

# Equilibria in the $B(C_6F_5)_3-H_2O$ system: synthesis and crystal structures of $H_2O \cdot B(C_6F_5)_3$ and the anions $[HOB(C_6F_5)_3]^-$ and $[(F_5C_6)_3B(\mu-OH)B(C_6F_5)_3]^-$

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Received (in Basel, Switzerland) 29th June 1998, Accepted 23rd September 1998

Addition of water to the Lewis acid  $B(C_6F_5)_3$  gives the neutral compound  $H_2O \cdot B(C_6F_5)_3 \cdot 2H_2O$  while the reaction between  $B(C_6F_5)_3$  and  $KOH-H_2O$  in the presence of dibenzo-18-crown-6 gives  $[K(\text{dibenzo-18-crown-6})]^+ [HOB(C_6F_5)_3]^-$  which crystallises together with the adduct  $H_2O \cdot B(C_6F_5)_3$ ; the new binuclear borate anion  $[(F_5C_6)_3B(\mu-OH)B(C_6F_5)_3]^-$  is formed as a salt with the cation  $[Ir(\eta^5-C_5H_5)(C_8H_{12})H]^+$  by addition of  $H_2O$  to  $B(C_6F_5)_3$  in the presence of  $[Ir(\eta^5-C_5H_5)(C_8H_{12})H]^+$ .

Large and very weakly or non-coordinating anions  $[BR_4]^-$  [ $R = 3,5-(CF_3)_2C_6H_3, C_6F_5$ ] have recently attracted interest due to their ability to stabilise electrophilic metal cations containing vacant coordination sites.<sup>1a-d</sup> These cations can be generated by interaction of the neutral Lewis acid  $B(C_6F_5)_3$  with a zirconium–methyl bond resulting in abstraction of the anionic methyl group and giving the anion  $[MeB(C_6F_5)_3]^-$ . Apart from the role as a co-catalyst for olefin polymerisation the Lewis acid  $B(C_6F_5)_3$  has been shown to have a versatile chemistry.<sup>2</sup> Despite the interest in  $B(C_6F_5)_3$ , however, little is known of its reaction with water. There is a report of the compound  $[NHEt_3][HOB(C_6F_5)_3]$ <sup>3</sup> and of the platinum complex,  $[Pt\{HOB(C_6F_5)_3\}Me(Bu_2bpy)]$  ( $Bu_2bpy = 4,4'$ -di-*tert*-butyl-2,2'-bipyridine), which is formed by reaction between  $[PtMe_2(Bu_2bpy)]$ ,  $B(C_6F_5)_3$  and  $H_2O$ . This latter complex has been structurally characterised and contains the anion  $[HOB(C_6F_5)_3]^-$  as a ligand co-ordinated to the platinum centre.<sup>4</sup> Finally, it has been reported that isobutylene and *p*-methylstyrene undergo a 'carbocationic' polymerisation initiated by  $B(C_6F_5)_3$  in the presence of water.<sup>5</sup> This implies the presence of acidic protons as reactive species. Herein we report the isolation and full characterisation of three new boron compounds by reactions between  $B(C_6F_5)_3$  and  $H_2O$  under various conditions which reveal the diverse nature of the  $B(C_6F_5)_3-H_2O$  system.

Slow evaporation of a  $CDCl_3$  solution of  $B(C_6F_5)_3$  and several equivalents of water gives colourless crystals of  $[H_2O \cdot B(C_6F_5)_3] \cdot 2H_2O$  **1**.<sup>6</sup> An X-ray crystal study reveals that one molecule of water is bound directly to the boron centre, whilst the remaining two water molecules are dispersed throughout the crystal lattice (Fig. 1).<sup>‡</sup> All hydrogen atoms have been directly located from the difference map and bond distances indicate hydrogen bonding from the hydrogen atoms in the coordinated water molecule to the oxygen atoms of the remaining two water molecules, as shown in Fig. 1. Variable temperature multinuclear NMR studies of  $B(C_6F_5)_3$  in the presence of  $H_2O$  shown that in **1** there is a rapid exchange of boron-bound water with the free water molecules.

