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


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Treatment of the diborane(4) compound B₂(NMe₂)₄ with aniline or 2,6-dimethylaniline results in the primary amido compounds B₂(NHR)₄ (R = Ph, 2,6-Me₂C₆H₃); subsequent treatment with n-BuLi in toluene in each case affords the first examples of anionic imidodiborates namely Li₄(thf)₆B₂(NPh)₄ and Li₄(thf)₄B₂(N-2,6-Me₂C₆H₃)₄; all complexes have been characterised crystallographically.

Tetra-amido substituted diborane(4) compounds, B₂(NR₂)₄, are important precursors for diborane(4) chemistry in general particularly the dimethylamido species B₂(NMe₂)₄.¹ Compound 1 has been structurally characterised by electron diffraction and important dimensions for other structurally characterised B₂N₄ compounds are listed in Table 1.

Of note are the conformations about the B–B bonds (τ in Table 1) which range from about 55 to 90°, 90° being completely staggered, presumably for steric reasons. Synthetic routes to B₂(NR₂)₄ compounds are of two main types involving either reductive coupling of BX(NR₂)₂ (X = halide) precursors or transamination reactions starting with compound 1.¹⁰-¹⁵ Transamination reactions provide the best access to primary amido substituted compounds of the type B₂(NHR)₄ although few examples, e.g. R = Me, n-hexyl and Ph, have been well characterised.¹⁶ 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 B₂(NH₂Bu)₄ (2, R = Ph; 3, R = 2,6-Me₂C₆H₃; 4, R = 4-IC₆H₄; 5, R = 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)

\[
B₂(NMe₂)₄ + 4 NH₂R \rightarrow B₂(NHR)₄ + 4 NHMe₂
\]

as colourless crystalline solids in high to moderate recrystallised yields.†

Reactions with NH₂Bu⁺ and NH₂-2,6-Pr₂C₆H₄ afforded mixtures of partially substituted species B₂(NMe₂)₄(NHR)₄ (R = Bu⁺, 2,6-Pr₂C₆H₄)‡ The structures of 2 and 3 were determined by X-ray crystallography and a view of compound 3 is shown in Fig. 1.

Table 1 Selected data for structurally characterised B₂(NR₂)₄ compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>τ°</th>
<th>B–B/Å</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>B₂(NMe₂)₄</td>
<td>90</td>
<td>1.762(11)</td>
<td>2</td>
</tr>
<tr>
<td>B₂[Ni(MeCH₂CH₂N(Me)]</td>
<td>61.6, 56.8</td>
<td>1.690(9), 1.696(9)</td>
<td>3</td>
</tr>
<tr>
<td>B₂[Ni(Cy)CH₂CH₂N(Cy)]</td>
<td>80.7</td>
<td>1.721(12)</td>
<td>4</td>
</tr>
<tr>
<td>B₂(piperidinyl)₂</td>
<td>73.5</td>
<td>1.750(8)</td>
<td>5</td>
</tr>
<tr>
<td>B₂(pyroldinyl)₂</td>
<td>76.4</td>
<td>1.739(4)</td>
<td>6</td>
</tr>
<tr>
<td>1,2-B₂(NMe₂)₂(pyroldinyl)₂</td>
<td>73</td>
<td>1.718(2)</td>
<td>7</td>
</tr>
<tr>
<td>1,2-B₂(NMe₂)₂(indolyl)₂</td>
<td>57</td>
<td>1.723(4)</td>
<td>7</td>
</tr>
<tr>
<td>[B₂[Ni(MeCH₂CH₂N(Me)]₂[GaCl₄]]</td>
<td>72.8</td>
<td>1.705(23)</td>
<td>8</td>
</tr>
</tbody>
</table>

* τ is defined as the angle between the N,B planes.

Scheme 1 2, R = Ph; 3, R = 2,6-Me₂C₆H₃; 4, R = 4-IC₆H₄; 5, R = benzyl.

In Fig. 1, Compounds 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 C₂ 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 τ 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

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) 1.690(9), B(1)–N(1A) 1.696(9), B(2)–N(2) 1.739(4), B(3)–N(3) 1.718(2), B(4)–N(4) 1.723(4) and B(1)/B(2) 64.0° and B(3)/B(4) 64.5°.

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the values of $r$ 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 $^{11}$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 containing the imidodiborate(4) anions, namely Li$_2$(thf)$_2$B$_2$(NPh)$_2$ (6) and Li$_2$(thf)$_2$B$_2$(N-tolene)$_2$ (7) (Scheme 2) were isolated from 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-bloc oxoanions in which an element–element bond is present in the central unit.

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$_2$N$_4$ plane in both imidodiborate structures thereby increasing the N–B–N angles with a consequent lengthening of the B–B bond. In 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 has explored the use of the dianions [B$_3$(N$_3$)$_{10}$]$_2^2$ derived from B$_3$(N$_3$)$_2$NHR, (R = 2,6-disubstituted aryl), as ligands towards early transition metal metallocenes. We note also the related work of Power and Nöth on the reduction of B$_3$(N$_3$)$_2$NH$_4$ towards early transition metal centres. We note also the related work of Power and Nöth which represent imido analogues of the borate BO$_3$ heptaoxide.

