

# Primary amido substituted diborane(4) compounds and imidodiborate(4) anions

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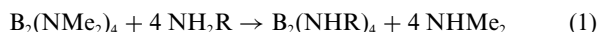
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Treatment of the diborane(4) compound  $B_2(NMe_2)_4$  with aniline or 2,6-dimethylaniline results in the primary amido compounds  $B_2(NHR)_4$  ( $R = Ph, 2,6-Me_2C_6H_3$ ); subsequent treatment with  $n-BuLi$  in toluene in each case affords the first examples of anionic imidodiborates namely  $Li_4(thf)_6B_2(NPh)_4$  and  $Li_4(thf)_6B_2(N-2,6-Me_2C_6H_3)_4$ ; all complexes have been characterised crystallographically.

Tetra-amido substituted diborane(4) compounds,  $B_2(NR_2)_4$ , are important precursors for diborane(4) chemistry in general particularly the dimethylamido species  $B_2(NMe_2)_4$  (**1**).<sup>1</sup> Compound **1** has been structurally characterised by electron diffraction and important dimensions for other structurally characterised  $B_2N_4$  compounds are listed in Table 1.

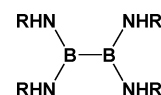
Of note are the conformations about the B–B bonds ( $\tau$  in Table 1) which range from about 55 to 90°, 90° being completely staggered, presumably for steric reasons. Synthetic routes to  $B_2(NR_2)_4$  compounds are of two main types involving either reductive coupling of  $BX(NR_2)_2$  ( $X = \text{halide}$ ) precursors or transamination reactions starting with compound **1**.<sup>1a–c,5</sup> Transamination reactions provide the best access to primary amido substituted compounds of the type  $B_2(NHR)_4$  although few examples, e.g.  $R = Me, n\text{-hexyl}$  and  $Ph$ , have been well characterised.<sup>1a</sup> Such species are nevertheless interesting as they offer potential routes to imidodiborate(4) anions and condensed species (ultimately BNR) as a result of amine elimination. Herein we describe the synthesis and structural characterisation of  $B_2(NHR)_4$  (**2**,  $R = Ph$ ; **3**,  $R = 2,6-Me_2C_6H_3$ ; **4**,  $R = 4-IC_6H_4$ ; **5**,  $R = \text{benzyl}$ ) together with the results of deprotonation of **2** and **3**.

Compounds **2–5** (Scheme 1) were prepared from **1** and the corresponding amine according to eqn (1)



as colourless crystalline solids in high to moderate recrystallised yields.<sup>†</sup>

Reactions with  $NH_2Bu^i$  and  $NH_2-2,6-Pr^i_2C_6H_3$  afforded mixtures of partially substituted species  $B_2(NMe_2)_x(NHR)_{4-x}$  ( $R = Bu^i, 2,6-Pr^i_2C_6H_3$ ).<sup>‡</sup> The structures of **2** and **3** were determined by X-ray crystallography and a view of compound **3** is shown



Scheme 1 **2**,  $R = Ph$ ; **3**,  $R = 2,6-Me_2C_6H_3$ ; **4**,  $R = 4-IC_6H_4$ ; **5**,  $R = \text{benzyl}$ .

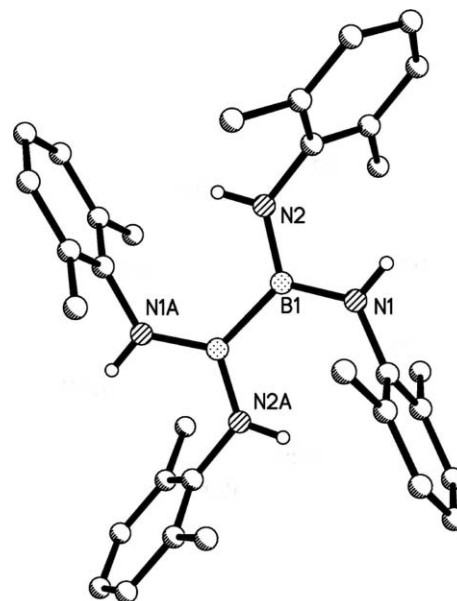


Fig. 1 A view of the molecular structure of compound **3**. Selected bond distances (Å) and angles (°) include: B(1)–B(1A) 1.732(4), B(1)–N(1) 1.420(2), B(1)–N(2) 1.431(2); N(1)–B(1)–N(2) 116.32(15).