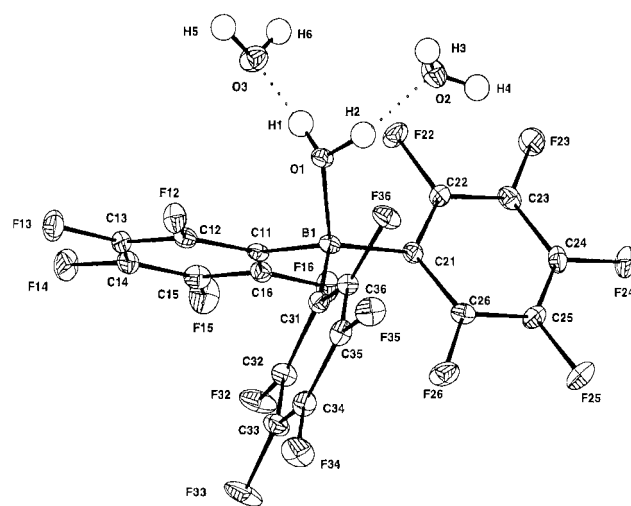
The existence of **1** and previously reported activity of the  $B(C_6F_5)_3-H_2O$  system<sup>5</sup> imply the formation of a Lewis acid–base adduct and subsequent ionisation to generate an acidic proton and complementary anion as depicted in Scheme 1.

Further evidence for the formation of the Brønsted acid is provided by the reaction between  $B(C_6F_5)_3$  and  $H_2O$  in the presence of the 'metal base'  $[Ir(\eta^5-C_5H_5)(C_8H_{12})H]^+$ ,<sup>7</sup> which gives the salt  $[Ir(\eta^5-C_5H_5)(C_8H_{12})H][F_5C_6)_3B(\mu-OH)B(C_6F_5)_3]$

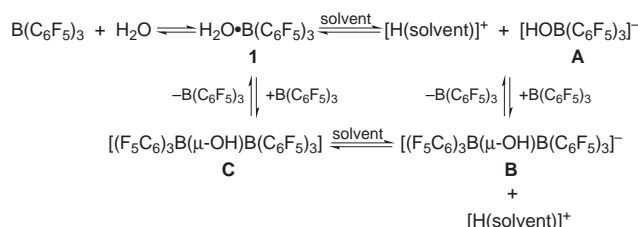
$2 \cdot 2CHCl_3$ , containing the previously unknown binuclear anion,  $[(F_5C_6)_3B(\mu-OH)B(C_6F_5)_3]^-$ . The single crystal structure of **2**§ (Fig. 2) shows that there is a large difference of size between the cation and anion. In the anion, the three pentafluorophenyl groups on each boron atom are staggered with respect to each other. The hydroxyl proton is coplanar with the B–O–B unit. The average B–O bond distance of 1.565(1) Å is consistent with other reported B–(μ-OH) bond lengths.<sup>4,8</sup> The B–O–B angle of 139.6(5)° is distinct from those of 144.8(5)° in a diborylcobaltocene complex<sup>8</sup> and 128.2(2)° in  $[Pt\{HOB(C_6F_5)_3\}Me(Bu_2bpy)]$ .<sup>4</sup>

In the cation, the hydride ligand on iridium is stereochemically active as evidenced by an angle of 20.2° between the Cp ring and the best plane of the coordinating carbon atoms in the cyclooctadiene ligand.