Notes and references
† In a typical reaction, a solution of B$_3$(N$_3$)$_2$NH$_4$ (0.396 g, 2.0 mmol) and aniline (0.920 g, 9.9 mmol) in toluene (20 cm$^3$) were refluxed under dinitrogen for 24 h. White crystals formed on cooling which were recrystallised from hexane/thf mixtures affording colourless crystals of B$_3$(N$_3$)$_2$NHR, (2) (93%). NMR (toluene, ppm): $^{11}$B $\delta = 7.37$; $^1$H $\delta = 7.02$ (m, 20H, Ph), $^{13}$C $\delta = 289.7$ (3) ppm. IR (solid) n(v–H) 3358 cm$^{-1}$, 11B NMR (CDCl$_3$, ppm) $\nu = 33.1$. IR (CH$_2$Cl$_2$) $\nu = 1546$, 1288, 1082, 794 cm$^{-1}$. (15 cm$^3$), $\nu = 1594$, 1467, 1322, 1160 cm$^{-1}$.

For a single crystal of 2, $\alpha = 11.484(11), b = 11.494(9), c = 15.965(12), U = 83.96(4), \beta = 75.16(4), \rho = 89.92(5)\text{A}^2, Z = 4, D = 1.279 M\rho cm$ $^{-3}$, $\lambda = 0.71073$ $\AA$, $\mu$(Mo-K$\alpha$) = 0.582 mm$^{-1}$, $F(000) = 824, T = 100(2)$ K, $R_F = 0.0421$ for 4711 reflections with $I > 2\sigma(I)$. Crystal data for 3: $\alpha = 3.052$ orthorhombic, space group P$n\bar{1}$c$n$, $a = 19.740(4), b = 8.759(8), c = 16.550(3)\text{A}^2, U = 2887.1(3)\text{A}^2, Z = 4, D = 1.152 M\rho cm$ $^{-3}$, $\lambda = 0.70730$ $\AA$, $\mu$(Mo-K$\alpha$) = 0.667 mm$^{-1}$, $F(000) = 1080, T = 293(2)$ K, $R_F = 0.0545$ for 2499 reflections with $I > 2\sigma(I)$. To a cooled (−78 °C) solution of 2 (0.262 g, 0.7 mmol) in toluene (15 cm$^3$), n-BuLi (1.7 cm$^3$ 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 $^{11}$B NMR revealed little in the way of side products.

Crystal data for 6: $\alpha = 3.052, b = 16.550(3)\text{A}^2, c = 19.740(4), \beta = 83.96(4), \gamma = 75.16(4), \rho = 89.92(5)\text{A}^2, Z = 4, D = 1.279 M\rho cm$ $^{-3}$, $\lambda = 0.71073$ $\AA$, $\mu$(Mo-K$\alpha$) = 0.582 mm$^{-1}$, $F(000) = 824, T = 100(2)$ K, $R_F = 0.0421$ for 4711 reflections with $I > 2\sigma(I)$. Crystal data for 3: $\alpha = 3.052$, orthorhombic, space group P$n\bar{1}$c$n$, $a = 19.740(4), b = 8.759(8), c = 16.550(3)\text{A}^2, U = 2887.1(3)\text{A}^2, Z = 4, D = 1.152 M\rho cm$ $^{-3}$, $\lambda = 0.70730$ $\AA$, $\mu$(Mo-K$\alpha$) = 0.667 mm$^{-1}$, $F(000) = 1080, T = 293(2)$ K, $R_F = 0.0545$ for 2499 reflections with $I > 2\sigma(I)$.
\begin{itemize}
  \item $U = 4899.6(4) \ \text{Å}^3$, $Z = 4$, $D_\text{c} = 1.147 \ \text{Mg m}^{-3}$, $\lambda = 0.71073 \ \text{Å}$, $\mu(\text{Mo-K}\alpha) = 0.073 \ \text{mm}^{-1}$, $F(000) = 1816$, $T = 172(2) \ \text{K}$, $R_1 = 0.0525$ [for 3436 reflections with $I > 2\sigma(I)$]. 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.

  \item Crystal data for: $C_{48}H_{68}B_2Li_4N_4O_4$, $M = 814.44$, orthorhombic, space group $Pbca$, $a = 16.9600(9)$, $b = 15.0470(8)$, $c = 18.4848(10) \ \text{Å}$, $U = 4717.3(4) \ \text{Å}^3$, $Z = 4$, $D_\text{c} = 1.147 \ \text{Mg m}^{-3}$, $\lambda = 0.71073 \ \text{Å}$, $\mu(\text{Mo-K}\alpha) = 0.070 \ \text{mm}^{-1}$, $F(000) = 1752$, $T = 173(2) \ \text{K}$, $R_1 = 0.0516$ [for 3535 reflections with $I > 2\sigma(I)$].

  \item 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%.

  \item CCDC reference numbers 277645–277648.

  \item See http://dx.doi.org/10.1039/b509653g for crystallographic data in CIF or other electronic format.
\end{itemize}