in Fig. 1. § Compound **2** contains two crystallographically independent molecules for which the B–B distances are 1.709(3) and 1.713(3) Å whilst molecules of **3** reside on a crystallographic  $C_2$  axis, the B–B distance being 1.732(4) Å. These B–B bond lengths are comparable to those in related compounds (Table 1) but more noteworthy are the angles  $\tau$  which for **2** are 64.0° [B(1)/B(2)] and 64.5° [B(3)/B(4)] and for **3** is 17.8°. Thus whilst

Table 1 Selected data for structurally characterised  $B_2(NR_2)_4$  compounds

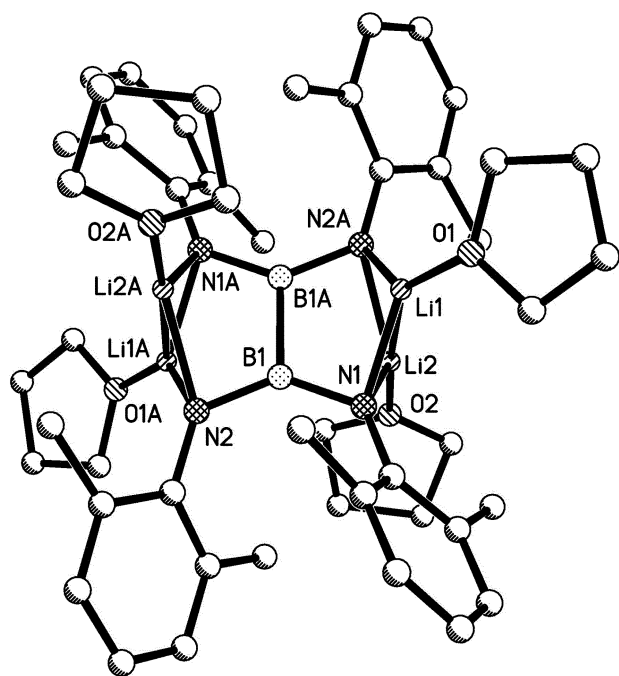
Compound	$\tau^a / ^\circ$	B–B/Å	Ref.
$B_2(NMe_2)_4$	90	1.762(11)	2
$B_2\{N(Me)CH_2CH_2N(Me)\}_2$	61.6, 56.8	1.690(9), 1.696(9)	3
$B_2\{N(Cy)CH_2CH_2N(Cy)\}_2$	80.7	1.721(12)	4
$B_2(\text{piperidinyl})_4$	73.5	1.750(8)	5
$B_2(\text{pyrrolidino})_4$	76.4	1.739(4)	6
$1,2-B_2(NMe_2)_2(\text{pyrrolyl})_2$	73	1.718(2)	7
$1,2-B_2(NMe_2)_2(\text{indolyl})_2$	57	1.723(4)	7
$[B_2\{N(Me)CH_2CH_2N(Me)\}_2\{GaCl_3\}]$	72.8	1.705(23)	8

<sup>a</sup>  $\tau$  is defined as the angle between the  $N_2B$  planes.

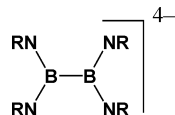
the values of  $\tau$  for **2** are similar to previously observed values (Table 1), the angle for **3** reveals a structure that is, uniquely, much closer to being eclipsed (as opposed to staggered).

Treatment of **2** or **3** in toluene with four equivalents of *n*-BuLi revealed a broadening of the  $^{11}\text{B}$  NMR resonance and a slight up-field chemical shift change to  $\delta$  31.2 and 28.8 ppm respectively as well as the appearance of some minor peaks in the region associated with four-coordinate boron centres.