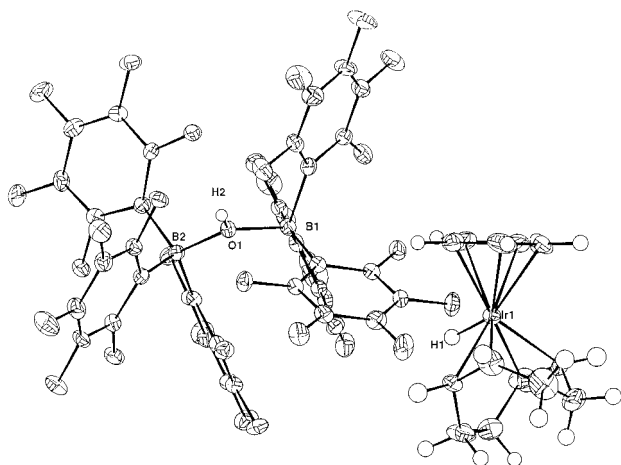
The only previously reported examples of hydroxy-bridged diborates are those prepared using the electrophilic chelates, *cis*-1,2-diborylalkenes<sup>9</sup> or in the coordination sphere of diborylcobaltocene.<sup>8</sup> The cation,  $[Ir(\eta^5-C_5H_5)(C_8H_{12})H]^+$ , has previously been synthesised by protonation of the metal base, using strong Brønsted acids such as triflic acid ( $CF_3SO_3H$ ).<sup>7</sup>



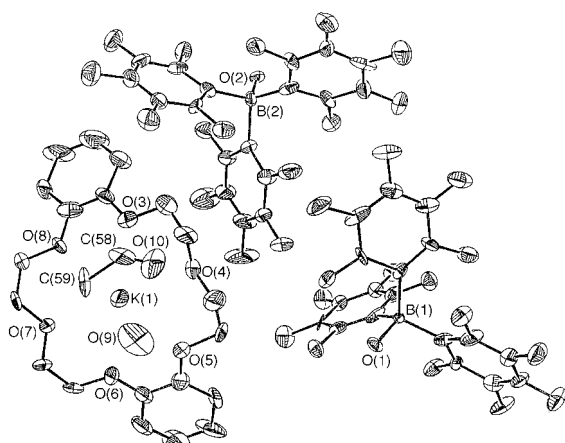
**Fig. 1** Asymmetric unit in the crystal structure of **1**·2  $H_2O$ . Selected bond lengths (Å) and angles (°): B(1)–O(1) 1.5769(14), O(1)–H(1) 0.88(2), O(1)–H(2) 0.86(2), O(1)–O(2) 2.572(2), O(1)–O(3) 2.597(2); B(1)–O(1)–H(1) 117.0(14), B(1)–O(1)–H(2) 117.8(12).



**Scheme 1**



**Fig. 2** Cation and anion of **2**. Chloroform molecules have been removed for clarity. Selected bond lengths (Å) and angles (°): Cp<sub>cent</sub>–Ir(1) 1.867(3), Ir(1)–H(1) 0.7773(19), B(1)–O(1) 1.566(6), B(2)–O(1) 1.564(6), O(1)–H(2) 0.78(6), B–C<sub>avg</sub> 1.644(8); B(1)–O(1)–B(2) 140.4(4), C–B–C<sub>avg</sub> 111(1).



**Fig. 3** Asymmetric unit in the crystal structure of **3**. Selected bond lengths (Å) and angles (°): B(1)–O(1) 1.521(10), B(2)–O(2) 1.480(11), B(1)–C 1.606–1.655, B(2)–C 1.583–1.699; C–B(1)–C 105.1–114.3, C–B(2)–C 105.6–113.6.

Formation of an anion with a bridging hydroxide between two B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> groups, **B** (Scheme 1), could take place either by binding a second equivalent of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> to the monoborate anion [HOB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>–</sup> **A**, or addition of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> to **1** to form the adduct **C** followed by ionisation to form **B**. The [HOB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>–</sup> anion has been characterised as a ligand,<sup>4</sup> *vide supra*, and we now describe its independent synthesis.

