $\text{Fc}$  = ferrocenyl; **1a**,  $\text{R} = {}^t\text{Bu}$ , **1b**,  $\text{R} = \text{Dipp}$ ) and  $1,1'\text{-Fc}\{\text{B}[\text{N}(\text{H}){}^t\text{Bu}]_2\}_2$  (**2**) are obtained by the reactions of  $[\text{Li}][\text{N}(\text{H})\text{R}]$  with the corresponding ferrocenyl dibromoboranes  $\text{FcBBr}_2$  and  $1,1'\text{-Fc}(\text{BBr}_2)_2$ . In a similar manner  $1,4\text{-}[\text{N}(\text{H}){}^t\text{Bu}]_2\text{BC}_6\text{H}_4\text{B}[\text{N}(\text{H}){}^t\text{Bu}]_2$  (**3**) is prepared in good yield by treatment of  $1,4\text{-Br}_2\text{BC}_6\text{H}_4\text{BBr}_2$  with five equivalents of  $[\text{Li}][\text{N}(\text{H}){}^t\text{Bu}]$  in toluene. Compound **3** is converted to the highly air-sensitive tetralithio derivative  $[\text{Li}_4][1,4\text{-}(\text{N}^t\text{Bu})_2\text{BC}_6\text{H}_4\text{B}(\text{N}^t\text{Bu})_2]$  (**4**), by deprotonation with  ${}^n\text{BuLi}$  in hexanes. Alkali-metal derivatives of a *monoanionic* boraamidinate  $[\text{M}][\text{PhB}(\text{NDipp})\{\text{N}(\text{H})\text{Dipp}\}]$  [ $\text{M} = \text{Li}$  (**5**),  $\text{K}$  (**6**)] are produced by reactions of  $\text{PhB}[\text{N}(\text{H})\text{Dipp}]_2$  with one equivalent of  ${}^n\text{BuLi}$  in hexanes or  $[\text{K}][\text{CH}_2\text{Ph}]$  in THF, respectively. The use of two equivalents of  $[\text{K}][\text{CH}_2\text{Ph}]$  generates the dipotassium reagent  $[\text{K}_2][\text{PhB}(\text{NDipp})_2]$  (**7**) in excellent yield. The X-ray structures of **1a**, **1b**, **2**, **4**·6THF, **5**·2THF and **7**·3THF were determined. The complex **4**·6THF incorporates one terminal and one bridging THF molecule for each  $\text{Li}^+$  cation. The boraamidinate ligand in **5**·2THF is connected in an *N*-monodentate fashion to the  $\text{Li}^+$  cation, which is solvated by two THF molecules. In the solid state **7**·3THF forms an extended structure as a result of  $\eta^1\text{-amide}-\eta^6\text{-arene}$  coordination to the two  $\text{K}^+$  cations, which are coordinated by one or two THF molecules, respectively.

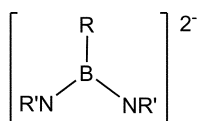
## Introduction

Boraamidates (*bams*)<sup>1</sup>  $[\text{RB}(\text{NR}')_2]^{2-}$  (**A**) are dianionic ligands that are isoelectronic with monoanionic amidinates  $[\text{RC}(\text{NR}')_2]^-$  (**B**).<sup>2</sup> The *bam* ligand adopts a wide range of bonding modes in main group and transition-metal complexes, most commonly chelating or bridging arrangements.<sup>1,3</sup> Replacement of the CR fragment in the ligand backbone with a BR unit imposes two

unique consequences: (a) fewer anionic ligands are necessary for stabilizing higher oxidation states<sup>4,5</sup> and (b) novel redox behaviour leading to the formation of persistent or, in some cases, stable radicals is observed.<sup>6</sup> As with amidinates, the electronic and steric properties of *bams* can be tuned by varying the substituents on either nitrogen or boron. Recently, we described the synthesis and structures of the first boraguanidinates,<sup>7</sup> i.e. isoelectronic analogues of guanidinates,<sup>8</sup> in which the substituent on boron is a dialkylamino group. Current investigations of *bam* ligands are focused on lanthanide complexes and their potential as catalysts.<sup>9,10</sup>

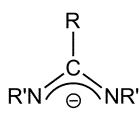
The synthesis of new types of *bams* is of interest in order to expand the chemistry of this versatile ligand. For example, the introduction of a linker group between two boron atoms would generate a tetraanionic ligand (**C**). In light of the formation of stable radicals that incorporate the anion radical  $[\text{PhB}(\text{N}^t\text{Bu})_2]^{\bullet-}$ ,<sup>6</sup> **C** is a potential source of biradical systems incorporating p-block elements.<sup>11</sup> A second modification of the *bam* ligand that warrants investigation is single deprotonation of *bamH*<sub>2</sub> to form a monoanionic ligand **D** that still contains an  $\text{-NH}$  functionality. In addition to being isoelectronic, these monoanions would have the same charge as the well-studied amidinate ligands.<sup>2</sup> Finally, the availability of hitherto unknown dipotassiated *bam* reagents is desirable in order to facilitate the separation of alkali-metal halide by-products in metathetical reactions with main group or transition-metal halides.<sup>12</sup>

With these objectives in mind we describe here the synthesis, spectroscopic and structural characterization of (a) the ferrocenyl aminoboranes  $\text{FcB}[\text{N}(\text{H})\text{R}]_2$  [ $\text{R} = {}^t\text{Bu}$  (**1a**),  $\text{Dipp}$  (**1b**);  $\text{Fc}$  = ferrocenyl,  $\text{Dipp} = 2,6\text{-diisopropylphenyl}$ ] and



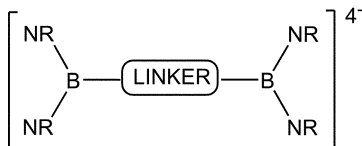
**A**

$\text{R} = \text{H, alkyl, aryl}$   
 $\text{R}' = \text{alkyl, aryl}$

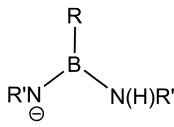


**B**

$\text{R} = \text{H, alkyl, aryl}$   
 $\text{R}' = \text{H, alkyl, aryl, trimethylsilyl}$



**C**



**D**

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† Dedicated to the late Professor Pascal le Floch in appreciation of his many outstanding contributions.

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§ CCDC reference numbers [CCDC 773247–773252]. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c0nj00279h

$\text{Fc}[\text{B}(\text{N}(\text{H})^t\text{Bu})_2]_2$  (**2**), (b)  $1,4\text{-}[\text{N}(\text{H})^t\text{Bu}]_2\text{BC}_6\text{H}_4\text{B}[\text{N}(\text{H})^t\text{Bu}]_2$  (**3**) and the tetralithiated derivative  $[\{\text{Li}(\text{THF})\}_4(\mu\text{-THF})_2]\text{-}[1,4\text{-}(\text{N}^t\text{Bu})_2\text{BC}_6\text{H}_4\text{B}(\text{N}^t\text{Bu})_2]$  (**4-6THF**), (c) alkali-metal derivatives of a monoanionic boraamidinate  $[\text{M}][\text{PhB}(\text{NDipp})\{\text{N}(\text{H})\text{Dipp}\}]_2$  ( $\text{M} = \text{Li}$  (**5**),  $\text{K}$  (**6**)), and (d) the dipotassium reagent  $[\text{K}_2(\text{THF})_3][\text{PhB}(\text{NDipp})_2]$  (**7**).

## Experimental section

### Reagents and general procedures

All reactions and the manipulation of moisture- and/or air-sensitive products were performed under an argon atmosphere using standard Schlenk line techniques or in an inert-atmosphere glove box. Solvents were dried with appropriate drying agents, distilled before use and stored over molecular sieves. Prior to use, all glassware was carefully dried. Dicyclopentadienyl iron ( $\text{Cp}_2\text{Fe}$ ) was purchased from Eastman Organic Chemical Company and all other chemicals were obtained from Aldrich Chemical Company and used as received. The reagents  $[\text{Li}][\text{N}(\text{H})\text{Dipp}]$  and  $[\text{Li}][\text{N}(\text{H})^t\text{Bu}]$  were prepared by the addition of  $^t\text{BuLi}$  (2.5 M in hexane) to an equimolar amount of  $\text{DippNH}_2$  or  $^t\text{BuNH}_2$ , respectively, in hexanes and purity was checked by  $^1\text{H}$  NMR spectroscopy. The reagents  $\text{FcBBr}_2$ ,<sup>13</sup>  $1,1'\text{-Fc}(\text{BBr}_2)_2$ ,<sup>14</sup>  $1,4\text{-Br}_2\text{BC}_6\text{H}_4\text{BBr}_2$ ,<sup>15</sup> benzylpotassium,<sup>16</sup> and  $\text{PhB}[\text{N}(\text{H})\text{Dipp}]_2$ <sup>17</sup> were prepared by literature methods. Deuterated solvents were purchased from Cambridge Isotope Laboratories, dried over molecular sieves for at least one week and degassed using the freeze–pump–thaw method.