After work up and recrystallisation from thf (tetrahydrofuran), crystalline samples of salts containing the imidodiborate(4) anions, namely  $\text{Li}_4(\text{thf})_6\text{B}_2(\text{NPh})_4$  (**6**) and  $\text{Li}_4(\text{thf})_4\text{B}_2(\text{N}-2,6\text{-Me}_2\text{C}_6\text{H}_3)_4$  (**7**)<sup>¶</sup> (Scheme 2) were isolated both of which were characterised by X-ray crystallography;\* the structure of **7** is shown in Fig. 2. Both structures are very similar consisting of a tetra-imidodiborate tetra-anion with the four Li centres complexing pairs of imido arms and being additionally solvated by thf molecules. To our knowledge **6** and **7** are the first structurally characterised examples not only of imidodiborate(4) anions but also from the family of imido analogues of p-block oxoanions in which an element–element bond is present in the central unit.<sup>9</sup>



**Fig. 2** A view of the molecular structure of compound **7**. Selected bond distances (Å) and angles (°) include: B(1)–B(1A) 1.814(4), B(1)–N(1) 1.442(2), B(1)–N(2) 1.445(2), Li(1)–N(1) 1.963(3), Li(1)–N(2A) 1.963(3), Li(2)–N(1) 2.054(3), Li(2)–N(2A) 2.057(3); N(1)–B(1)–N(2) 133.96(16).



**Scheme 2** **6**, R = Ph; **7**, R = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>.

In the unit cells of **6** and **7** the imidodiborate(4) tetra-anion lies on a crystallographic centre of inversion such that the B<sub>2</sub>N<sub>4</sub> units are strictly planar (*i.e.*  $\tau = 0^\circ$ ). The B–B distances (**6**, 1.781(4) Å and **7**, 1.814(4) Å) are significantly longer (> 0.05 Å) than the corresponding distances in **2** and **3** as are the B–N distances albeit to a lesser degree (> 0.02 Å, see Fig. captions). Furthermore, the N–B–N angles in **6** [133.24(16)°] and **7** [133.96(16)°] are considerably enlarged relative to the corresponding angles in **2** [113.11(19), 112.87(18), 112.15(17), 113.30(17)°] and **3** [116.32(15)°]. The most likely explanation for these features lies

in the presence of the ion-contacted lithium atoms which bridge the imido nitrogen centres in a 1,2-fashion above and below the B<sub>2</sub>N<sub>4</sub> plane in both imidodiborate structures thereby increasing the N–B–N angles with a consequent lengthening of the B–B bond. In **6** a total of six thf molecules are coordinated to the four lithium centres whereas for **7** it is only four presumably as a result of the larger steric bulk of the aryl group in the latter.

We note that there is apparently very little previous work on the deprotonation of primary amido diborane(4) compounds although a recent study by Patton and co-workers<sup>10</sup> has explored the use of the dianions  $[\text{B}_2(\text{NMe}_2)_2(\text{NR})_2]^{2-}$ , derived from  $\text{B}_2(\text{NMe}_2)_2(\text{NHR})_2$  (R = 2,6-disubstituted aryl), as ligands towards early transition metal centres. We note also the related work of Power<sup>11</sup> and Nöth<sup>7</sup> on the reduction of  $\text{B}_2\text{Ph}_2(\text{NMe}_2)_2$  and  $\text{B}_2(\text{NMe}_2)_2(\text{NR})_2$  respectively affording the corresponding di-anions, an example being  $[\text{Li}(\text{Et}_2\text{O})][\text{B}_2(\text{NMe}_2)_2(\text{pyrrolyl})_2]^{2-}$ ,<sup>7</sup> featuring B=B double bonding. It is noteworthy in the examples described by Nöth that on reduction, and compared to their neutral precursors, B–N bond distances get longer and the B<sub>2</sub>N<sub>4</sub> units become planar, as seen for **6** and **7**, whereas the B–B bonds get shorter and N–B–N angles decrease slightly. Finally we note the work on the formation of the related imidoborate anions  $[\text{B}(\text{NR})_3]^{3-}$  reported by Russell<sup>12</sup> and Nöth<sup>13</sup> which represent imido analogues of the borate  $\text{BO}_3^{3-}$ , and note also that the oxo-anion related to **6/7**, *i.e.*  $\text{B}_2\text{O}_4^{4-}$  is not currently known.