### Instrumentation

All NMR spectra were collected at room temperature using a Bruker DRX 400 spectrometer. All chemical shifts are reported in parts per million (ppm) with higher frequency taken as positive. Chemical shifts for  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra are reported with respect to tetramethylsilane and were calibrated based on the signal of the residual solvent peak. A solution of 1.0 M  $\text{LiCl}$  in  $\text{D}_2\text{O}$  was used as the external standard for  $^7\text{Li}$  NMR spectra and  $^{11}\text{B}\{^1\text{H}\}$  NMR chemical shifts are reported with respect to a solution of  $\text{BF}_3\cdot\text{OEt}_2$  in  $\text{C}_6\text{D}_6$ . Elemental and mass spectrometry analyses (using a Waters GCT Premier spectrometer) were carried out by the Analytical Services Laboratory of the Department of Chemistry, University of Calgary.

### Crystal structure determinations

Single crystals of  $\text{FcB}[\text{N}(\text{H})^t\text{Bu}]_2$  (**1a**),  $\text{FcB}[\text{N}(\text{H})\text{Dipp}]_2$  (**1b**),  $1,1'\text{-Fc}[\text{B}(\text{N}(\text{H})^t\text{Bu})_2]_2$  (**2**),  $[\{\text{Li}(\text{THF})\}_4(\mu\text{-THF})_2][1,4\text{-}(\text{N}^t\text{Bu})_2\text{BC}_6\text{H}_4\text{B}(\text{N}^t\text{Bu})_2]$  (**4-6THF**),  $[\text{Li}(\text{THF})_2][\text{PhB}(\text{NDipp})\{\text{N}(\text{H})\text{Dipp}\}]$  (**5-2THF**) and  $[\text{K}_2(\text{THF})_3][\text{PhB}(\text{NDipp})_2]$  (**7-3THF**) suitable for X-ray analysis were covered with Paratone oil and mounted on a glass fibre in a stream of  $\text{N}_2$  at 173 K on a Nonius KappaCCD diffractometer ( $\text{MoK}\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ ) using COLLECT (Nonius, B.V. 1998) software. The unit cell parameters were calculated and refined from the full data set. All crystal cell refinement and data reduction were carried out using the Nonius DENZO package. After data reduction, the data were corrected for absorption based on equivalent reflections using SCALEPACK (Nonius, B.V. 1998). The structures

were solved by direct methods using SHELXS-97<sup>18a</sup> and refinement was carried out on  $F^2$  against all independent reflections by the full-matrix least-squares method using the SHELXL-97<sup>18b</sup> program. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were calculated geometrically and refined using a riding model. For complexes **4-6THF** and **7-3THF**, electron density in two regions was attributed to disordered solvent molecules (**4-6THF**: diethyl ether; **7-3THF**: hexane) for which no suitable model could be found. These regions of electron density were removed from the reflections data using the program SQUEEZE (PLATON),<sup>18c</sup> leaving a total void of  $355.7 \text{ \AA}^3$  and  $327.4 \text{ \AA}^3$ , respectively. Crystallographic data for **1a**, **1b** and **2** are summarised in Table 1 and those for **4-6THF**, **5-2THF** and **7-3THF** are given in Table 2.

### Syntheses

**$\text{FcB}[\text{N}(\text{H})^t\text{Bu}]_2$ , **1a**.** A solution of  $\text{FcBBr}_2$  (1.37 g, 3.85 mmol) in toluene (15 mL) was added to a stirred slurry of  $[\text{Li}][\text{N}(\text{H})^t\text{Bu}]$  (0.609 g, 7.70 mmol) in toluene (15 mL) at *ca.*  $-80^\circ\text{C}$ . After 1 h, the cold bath was removed and the reaction mixture was allowed to warm to room temperature and stirred for 4 h. After filtration to remove  $\text{LiBr}$ , volatiles were taken off *in vacuo* yielding an orange solid (1.005 g, 2.96 mmol, 76%). Orange, X-ray quality crystals of **1a** were grown from a concentrated hexanes/toluene solution at  $5^\circ\text{C}$ . HRMS: calculated  $m/z$  for  $[\text{C}_{18}\text{H}_{29}\text{BN}_2]$ : 340.1773. Found: 340.1757.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta$  4.28 (t, 2H,  $\text{C}_5\text{H}_4$ ,  $^3J_{\text{H-H}} = 1.59 \text{ Hz}$ ), 4.12 (t, 2H,  $\text{C}_5\text{H}_4$ ,  $^3J_{\text{H-H}} = 1.59 \text{ Hz}$ ), 4.06 (s, 5H,  $\text{C}_5\text{H}_5$ ), 3.35 (2H, br s,  $-\text{NH}$ ), 1.21 (s, 18H,  $-\text{C}(\text{CH}_3)_3$ ).  $^{11}\text{B}$  NMR ( $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta$  29.2.  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta$  74.4 ( $\text{C}_5\text{H}_4$ ), 69.4 ( $\text{C}_5\text{H}_4$ ), 69.2 ( $\text{C}_5\text{H}_5$ ), 49.0 ( $-\text{C}(\text{CH}_3)_3$ ), 33.6 ( $-\text{C}(\text{CH}_3)_3$ ).

**$\text{FcB}[\text{N}(\text{H})\text{Dipp}]_2$ , **1b**.** A solution of  $\text{FcBBr}_2$  (0.720 g, 2.02 mmol) in toluene (10 mL) was added to a stirred slurry of  $[\text{Li}][\text{N}(\text{H})\text{Dipp}]$  (0.742 g, 4.05 mmol) in toluene (15 mL) at *ca.*  $-80^\circ\text{C}$ . After 1 h the cold bath was removed and the reaction was allowed to warm to room temperature and stirred for 18 h. The reaction mixture was filtered to remove  $\text{LiBr}$  and volatiles were taken off *in vacuo* yielding an orange solid (0.746 g, 1.36 mmol, 67%). Orange, X-ray quality crystals of **1b** were grown from a concentrated toluene solution at  $5^\circ\text{C}$ . Anal. Calcd. for  $\text{C}_{34}\text{H}_{45}\text{BN}_2\text{Fe}$ : C, 74.46; H, 8.27; N, 5.11%. Found: C, 74.31; H, 8.05; N, 5.06%.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta$  7.21–7.03 (m, 6H, Dipp), 4.28 (br, 2H,  $-\text{CH}(\text{CH}_3)_2$ ), 4.07 (s, 5H,  $\text{C}_5\text{H}_5$ ), 4.01 (t, 2H,  $\text{C}_5\text{H}_4$ ,  $^3J_{\text{H-H}} = 1.67 \text{ Hz}$ ), 3.87 (t,  $\text{C}_5\text{H}_4$ ,  $^3J_{\text{H-H}} = 1.67 \text{ Hz}$ ), second  $^1\text{Pr}$  septet under resonance at 3.87 ppm, 3.41 (2H, br s,  $-\text{NH}$ ), 1.37–1.04 (br, 24H,  $-\text{CH}(\text{CH}_3)_2$ ).  $^{11}\text{B}$  NMR ( $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta$  30.3.  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta$  147.6 (Dipp), 146.1 (Dipp), 123.6 (Dipp), 73.9 ( $\text{C}_5\text{H}_4$ ), 71.0 ( $\text{C}_5\text{H}_4$ ), 68.9 ( $\text{C}_5\text{H}_5$ ), 28.9 ( $-\text{CH}(\text{CH}_3)_2$ ), 25.7 ( $-\text{CH}(\text{CH}_3)_2$ ), 24.7 ( $-\text{CH}(\text{CH}_3)_2$ ), 23.7 ( $-\text{CH}(\text{CH}_3)_2$ ), 23.1 ( $-\text{CH}(\text{CH}_3)_2$ ).

**$\text{Fc}[\text{B}(\text{N}(\text{H})^t\text{Bu})_2]_2$ , **2**.** A solution of  $1,1'\text{-Fc}(\text{BBr}_2)_2$  (0.268 g, 0.51 mmol) in toluene (10 mL) was added to a stirred slurry of  $[\text{Li}][\text{N}(\text{H})^t\text{Bu}]$  (0.161 g, 2.03 mmol) in toluene (10 mL) at *ca.*  $-80^\circ\text{C}$ . After 1 h the cold bath was removed and the reaction mixture was allowed to warm to room temperature and stirred

**Table 1** Selected crystal data and refinement parameters for **1a**, **1b** and **2**<sup>a</sup>

	<b>1a</b>	<b>1b</b>	<b>2</b>
Empirical formula	C <sub>18</sub> H <sub>49</sub> BFeN <sub>2</sub>	C <sub>34</sub> H <sub>45</sub> BFeN <sub>2</sub>	C <sub>26</sub> H <sub>48</sub> B <sub>2</sub> FeN <sub>4</sub>
Fw	340.09	548.38	494.15
Cryst. system	Orthorhombic	Monoclinic	Triclinic
Space group	<i>Pna</i> 2 <sub>1</sub>	<i>C2/c</i>	<i>P1</i>
<i>a</i> /Å	17.365(4)	21.451(4)	10.265(2)
<i>b</i> /Å	5.996(1)	10.016(2)	12.189(2)
<i>c</i> /Å	35.480(7)	28.699(6)	13.101(3)
$\alpha$ /°	90.00	90.00	109.70(3)
$\beta$ /°	90.00	99.88(3)	102.12(3)
$\gamma$ /°	90.00	90.00	103.19(3)
<i>V</i> /Å <sup>3</sup>	3670(1)	6075(2)	1427(1)
<i>Z</i>	8	8	2
<i>T</i> /°C	−100	−100	−100
$\rho_{\text{calcd}}$ /g cm <sup>−3</sup>	1.231	1.199	1.150
$\mu(\text{MoK}\alpha)/\text{mm}^{-1}$	0.820	0.521	0.548
Crystal size/mm <sup>3</sup>	0.28 × 0.08 × 0.04	0.20 × 0.16 × 0.04	0.40 × 0.40 × 0.32
<i>F</i> (000)	1456	2352	536
$\theta$ Range/°	3.28–25.02	2.25–27.46	2.97–25.03
Reflns collected	22 275	30 049	24 390
Unique reflns	5629	6921	5021
<i>R</i> <sub>int</sub>	0.0 <sup>d</sup>	0.0583	0.0200
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup>b</sup>	0.0428	0.0525	0.0366
<i>wR</i> <sub>2</sub> (all data) <sup>c</sup>	0.1121	0.1380	0.0966
GOF on <i>F</i> <sup>2</sup>	1.126	1.081	1.043
Completeness	0.943	0.995	0.996

<sup>a</sup>  $\lambda(\text{MoK}\alpha) = 0.71073$  Å. <sup>b</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>c</sup>  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{\frac{1}{2}}$ . <sup>d</sup> Flack parameter: 0.50(2).

**Table 2** Selected crystal data and refinement parameters for **4-6THF**, **5-2THF** and **7-3THF**<sup>a</sup>

	<b>4-6THF</b>	<b>5-2THF</b>	<b>7-3THF</b>
Empirical formula	C <sub>46</sub> H <sub>88</sub> B <sub>2</sub> Li <sub>4</sub> N <sub>4</sub> O <sub>6</sub>	C <sub>38</sub> H <sub>56</sub> BLiN <sub>2</sub> O <sub>2</sub>	C <sub>42</sub> H <sub>63</sub> BK <sub>2</sub> N <sub>2</sub> O <sub>3</sub>
Fw	842.58	590.60	732.95
Cryst. system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P2</i> <sub>1</sub> / <i>c</i>	<i>P2</i> <sub>1</sub> / <i>n</i>	<i>P2</i> <sub>1</sub> / <i>c</i>
<i>a</i> /Å	10.003(2)	14.028(3)	10.456(2)
<i>b</i> /Å	14.712(3)	16.356(3)	15.323(3)
<i>c</i> /Å	19.859(4)	16.606(3)	27.854(6)
$\beta$ /°	91.29(3)	103.66(3)	90.91(3)
<i>V</i> /Å <sup>3</sup>	2922(1)	3702(1)	4462(2)
<i>Z</i>	2	4	4
<i>T</i> /°C	−100	−100	−100
$\rho_{\text{calcd}}$ /g cm <sup>−3</sup>	0.958	1.060	1.091
$\mu(\text{MoK}\alpha)/\text{mm}^{-1}$	0.060	0.063	0.248
Crystal size/mm <sup>3</sup>	0.20 × 0.20 × 0.20	0.14 × 0.14 × 0.12	0.20 × 0.12 × 0.08
<i>F</i> (000)	924	1288	1584
$\theta$ Range/°	2.65–25.03	2.79–25.03	2.57–25.03
Reflns collected	32 486	56 077	37 588
Unique reflns	5107	6541	7805
<i>R</i> <sub>int</sub>	0.0188	0.0666	0.0417
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup>b</sup>	0.0679	0.0740	0.0859
<i>wR</i> <sub>2</sub> (all data) <sup>c</sup>	0.2254	0.1958	0.2078
GOF on <i>F</i> <sup>2</sup>	1.074	1.059	1.093
Completeness	0.990	0.998	0.991

<sup>a</sup>  $\lambda(\text{MoK}\alpha) = 0.71073$  Å. <sup>b</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>c</sup>  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{\frac{1}{2}}$ .

for 18 h. The reaction mixture was filtered to remove LiBr and volatiles were taken off *in vacuo* yielding an orange solid (0.136 g, 0.28 mmol, 54%). Orange, X-ray quality crystals of **2** were grown from a concentrated toluene solution at 5 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  4.28 (t, 4H, C<sub>5</sub>H<sub>4</sub>, <sup>3</sup>*J*<sub>H-H</sub> = 1.73 Hz), 4.21 (t, 4H, C<sub>5</sub>H<sub>4</sub>, <sup>3</sup>*J*<sub>H-H</sub> = 1.73 Hz), 3.47 (4H, br s, −NH), 1.25 (s, 36H, −C(CH<sub>3</sub>)<sub>3</sub>). <sup>11</sup>B NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  29.2. <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  75.2 (C<sub>5</sub>H<sub>4</sub>), 69.8 (C<sub>5</sub>H<sub>4</sub>), 49.1 (−C(CH<sub>3</sub>)<sub>3</sub>), 33.7 (−C(CH<sub>3</sub>)<sub>3</sub>).

**1,4-[N(H)<sup>t</sup>Bu]<sub>2</sub>BC<sub>6</sub>H<sub>4</sub>B[N(H)<sup>t</sup>Bu]<sub>2</sub>, 3.** A solution of 1,4-Br<sub>2</sub>BC<sub>6</sub>H<sub>4</sub>BBr<sub>2</sub> (0.858 g, 2.05 mmol) in toluene (15 mL) was added to a slurry of [Li][N(H)<sup>t</sup>Bu] (0.898 g, 10.0 mmol) in toluene (10 mL) at *ca.* −80 °C. After 30 min the reaction mixture was allowed to warm to room temperature and stirred for 18 h. Volatiles were removed *in vacuo* and the product was extracted in hexanes. After filtration to remove LiBr and excess [Li][N(H)<sup>t</sup>Bu], volatiles were removed *in vacuo* resulting in an oily solid that completely solidified overnight at room

temperature to give **3** as a colourless solid (0.597 g, 1.54 mmol, 75%). HRMS: calculated  $m/z$  for  $[C_{22}H_{44}N_2B]$ : 386.3752. Found: 386.3752.  $^1H$  NMR ( $C_6D_6$ , 25 °C):  $\delta$  7.66 (s, 4H,  $-C_6H_4-$ ), 2.88 (br s, 4H,  $-NH$ ), 1.16 (s, 36H,  $-C(CH_3)_3$ ).  $^1H$  NMR (THF- $d_8$ , 25 °C):  $\delta$  7.22 (s, 4H,  $-C_6H_4-$ ), 2.93 (br s, 4H,  $-NH$ ), 1.13 (s, 36H,  $-C(CH_3)_3$ ).  $^{11}B$  NMR ( $C_6D_6$ , 25 °C):  $\delta$  30.0.  $^{13}C$  NMR ( $C_6D_6$ , 25 °C):  $\delta$  *ipso* carbon not observed, 132.0 ( $-C_6H_4-$ ), 49.3 ( $-C(CH_3)_3$ ), 33.6 ( $-C(CH_3)_3$ ).