## Acknowledgements

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## Notes and references

<sup>†</sup> In a typical reaction, a solution of  $\text{B}_2(\text{NMe}_2)_4$  (0.396 g, 2.0 mmol) and aniline (0.920 g, 9.9 mmol) in toluene (20 cm<sup>3</sup>) were refluxed under dinitrogen for 24 h. White crystals formed on cooling which were recrystallised from hexane/thf mixtures affording colourless crystals of  $\text{B}_2(\text{NHPH})_4$  (**2**) (93%). NMR (toluene, ppm):  $^{11}\text{B}$   $\delta$  33.7;  $^1\text{H}$   $\delta$  7.02 (m, 20H, Ph), 0.28 (s, 4H, NH). IR (solid)  $\nu(\text{N-H})$  3358 cm<sup>-1</sup>. MS(EI)  $m/z$  390.  $\text{C}_{24}\text{H}_{24}\text{B}_2\text{N}_4$  requires C, 73.90; H, 6.20; N, 14.35; found C, 73.90, H, 6.40; N, 14.30%. Data for **3**: 80%.  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , ppm)  $\delta$  29.7. IR (solid)  $\nu(\text{N-H})$  3395, 3330 cm<sup>-1</sup>. HRMS(EI)  $m/z$  502.34391 (calc. 502.32440).  $\text{C}_{32}\text{H}_{40}\text{B}_2\text{N}_4$  requires C, 76.50; H, 8.05; N, 11.15; found C, 72.90, H, 8.10; N, 10.60%. Data for **4**: 46%.  $^{11}\text{B}$  NMR (toluene, ppm)  $\delta$  32.4. IR (solid)  $\nu(\text{N-H})$  3343 cm<sup>-1</sup>. MS(EI)  $m/z$  894.  $\text{C}_{24}\text{H}_{20}\text{B}_2\text{N}_4\text{I}_4$  requires C, 32.25; H, 2.25; N, 6.25; found C, 33.00, H, 3.60; N, 7.05%. Data for **5**: 80%.  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , ppm)  $\delta$  33.1. IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu(\text{N-H})$  3441, 3392 cm<sup>-1</sup>. HRMS(EI)  $m/z$  446.28131 (calc. 446.21604).  $\text{C}_{28}\text{H}_{32}\text{B}_2\text{N}_4$  requires C, 75.35; H, 7.20; N, 12.55; found C, 75.20, H, 7.55; N, 12.50%.

<sup>‡</sup> The structure of  $\text{B}_2(\text{NMe}_2)(\text{NH}-2,6\text{-Pr}^i_2\text{C}_6\text{H}_3)_3$  was confirmed by X-ray crystallography, details of which will be reported in a future publication; C. Feng, unpublished results.

<sup>§</sup> Crystal data for **2**:  $\text{C}_{24}\text{H}_{24}\text{B}_2\text{N}_4$ ,  $M = 390.09$ , triclinic, space group  $P\bar{1}$ ,  $a = 11.484(11)$ ,  $b = 11.494(9)$ ,  $c = 15.965(12)$  Å,  $\alpha = 83.96(4)$ ,  $\beta = 75.16(4)$ ,  $\gamma = 89.92(5)^\circ$ ,  $U = 2025(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.279$  Mg m<sup>-3</sup>,  $\lambda = 0.71073$  Å,  $\mu(\text{Mo-K}\alpha) = 0.582$  mm<sup>-1</sup>,  $F(000) = 824$ ,  $T = 100(2)$  K,  $R_1 = 0.0421$  [for 4711 reflections with  $I > 2\sigma(I)$ ].<sup>14–17</sup> Crystal data for **3**:  $\text{C}_{32}\text{H}_{40}\text{B}_2\text{N}_4$ ,  $M = 502.30$ , orthorhombic, space group  $Pccn$ ,  $a = 19.740(4)$ ,  $b = 8.8681(18)$ ,  $c = 16.550(3)$  Å,  $U = 2897.1(10)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.152$  Mg m<sup>-3</sup>,  $\lambda = 0.71073$  Å,  $\mu(\text{Mo-K}\alpha) = 0.067$  mm<sup>-1</sup>,  $F(000) = 1080$ ,  $T = 293(2)$  K,  $R_1 = 0.0545$  [for 2499 reflections with  $I > 2\sigma(I)$ ].<sup>14–17</sup>

<sup>¶</sup> To a cooled (–78 °C) solution of **2** (0.262 g, 0.7 mmol) in toluene (15 cm<sup>3</sup>), *n*-BuLi (1.7 cm<sup>3</sup> of a 1.6 M solution, 2.7 mmol) was added and the resulting pale yellow coloured solution allowed to warm to room temperature with stirring. After 40 min, the reaction mixture was brought briefly to reflux and then left to stir for 3 h. Removal of the toluene afforded a yellow powder which was recrystallised from cooled thf solutions affording **6** as colourless crystals. Compound **7** was prepared in an analogous fashion from **3**. Isolated crystalline yields of both **6** and **7** were low preventing satisfactory elemental analytical data from being obtained although monitoring of both reactions by  $^{11}\text{B}$  NMR revealed little in the way of side products.

\* Crystal data for **6**:  $\text{C}_{48}\text{H}_{68}\text{B}_2\text{Li}_4\text{N}_4\text{O}_6$ ,  $M = 846.44$ , orthorhombic, space group  $Phca$ ,  $a = 17.9789(4)$ ,  $b = 13.8833(6)$ ,  $c = 19.6293(9)$  Å,

$U = 4899.6(4) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_c = 1.147 \text{ Mg m}^{-3}$ ,  $\lambda = 0.71073 \text{ \AA}$ ,  $\mu(\text{Mo-K}\alpha) = 0.073 \text{ mm}^{-1}$ ,  $F(000) = 1816$ ,  $T = 172(2) \text{ K}$ ,  $R1 = 0.0525$  [for 3436 reflections with  $I > 2\sigma(I)$ ].<sup>14–17</sup> All three independent thf molecules are disordered and were modelled for two positions for each molecule of thf. The site occupancy factor for each part was refined using free variables such that the total SOF for each molecule is equal to one. The % occupancy for thf molecules containing O1, O2 and O3 was 51/49, 64/36 and 53/47% respectively. Crystal data for **7**:  $\text{C}_{48}\text{H}_{68}\text{B}_2\text{Li}_4\text{N}_4\text{O}_4$ ,  $M = 814.44$ , orthorhombic, space group  $Pbca$ ,  $a = 16.9600(9)$ ,  $b = 15.0470(8)$ ,  $c = 18.4848(10) \text{ \AA}$ ,  $U = 4717.3(4) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_c = 1.147 \text{ Mg m}^{-3}$ ,  $\lambda = 0.71073 \text{ \AA}$ ,  $\mu(\text{Mo-K}\alpha) = 0.070 \text{ mm}^{-1}$ ,  $F(000) = 1752$ ,  $T = 173(2) \text{ K}$ ,  $R1 = 0.0516$  [for 3535 reflections with  $I > 2\sigma(I)$ ].<sup>14–17</sup> The thf molecule containing O1 is disordered and was modelled for two positions. The site occupancy factor for each part was refined using free variables such that the total SOF is equal to one. The % occupancy was 41% vs. 59%. CCDC reference numbers 277645–277648. See <http://dx.doi.org/10.1039/b509653g> for crystallographic data in CIF or other electronic format.

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