**[{Li(THF)}<sub>4</sub>( $\mu$ -THF)<sub>2</sub>][1,4-( $N^iBu$ )<sub>2</sub>BC<sub>6</sub>H<sub>4</sub>B( $N^iBu$ )<sub>2</sub>], **4-6THF**. A 2.5 M solution of  $nBuLi$  in hexanes (2.23 mL, 5.60 mmol) was added to a solution of **3** (0.54 g, 1.40 mmol) in hexanes (10 mL) at 0 °C. The reaction was warmed to room temperature, stirred for 18 h and volatiles were removed *in vacuo* giving a colourless solid. Purification by recrystallization from THF gave **4-6THF** (0.409 g, 0.485 mmol, 35%). X-Ray quality crystals were grown from a solution of **4** in a THF/Et<sub>2</sub>O solution. Accurate CHN analysis could not be obtained owing to the highly air-sensitive nature of **4**.  $^1H$  NMR (THF- $d_8$ , 25 °C):  $\delta$  6.98 (s, 4H,  $-C_6H_4-$ ), 3.61 ( $-OCH_2CH_2$ ), 1.77 ( $-OCH_2CH_2$ ), 0.93 (s, 36H,  $-C(CH_3)_3$ ).  $^{11}B$  NMR (THF- $d_8$ , 25 °C):  $\delta$  33.6.  $^7Li$  NMR (THF- $d_8$ , 25 °C):  $\delta$  1.22.  $^{13}C$  NMR ( $C_6D_6$ , 25 °C):  $\delta$  *ipso* carbon not observed, 132.3 ( $-C_6H_4-$ ), 68.4 ( $-OCH_2CH_2$ ), 51.4 ( $-C(CH_3)_3$ ), 38.8 ( $-C(CH_3)_3$ ), 26.5 ( $-OCH_2CH_2$ ).**

**[Li][PhB(NDipp){N(H)Dipp}], **5****. A 2.5 M solution of  $nBuLi$  in hexanes (2.5 mL, 2.5 mmol) was added to a solution of PhB[N(H)Dipp]<sub>2</sub> (1.01 g, 2.5 mmol) in hexanes (15 mL) at *ca.* -30 °C. The reaction mixture was warmed to room temperature over *ca.* 20 min and stirred for an additional 1.5 h. Removal of volatiles *in vacuo* gave **5** as a colourless solid (0.991 g, 2.07 mmol, 89%). Anal. Calcd. for  $C_{30}H_{40}BN_2Li$ : C, 80.72; H, 9.03; N, 6.28%. Found: C, 79.36; H, 8.98; N, 6.18%.  $^1H$  NMR (THF- $d_8$ , 25 °C):  $\delta$  7.30 (m, 2H, aryl protons), 7.0–6.96 (m, 5H, aryl protons), 6.8–6.74 (m, 3H, aryl proton), 6.58 (t, 1H, aryl proton), 3.91 (sept., 2H,  $-CH(CH_3)_2$ ,  $^3J_{H-H}$  = 6.87 Hz), 3.58 ( $-NH$ , under residual solvent peak of THF), 3.41 (sept., 2H,  $-CH(CH_3)_2$ ,  $^3J_{H-H}$  = 6.72 Hz), 1.29 (d, 6H,  $-CH(CH_3)_2$ ,  $^3J_{H-H}$  = 6.87 Hz), 0.81 (d, 12H,  $-CH(CH_3)_2$ ,  $^3J_{H-H}$  = 6.72 Hz).  $^7Li$  NMR (THF- $d_8$ , 25 °C):  $\delta$  0.23.  $^{11}B$  NMR (THF- $d_8$ , 25 °C):  $\delta$  26.4.  $^{13}C$  NMR (THF- $d_8$ , 25 °C): 156.6 (aryl), 144.0 (aryl), 143.0 (aryl), 141.5 (aryl), 134.2 (aryl), 127.9 (aryl), 126.9 (aryl), 123.1 (aryl), 123.0 (aryl), 122.9 (aryl), 117.7 (aryl), 28.8 ( $-C(CH_3)_2$ ), 28.3 ( $-C(CH_3)_2$ ), 25.3 ( $-C(CH_3)_2$ ), 25.0 ( $-C(CH_3)_2$ ), 24.3 ( $-C(CH_3)_2$ ).

**[K][PhB{N(H)Dipp}{NDipp}], **6****. A solution of [K][CH<sub>2</sub>Ph] (0.166 g, 1.27 mmol) in THF (10 mL) was added to a solution of PhB[N(H)Dipp]<sub>2</sub> (0.562 g, 1.27 mmol) in THF (10 mL) at room temperature. After 10 min, volatiles were removed *in vacuo* and the resulting product was treated with 10 mL of hexanes. Removal of volatiles *in vacuo* gave **6** as a cream-coloured solid (0.578 g, 1.05 mmol, 82%, based on **6-THF**).  $^1H$  NMR (THF- $d_8$ , 25 °C):  $\delta$  7.34 (m, 2H, aryl protons of Ph group), 6.95–6.78 (m, 8H, aryl protons), 6.32 (t, 1H, aryl proton), 3.79 (overlapping sept., 4H,  $-CH(CH_3)_2$ ), 3.62 (m,  $-OCH_2CH_2$ ),  $-NH$  is observed at 3.62 ppm when the reaction is carried out in THF- $d_8$ , 1.78 (m,  $-OCH_2CH_2$ ), 1.10

(d, 6H,  $-CH(CH_3)_2$ ,  $^3J_{H-H}$  = 6.12 Hz), 1.03 (d, 18H,  $-CH(CH_3)_2$ ,  $^3J_{H-H}$  = 5.96 Hz).  $^{11}B$  NMR (THF- $d_8$ , 25 °C):  $\delta$  24.9.  $^{13}C$  NMR (THF- $d_8$ , 25 °C): 145.7 (aryl), 138.8 (aryl), 134.4 (aryl), 127.3 (aryl), 126.1 (aryl), 123.1 (aryl), 122.7 (aryl), 114.3 (aryl), 68.4 ( $-OCH_2CH_2$ ), 28.9 ( $-C(CH_3)_2$ ), 28.0 ( $-C(CH_3)_2$ ), 26.5 ( $-OCH_2CH_2$ ), 24.9 ( $-C(CH_3)_2$ ), 24.3 ( $-C(CH_3)_2$ ).

**[K<sub>2</sub>][PhB(NDipp)<sub>2</sub>], **7****. A solution of [K][CH<sub>2</sub>Ph] (0.385 g, 2.96 mmol) in THF (10 mL) was added to a solution of PhB[N(H)Dipp]<sub>2</sub> (0.650 g, 1.48 mmol) in THF (10 mL) at room temperature. After 20 min volatiles were removed *in vacuo* and the resulting product was treated with 10 mL of hexanes. Removal of volatiles *in vacuo* gave **7** as a yellow solid (0.705 g, 1.36 mmol, 93%). Anal. Calcd. for  $C_{30}H_{39}BN_2K_2$ : C, 69.74; H, 7.61; N, 5.42%. Found: C, 68.19; H, 7.63; N, 5.22%.  $^1H$  NMR (THF- $d_8$ , 25 °C):  $\delta$  7.52 (d, 2H, *ortho*-aryl protons of Ph group), 6.89 (m, 2H, *meta*-aryl protons of the Ph group), 6.77 (t, 1H, *para*-aryl proton of Ph group), 6.64 (d, 4H, *meta*-protons of Dipp groups), 6.01 (t, 2H, *para*-protons of Dipp groups), 4.04 (sept., 4H,  $-CH(CH_3)_2$ ,  $^3J_{H-H}$  = 6.17 Hz), 3.62 (m,  $-OCH_2CH_2$ ), 1.78 (m,  $-OCH_2CH_2$ ), 1.08 (d, 12H,  $-CH(CH_3)_2$ ,  $^3J_{H-H}$  = 6.17 Hz), 0.92 (d, 12H,  $-CH(CH_3)_2$ ,  $^3J_{H-H}$  = 6.17 Hz).  $^{11}B$  NMR (THF- $d_8$ , 25 °C):  $\delta$  24.2.  $^{13}C$  NMR (THF- $d_8$ , 25 °C): 162.9 (aryl), 139.2 (aryl), 135.1 (aryl), 126.8 (aryl), 124.0 (aryl), 122.3 (aryl), 109.3 (aryl), 68.4 ( $-OCH_2CH_2$ ), 27.8 ( $-C(CH_3)_2$ ), 26.8 ( $-OCH_2CH_2$ ), 25.2 ( $-C(CH_3)_2$ ), 24.8 ( $-C(CH_3)_2$ ).

## Results and discussion

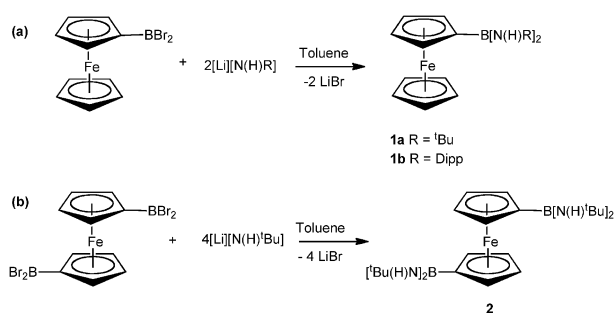
### Synthesis, spectroscopic characterization and X-ray structures of FcB[N(H)R]<sub>2</sub> (**1a**, R = $^iBu$ , **1b**, R = Dipp) and **1,1'-Fc{B[N(H) $^iBu$ ]<sub>2</sub>}<sub>2</sub> (**2**)**

Ferrocene ( $Cp_2Fe$ ) was the first linker group considered for the preparation of bis-*bams* because of the ready availability of ferrocenyl bis(dibromoborane) 1,1'-Fc(BBr<sub>2</sub>)<sub>2</sub>.<sup>14</sup> In order to provide a benchmark for the evaluation of the influence of the Fc group compared to the Ph on redox behaviour of the dianions  $[ArB(N^iBu)_2]^{2-}$  (Ar = Ph,<sup>6</sup> Fc), the initial targets were the ferrocenyl *bams*  $[FcB(NR)_2]^{2-}$  (R =  $^iBu$ , Dipp).

Substitution of the halogen atoms in ferrocenyl dihaloboranes for dialkylamino groups has previously been accomplished by the reaction of 1,1'-Fc(BBr<sub>2</sub>)<sub>2</sub> with different amounts of secondary amine.<sup>13b</sup> More recently, it was demonstrated that FcBBr<sub>2</sub> reacts with two equivalents of lithium anilide to afford FcB[N(H)Ph]<sub>2</sub>;<sup>19</sup> the mono-substituted *tert*-butyl derivative, FcBBr[N(H) $^iBu$ ], was also prepared. However, no structural characterisation for either compound was reported. In the current study the new ferrocenyl aminoboranes FcB[N(H)R]<sub>2</sub> (**1a**, R =  $^iBu$ ; **1b**, R = Dipp) were synthesized in 65–75% yields by the reaction of FcBBr<sub>2</sub> with two equivalents of [Li][N(H)R] (R =  $^iBu$ , Dipp) in toluene (Scheme 1a). A similar protocol was used to prepare 1,1'-ferrocenyl bis-[di-(*tert*-butylamino)borane], **2**, in 54% yields from 1,1'-Fc(BBr<sub>2</sub>)<sub>2</sub> and four equivalents of [Li][N(H) $^iBu$ ] (Scheme 1b).

The identities of **1a**, **1b** and **2** were established by  $^1H$ ,  $^{13}C$  and  $^{11}B$  NMR data together with C,H,N analyses or, in the case of **1a**, high resolution mass spectra. The  $^1H$  NMR spectra





Scheme 1

of the *tert*-butylamino derivatives **1a** and **2** show resonances for C<sub>5</sub>H<sub>5</sub>, C<sub>5</sub>H<sub>4</sub>, NH and C(CH<sub>3</sub>)<sub>3</sub> protons with appropriate relative intensities, while the derivative **1b** showed the expected resonances for the C<sub>6</sub>H<sub>3</sub> and CH(CH<sub>3</sub>)<sub>2</sub> protons of the Dipp groups, in addition to those for C<sub>5</sub>H<sub>5</sub>, C<sub>5</sub>H<sub>4</sub>, and NH. The <sup>11</sup>B NMR chemical shifts of **1a**, **1b** and **2** are in the narrow range 29–30 ppm.

X-Ray quality orange crystals of **1a**, **1b**, and **2** were grown from toluene or hexanes/toluene solutions. The molecular structures are depicted in Fig. 1 and 2; selected bond lengths and angles are compared in Table 3.

The unit cell of **1a** contains two independent molecules, as was found for FcBBr<sub>2</sub>.<sup>20</sup> For both **1a** and **1b**, planar geometry is observed at boron; the bond angles at boron are close to trigonal for **1b** (*ca.* 119–122°), but significantly distorted (*ca.* 114–123°) in **1a**. The B–N bond lengths in both **1a** and **1b** are intermediate between a single and double bond as expected for N(2p) → B(2p) π-bonding. Crystallographic analysis of 1,1'-Fc(BBr<sub>2</sub>)<sub>2</sub> has revealed that Lewis acidic ferrocenyl boranes have weak iron–boron interactions resulting in the tilting of the B–C bond towards the metal centre, as indicated by a B–C1–C2–C3 dihedral angle of *ca.* 10°. <sup>21</sup> The amino substituents in **1a** and **1b** significantly decrease the Lewis acidity of the boron centre, reducing this angle to *ca.* 4° in **1a** and even further in **1b** where the boron moiety lies in the plane of the Cp ring. The structural parameters of the 1,1'-diborylated ferrocene **2** are very similar to the analogous mono-borylated derivative **1a**, with no notable differences in B–N bond lengths or angles.

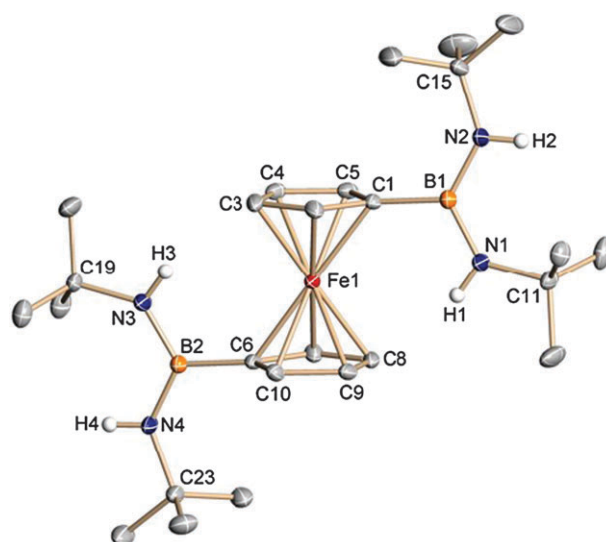


Fig. 2 Molecular structure of 1,1'-Fc{B[N(H)<sup>t</sup>Bu]<sub>2</sub>}<sub>2</sub> (**2**) with hydrogen atoms omitted for clarity, other than those located on the nitrogen atoms. Thermal ellipsoids are shown at 30% probability.

Table 3 Selected bond lengths (Å) and bond angles (°) for **1a**, **1b** and **2**

	<b>1a</b>	<b>1b</b>	<b>2</b>
B1–N1	1.421(6)	1.418(4)	1.415(3)
B1–N2	1.414(7)	1.419(3)	1.413(3)
B2–N3 <sup>a</sup>	1.437(6)	N/A	1.414(3)
B2–N4 <sup>a</sup>	1.394(7)	N/A	1.414(3)
N1–B1–N2	122.5(4)	118.8(2)	122.0(2)
N1–B1–C1	114.8(4)	119.1(2)	116.8(2)
N2–B1–C1	122.6(4)	122.1(2)	121.3(2)
N3–B2–N4 <sup>a</sup>	123.2(4)	N/A	122.2(2)
N3–B2–C19 <sup>a</sup>	114.0(4)	N/A	116.5(2)
N4–B2–C19 <sup>a</sup>	122.7(4)	N/A	121.3(2)

<sup>a</sup> These values correspond to the second molecule in the asymmetric unit of **1a**.

The attempted dilithiation of **1a** with two equivalents of <sup>n</sup>BuLi, which readily deprotonates PhB[N(H)<sup>t</sup>Bu]<sub>2</sub>,<sup>22</sup> in hexanes, toluene or THF was unsuccessful. No reaction was

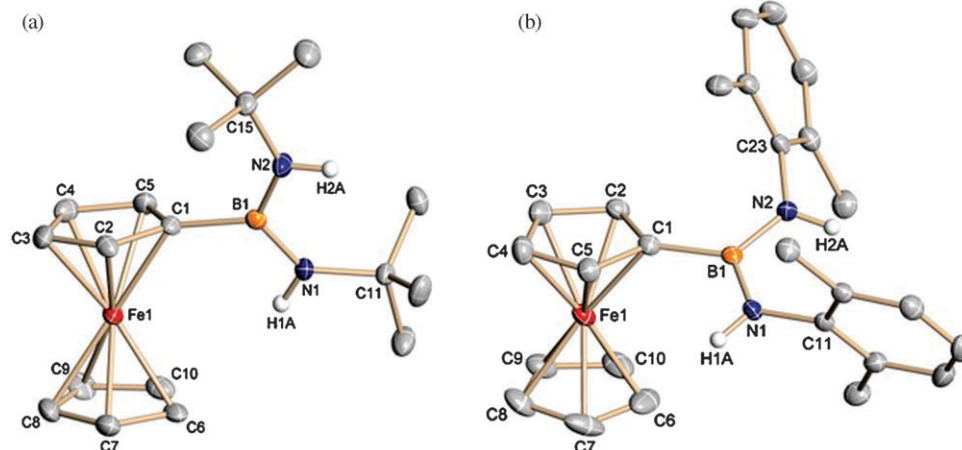


Fig. 1 Molecular structures of FcB[N(H)<sup>t</sup>Bu]<sub>2</sub> (**1a**, left) and FcB[N(H)Dipp]<sub>2</sub> (**1b**, right). For clarity, only H atoms attached to N and α-carbons of Dipp groups are shown. Thermal ellipsoids are shown at 30% probability.

observed even after extended reaction times at elevated temperatures, suggesting that replacement of the Ph substituent by the electron-rich metallocene decreases the acidity of the  $-\text{NH}$  protons to such an extent that  $^n\text{BuLi}$  is insufficient as a metallating reagent. Subsequently, **1a** was treated with the stronger base  $^n\text{BuLi}$ . With this reagent, however, competition between metallation of the  $-\text{NH}^t\text{Bu}$  groups and the Cp ring was indicated by multiple products in the  $^1\text{H}$  NMR spectra.<sup>23</sup> The deprotonation of **1b** with  $[\text{Li}][\text{N}(\text{SiMe}_3)_2]$  was also attempted as this reagent does not react with ferrocene;<sup>24</sup> however, no reaction was observed. Given the difficulties encountered in the attempted deprotonation of **1a** and **1b**, we turned our attention to the use of the phenylene ( $-\text{C}_6\text{H}_4-$ ) group as a linker for bis-*bam* ligands of the type **C**.

### Synthesis, X-ray structure and reactions of $[\text{Li}_4][(\text{N}^t\text{Bu})_2\text{C}_6\text{H}_4\text{B}(\text{N}^t\text{Bu})_2]\cdot 6\text{THF}$ (**4-6THF**)

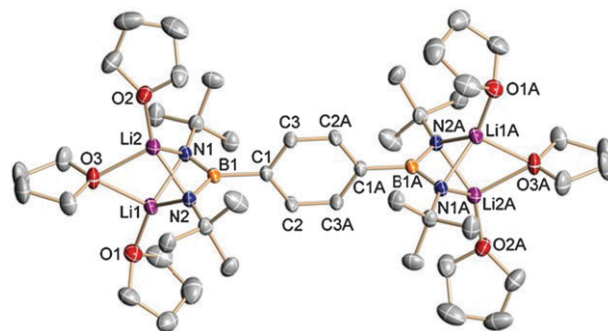
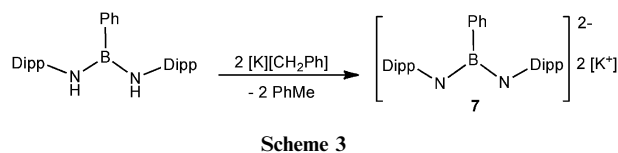
The reaction of 1,4- $\text{Br}_2\text{BC}_6\text{H}_4\text{BBR}_2$ , and five equivalents of  $[\text{Li}][\text{N}(\text{H})^t\text{Bu}]$  in toluene, produces an oil that solidifies overnight at room temperature to give **3** in 75% yield (Scheme 2). If only four equivalents of amide are used, the product **3** is contaminated with minor impurities. The necessity of using an excess of amide has previously been noted in the synthesis of dilithio *bams*;<sup>17,22</sup> any unreacted amide is removed by filtration. Multinuclear NMR spectra and high-resolution mass spectrometric data were consistent with complete replacement of all four Br substituents in 1,4- $\text{Br}_2\text{BC}_6\text{H}_4\text{BBR}_2$  by  $-\text{N}(\text{H})^t\text{Bu}$  groups. The  $^1\text{H}$  NMR spectrum of **3** exhibits singlets at 7.66, 2.88 and 1.16 ppm with relative intensities of 4 : 4 : 36 corresponding to  $\text{C}_6\text{H}_4$ ,  $\text{NH}$  and  $\text{C}(\text{CH}_3)_3$  protons, respectively. A single resonance is observed in the  $^{11}\text{B}$  NMR spectrum at 30 ppm.

Tetra-lithiation of **3** using four equivalents of  $^n\text{BuLi}$  in hexanes results in a colourless precipitate of **4**, the first example of a tetra-lithio bis-boraamidinate (Scheme 2). The molecular structure of **4** is illustrated in Fig. 3 and pertinent bond lengths and angles are found in Table 4, along with those of  $\{\text{Li}_2[\text{PhB}(\text{N}^t\text{Bu})_2]\}_2$  for comparison.

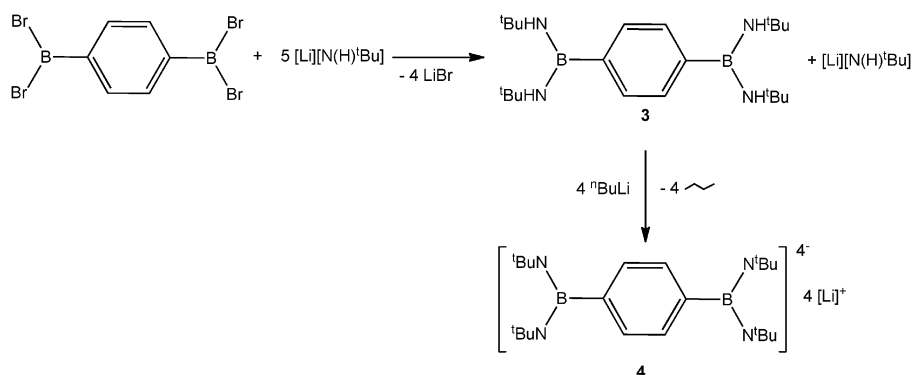
As depicted in Fig. 3, the  $-\text{C}_6\text{H}_4-$  unit of **4-6THF** lies on an inversion centre. The structural parameters involving the boron centres for **4-6THF** are similar to those of the unsolvated complex  $\{\text{Li}_2[\text{PhB}(\text{N}^t\text{Bu})_2]\}_2$ .<sup>22</sup> The geometry about boron is planar, but greatly distorted from trigonal, with bond angles in the range  $109.8$ – $125.5^\circ$ . The B–N bond lengths are

intermediate between a single and double bond, as expected. The arrangement of solvent THF molecules in **4-6THF** (*i.e.* one terminal and one bridging THF per  $\text{Li}^+$  ion) has been observed previously in the mono-*bam* complex  $[\text{Li}(\text{THF})_2(\mu\text{-THF})][\text{PhB}(\text{NDipp})_2]$ .<sup>17</sup> Although the average N–Li distance in both unsolvated  $\{\text{Li}_2[\text{PhB}(\text{N}^t\text{Bu})_2]\}_2$ <sup>22</sup> and highly solvated  $[\text{Li}(\text{THF})_2(\mu\text{-THF})][\text{PhB}(\text{NDipp})_2]$ <sup>17</sup> are nearly identical, the average length of this bond in the bis-*bam* **4-6THF** is approximately  $0.05 \text{ \AA}$  shorter than in either of the mono-*bams*.

The new bis-*bam* reagent **4-6THF** is extremely air-sensitive and rapidly turns pink in solution or in the solid state upon exposure to air, indicative of oxidation to a radical species even in the presence of only trace amounts of oxygen (*i.e.*  $\sim 8 \text{ ppm}$ ). This observation is reminiscent of the behaviour of  $\{\text{Li}_2[\text{PhB}(\text{N}^t\text{Bu})_2]\}_2$ .<sup>6b</sup> In that case, the pink colour was attributed to the  $\text{Li}^+$  derivative of the anion radical  $[\text{PhB}(\text{N}^t\text{Bu})_2]^{\bullet-}$  formed upon one-electron oxidation of the corresponding dianion. This persistent radical is also formed upon treatment of  $\{\text{Li}_2[\text{PhB}(\text{N}^t\text{Bu})_2]\}_2$  with one-half equivalent of  $\text{I}_2$  and it was identified on the basis of a simulation of the



**Fig. 3** Molecular structure of  $[\text{Li}_4][(\text{N}^t\text{Bu})_2\text{C}_6\text{H}_4\text{B}(\text{N}^t\text{Bu})_2]\cdot 6\text{THF}$ , **4-6THF**. Hydrogen atoms omitted for clarity. Symmetry transformations used to generate equivalent atoms:  $-x + 1$ ,  $-y + 1$ ,  $-z$ . Thermal ellipsoids are shown at 30% probability.



**Table 4** Selected bond lengths (Å) and bond angles (°) for **4**·6THF and  $\{\text{Li}_2[\text{PhB}(\text{N}^t\text{Bu})_2]\}_2^a$ 

	<b>4</b>	$\{\text{Li}_2[\text{PhB}(\text{N}^t\text{Bu})_2]\}_2^a$
B1–N1	1.437(3)	1.448(3)
B1–N2	1.442(3)	1.449(3)
Li1–N1	1.970(4)	2.077(4)
Li1–N2	1.992(4)	2.052(4)
Li2–N1	2.013(4)	2.027(4)
Li2–N2	1.989(4)	2.022(4)
N1–B1–N2	109.8(2)	109.5(2)
N1–B1–C1	125.5(2)	124.9(2)
N2–B1–C1	124.8(2)	125.5(1)

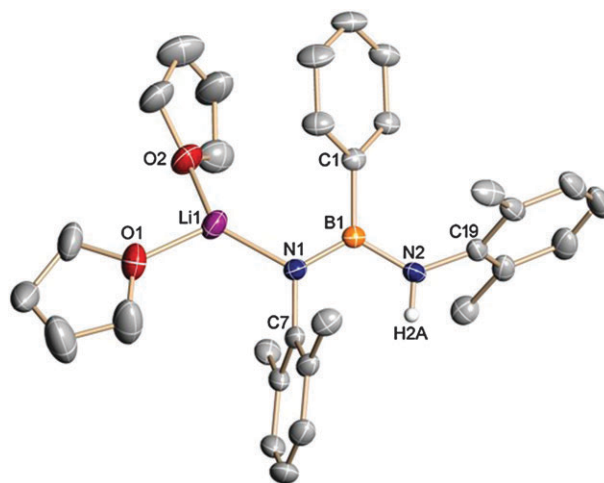
<sup>a</sup> Data taken from ref. 22.

EPR spectrum.<sup>6b</sup> The controlled oxidation of **4**·6THF with one-half equivalent of  $\text{I}_2$  at  $-80^\circ\text{C}$  in THF also generates a pink solution. However, this solution exhibits a very complex EPR spectrum and attempts to simulate it assuming the formation of the expected one-electron oxidation product suggested the presence of more than one radical species, whose identities could not be established. The complexity of the redox behaviour of **4**·6THF presumably results from the presence of more than one redox-active site.

#### Synthesis and spectroscopic characterization of $[\text{M}][\text{PhB}(\text{NDipp})\{\text{N}(\text{H})\text{Dipp}\}]$ (**5**, $\text{M} = \text{Li}$ ; **6**, $\text{M} = \text{K}$ ) and X-ray structure of **5**·2THF

In view of the isoelectronic relationship and similar charges of monoanionic boraamidates of the type  $[\text{bam}(\text{H})]^-$  (**D**) and the corresponding amidinates (**B**), we have developed efficient syntheses of alkali-metal derivatives of this new class of ligand. The equimolar reaction of  $\text{PhB}[\text{N}(\text{H})\text{Dipp}]_2$  with  $^n\text{BuLi}$  in hexanes proceeds cleanly to give  $[\text{Li}][\text{PhB}(\text{NDipp})\{\text{N}(\text{H})\text{Dipp}\}]$  (**5**), in *ca.* 90% yield. The  $^1\text{H}$  NMR spectrum of **5** is consistent with a mono-lithiated derivative. In addition to aryl resonances that integrate to the expected values, there are two septets integrating to 2H each (attributed to  $\text{CH}(\text{CH}_3)_2$  protons), a broad singlet assigned to the remaining  $-\text{NH}$  group and three methyl resonances with relative intensities of 6 : 6 : 12 ( $\text{CH}(\text{CH}_3)_2$  protons). The  $^{11}\text{B}$  and  $^7\text{Li}$  NMR spectra exhibit single resonances at 26.4 and 0.23 ppm, respectively. X-Ray quality crystals of **5**·2THF were obtained from a concentrated THF/hexane solution cooled to *ca.*  $-18^\circ\text{C}$  and the molecular structure is illustrated in Fig. 4. Selected bond lengths and angles are compared with those of  $\text{PhB}[\text{N}(\text{H})\text{Dipp}]_2$  ( $^{\text{Dipp}}\text{bamH}_2$ ) and  $[\text{Li}_2(\text{THF})_3][\text{PhB}(\text{NDipp})_2]$  in Table 5.

The molecular structure of **5**·2THF is comprised of the monoanionic  $[\text{Dipp}^-\text{bamH}]^-$  ligand bonded in an *N*-monodentate fashion to the lithium cation, which is solvated by two THF molecules. Monodentate structures of lithium amidinates are known, however they contain even bulkier groups on nitrogen, such as substituted terphenyls.<sup>25,26</sup> Two notable examples for direct comparison with **5**·2THF are lithium formamidinate  $[\text{Li}(\text{THF})_2][\text{HC}(\text{NDipp})_2]$ <sup>27</sup> and lithium amidinate  $[\text{Li}(\text{THF})_2][p\text{-TolC}(\text{NDipp})_2]$ <sup>28</sup> ( $\text{Tol} = -\text{C}_6\text{H}_4\text{Me}$ ), in which the lithium ion interacts with both nitrogen atoms. In the formamidinate, however, monodentate structures were obtained when the THF molecules coordinated to the lithium cation were replaced with TMEDA.<sup>29</sup> The most notable

**Fig. 4** Molecular structure of  $[\text{Li}(\text{THF})_2][\text{PhB}(\text{NDipp})\{\text{N}(\text{H})\text{Dipp}\}]$ , **5**·2THF. For clarity, hydrogen atoms on carbon atoms have been omitted and only  $\alpha$ -carbons of Dipp groups shown. Thermal ellipsoids are shown at 30% probability.**Table 5** Selected bond lengths (Å) and bond angles (°) for **5**·2THF,  $^{\text{Dipp}}\text{bamH}_2$  and  $[\text{Li}_2(\text{THF})_3][^{\text{Dipp}}\text{bam}]$ 

	<b>5</b> ·2THF	$^{\text{Dipp}}\text{bamH}_2^a$	$[\text{Li}_2(\text{THF})_3][^{\text{Dipp}}\text{bam}]^a$
B1–N1	1.396(4)	1.420(3)	1.415(5)
B1–N2	1.448(4)	1.414(3)	1.446(4)
N1–Li1	1.908(5)	N/A	2.022(6)
N2–Li2	N/A	N/A	2.049(7)
N1–B1–N2	121.1(2)	118.5(2)	111.4(3)
N1–B1–C1	119.1(2)	118.7(2)	125.2(3)
N2–B1–C1	119.7(2)	122.8(2)	122.9(3)
B1–N1–C7	120.0(2)	124.6(2)	130.4(3)
B1–N1–Li1	120.0(2)	N/A	83.7(3)
C7–N1–Li1	119.1(2)	N/A	135.5(3)
C19–N2–B1	130.2(2)	128.0(2)	126.4(3)
C19–N2–Li2	N/A	N/A	124.4(3)
B1–N2–Li2	N/A	N/A	79.2(2)
N1–Li1–O1	121.1(3)	N/A	163.0(4)
N1–Li1–O2	131.3(3)	N/A	87.6(2)
O1–Li1–O2	104.3(3)	N/A	98.6(3)

<sup>a</sup> Data taken from ref. 17.

structural differences between **5**·2THF and  $[\text{Li}_2(\text{THF})_3][^{\text{Dipp}}\text{bam}]$ <sup>17</sup> are the coordination numbers of the anionic nitrogen and the lithium centres, which are both three-coordinate in the former but four-coordinate in the latter. The nitrogen atoms interact with both lithium centres in  $[\text{Li}_2(\text{THF})_3][^{\text{Dipp}}\text{bam}]$ , while the coordination sphere of the lithium cations is completed by two THF molecules (one terminal and one bridging THF) in **5**·2THF.

The geometry about B1 in **5**·2THF is trigonal planar (bond angles are *ca.*  $119$ – $121^\circ$ ), *cf.*  $118.5$ – $123^\circ$  for  $^{\text{Dipp}}\text{bamH}_2$ , and *ca.*  $111$ – $125^\circ$  in  $[\text{Li}_2(\text{THF})_3][^{\text{Dipp}}\text{bam}]$ .<sup>17</sup> The geometry about N1 is also planar. The B1–N1 distance is shorter than B1–N2 by *ca.*  $0.05$  Å. There is a slight elongation of the B–N bond distance of the protonated nitrogen atom in **5**·2THF when compared to that in  $^{\text{Dipp}}\text{bamH}_2$ . There is no significant difference between the B–N bond lengths in **5**·2THF and  $[\text{Li}_2(\text{THF})_3][^{\text{Dipp}}\text{bam}]$ , however, the N1–Li bond length is

ca. 0.13 Å shorter in the monolithiated [<sup>Dipp</sup>bamH]<sup>−</sup> than the average value in the dilithiated [<sup>Dipp</sup>bam]<sup>2−</sup>.

The mono-potassiated derivative, [K][PhB(NDipp){N(H)Dipp}] (**6**), was prepared in 82% yield from the 1 : 1 reaction of <sup>Dipp</sup>bamH<sub>2</sub> and benzylpotassium in THF. The deep red colour of [K][CH<sub>2</sub>Ph] is immediately consumed upon addition to <sup>Dipp</sup>bamH<sub>2</sub>, yielding a golden solution; potassium hexamethyldisilazide (KHMDs) can also be used as the deprotonating reagent. Numerous attempts to obtain X-ray quality crystals from the resulting pale yellow solid failed and, instead, only an amorphous powder precipitated from solution. However, <sup>1</sup>H NMR data are consistent with the formation of the mono-potassiated derivative; aryl resonances integrating to 11H, overlapping septets integrating to 4H, a 1H singlet for the remaining −NH proton and two doublets (6 : 18 relative intensities) for the methyl protons of the isopropyl groups are observed. The <sup>11</sup>B NMR spectrum displays a single resonance at 24.9 ppm, which is shifted upfield from <sup>Dipp</sup>bamH<sub>2</sub> (<sup>11</sup>B δ 29 ppm).<sup>17</sup>

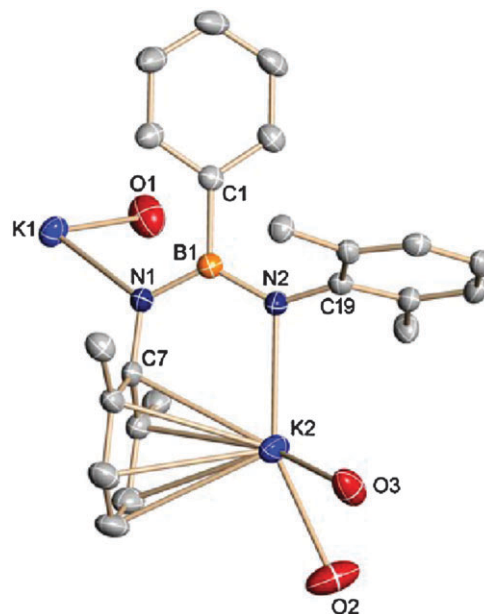
### Synthesis, spectroscopic characterization and X-ray structure of [K<sub>2</sub>(THF)<sub>3</sub>][PhB(NDipp)<sub>2</sub>], 7·3THF

The metathetical chemistry of *bam* ligands has primarily been based on dilithiated reagents.<sup>1</sup> However, lithium halides are difficult to separate from the main products of these reactions and, in some cases, they become incorporated in the products.<sup>5,9</sup> These difficulties provided the incentive for the synthesis of the first dipotassiated derivative of a *bam* ligand.

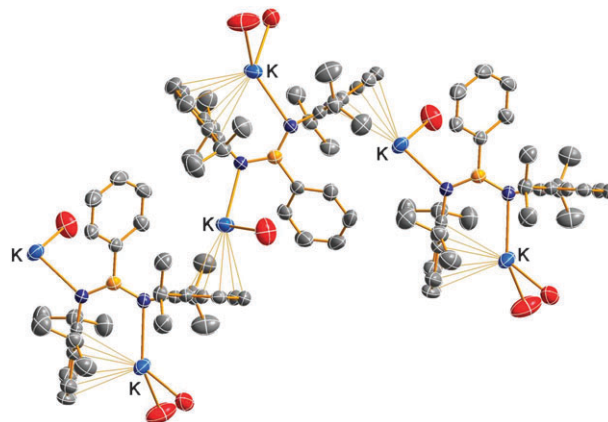
The reagents KH, [K][HMDs] and [K][CH<sub>2</sub>Ph] were evaluated as a base for the deprotonation of <sup>Dipp</sup>bamH<sub>2</sub>. Potassium hydride was unreactive, while [K][HMDs] gave only the mono-potassiated derivative, **6**. However, benzylpotassium proved to be effective, producing [K<sub>2</sub>][PhB(NDipp)<sub>2</sub>] (**7**) in ca. 90% yield as a yellow solid, which is soluble in THF and to a lesser extent in toluene, but insoluble in hexanes and Et<sub>2</sub>O (Scheme 3). The <sup>1</sup>H NMR spectrum of this solid is consistent with double deprotonation and only one resonance is observed in the <sup>11</sup>B NMR spectrum at 24.2 ppm. X-Ray quality crystals of 7·3THF were obtained by cooling a concentrated solution of **7** in a mixture of THF and either hexanes or toluene. The molecular structure of 7·3THF is shown in Fig. 5, the extended structure is illustrated in Fig. 6, and selected structural parameters are presented in Table 6.

Although three molecules of THF are incorporated into the structure of **7** during crystallization, the <sup>1</sup>H NMR spectrum of the crude product suggests that the potassium cations are not solvated; however, attempts to crystallize **7** in the absence of THF were unsuccessful. A similar observation has been made in the preparation of [K][N(H)Trip] (Trip = 2,6-(2,4,6-*i*Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), for which no solvation of the potassium cation was observed in the crude material (by <sup>1</sup>H NMR and elemental analysis) although the reaction was carried out in THF.<sup>30</sup>

In the solid state, 7·3THF forms an extended structure resulting from arene–metal interactions. The potassium cation is coordinated in an η<sup>1</sup>-amide–η<sup>6</sup>-arene fashion, similar to the bonding mode observed for potassium formamidinates [K][HC(NMes<sub>2</sub>){HC(NMes<sub>2</sub>)H}]<sup>31</sup> and {K[HC(NDipp)<sub>2</sub>]<sub>2</sub>·K(THF)<sub>2</sub>}<sub>n</sub><sup>32</sup> (Mes = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) as well as for the potassium



**Fig. 5** Crystal structure of a discrete [K<sub>2</sub>(THF)<sub>3</sub>][PhB(NDipp)<sub>2</sub>] unit (7·3THF). For clarity, all hydrogen atoms and carbon atoms of THF solvent molecules have been omitted and only α-carbon atoms on Dipp groups are shown. Thermal ellipsoids are shown at 30% probability. Symmetry elements used to generate equivalent atoms:  $-x, y + \frac{1}{2}, -z + \frac{1}{2}$ ;  $-x, y - \frac{1}{2}, -z + \frac{1}{2}$ .



**Fig. 6** Representation of the extended solid-state structure of [K<sub>2</sub>(THF)<sub>3</sub>][PhB(NDipp)<sub>2</sub>] (7·3THF). For clarity all hydrogen atoms and selected carbon atoms have been omitted. Thermal ellipsoids are shown at 30% probability.

**Table 6** Selected bond lengths (Å) and bond angles (°) for 7·3THF

B1–N1	1.407(5)	N1–B1–N2	124.7(4)
B1–N2	1.422(5)	N1–B1–C1	116.3(3)
N1–K1	2.673(3)	N2–B1–C1	119.0(4)
N2–K2	2.709(3)	C7–N1–B1	121.6(3)
K1–centroid	2.905(3)	C7–N1–K1	118.8(2)
K2–centroid	2.834 (3)	B1–N1–K1	115.4(3)
K1–O1	2.773(4)	C19–N2–B1	134.2(3)
K2–O2	2.704(4)	C19–N2–K2	101.1(2)
K2–O3	2.655(4)	B1–N2–K2	119.8(2)

amidinate [K][PhC(NSiMe<sub>3</sub>)(NDipp)].<sup>33</sup> The potassium–nitrogen bond distances are comparable to that found in



[K][HC(NMes<sub>2</sub>)] (2.719(1) Å).<sup>31</sup> The K(1)–centroid and K(2)–centroid contacts of 2.905(3) and 2.834(3) Å, respectively, are similar to the values reported for [K][HC(NMes<sub>2</sub>){HC(NMes<sub>2</sub>H)}] and [K][PhC(NSiMe<sub>3</sub>)(NDipp)].<sup>31</sup> The potassium ions K(1)<sup>+</sup> and K(2)<sup>+</sup> are solvated by one or two THF molecules, respectively.

The distorted trigonal planar geometry about boron is similar to that of the boron atom in [Li<sub>2</sub>(THF)<sub>3</sub>][PhB(NDipp)<sub>2</sub>].<sup>17</sup> However, since the nitrogen atoms only interact with a single potassium cation, their geometry differs significantly from that of the dilithiated analogue, in which the nitrogen atoms are a part of two puckered four-membered rings with the boron centre and a lithium atom.<sup>17</sup> Both nitrogen atoms in 7·3THF have bond angles that deviate substantially from trigonal geometry, *ca.* 115–121° for N1 and 101–134° for N2.

## Conclusions

We have described the syntheses and structures of several new reagents that will be useful in the future development of the chemistry of *bams*. These include the bis-[di-(*tert*-butylamino)-boranes] 1,1'-Fc{B[N(H)<sup>t</sup>Bu]<sub>2</sub>}<sub>2</sub> and [N(H)<sup>t</sup>Bu]<sub>2</sub>BC<sub>6</sub>H<sub>4</sub>B[N(H)<sup>t</sup>Bu]<sub>2</sub> as well as the extremely air-sensitive tetralithio derivative of the latter. Efficient syntheses of alkali-metal derivatives of the monoanion [PhB(NDipp){N(H)Dipp}]<sup>−</sup> and the first dipotassium salt of a *bam* [K<sub>2</sub>][PhB(NDipp)<sub>2</sub>] are also reported. In the [Li(THF)<sub>2</sub>]<sup>+</sup> derivative the <sup>Dipp</sup>*bam*H<sup>−</sup> ligand forms an *N*-monodentate complex with the cation, while the <sup>Dipp</sup>*bam*<sup>2−</sup> dianion in the dipotassium salt forms an extended structure via η<sup>1</sup>-amide–η<sup>6</sup>-arene coordination to the cations. Main group, transition-metal and lanthanide complexes of the monoanionic *bam* ligand will be of especial interest in comparison with the well-studied chemistry of isoelectronic amidinate analogues. The dipotassium reagent will be advantageous compared to dilithium derivatives in metathetical reactions with element halides.

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