In a further study, B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in a CH<sub>2</sub>Cl<sub>2</sub> solution containing dibenzo-18-crown-6 was treated with solid KOH pellets and gave colourless crystals which may be formulated as {[H<sub>2</sub>O·B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]}{[K(dibenzo-18-crown-6)]<sup>+</sup>[HOB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>–</sup>·H<sub>2</sub>O·MeCHO **3** (Fig. 3).<sup>‡</sup> We assume the acetaldehyde present in the crystal is derived either from reaction of the solvent CH<sub>2</sub>Cl<sub>2</sub> with KOH followed by decomposition of the resultant diol or by decomposition of the crown ether under highly basic conditions. There is no interaction of the aldehyde with any of the boron-containing species, although many Lewis base adducts of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> with aldehydes and ketones have been reported.<sup>10</sup> The structure of **3** definitively shows the presence of only one cation and charge balance therefore requires there to be only one monoanion. Hydrogen atoms cannot be located on either of the two {OB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>} units of **3**, but we can infer that there is one molecule of [H<sub>2</sub>O·B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] and one of the anion [HOB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>–</sup> present. The larger B–O distance in **3** is not consistent with that of the aqua complex **1** and it is possible that there is some mixing-in of both species at each site, particularly as the aryl ring torsion angles of the two species are equivalent to within a few degrees.

In conclusion, these preliminary studies show that reaction of H<sub>2</sub>O with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> gives a stable adduct and that this adduct can coexist with its conjugate base although the factors affecting the equilibrium are not fully understood at present. The formation of mono- or di-borate anions may be a function of cation size or relative metal basicity under the reaction conditions. Further investigations are in progress to elucidate these factors.

We thank the Wilkinson Trust (A. A. D.), the University of Oxford for a Violette and Samuel Glasstone Fellowship (J. R. G.), St. John's College, Oxford (L. H. D.) and the EPSRC for financial support.

## Notes and references

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<sup>‡</sup> *Crystal data 1*: C<sub>18</sub>H<sub>6</sub>BF<sub>15</sub>O<sub>3</sub>, *M*<sub>w</sub> = 566.02, triclinic, space group *P*1, *a* = 9.999(4), *b* = 10.250(4), *c* = 10.908(5) Å, α = 90.097(2), β = 103.680(2), γ = 116.27(2)°, *V* = 966.7(3) Å<sup>3</sup>, *Z* = 2, *D*<sub>c</sub> = 1.94 g cm<sup>–3</sup>, *F*(000) = 544, μ(Mo–Kα) = 0.220 mm<sup>–1</sup>, *T* = 120 K; crystal 0.3 × 0.35 × 0.35 mm; 4494 total reflections, 3442 unique [*I* > 3σ(*I*)], *R*<sub>int</sub> = 0.013; *R* = 0.0309 and *R*<sub>w</sub> = 0.0380.

*2·2CHCl<sub>3</sub>*: C<sub>49</sub>H<sub>19</sub>B<sub>2</sub>F<sub>30</sub>IrO·2CHCl<sub>3</sub>, *M*<sub>w</sub> = 1407.17 + 238.74, monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 12.070(4), *b* = 24.789(5), *c* = 17.341(4) Å, β = 93.547(2)°, *V* = 5178.5(3) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 2.11 g cm<sup>–3</sup>, *F*(000) = 2904, μ(Mo–Kα) = 0.303 mm<sup>–1</sup>, *T* = 120 K; crystal 0.3 × 0.35 × 0.35 mm; 29435 total reflections, 8800 unique [*I* > 3σ(*I*)], *R*<sub>int</sub> = 0.0519, *R*<sub>w</sub> = 0.0589. Hydroxyl and hydride hydrogen atoms located but not refined. Structures of **1** and **2** solved with SIR-92<sup>11</sup> and refined with CRYSTALS.<sup>12,13</sup>

**3**: C<sub>58</sub>H<sub>33</sub>B<sub>2</sub>F<sub>30</sub>KO<sub>10</sub>, *M*<sub>w</sub> = 1520.42, monoclinic, space group *P*2<sub>1</sub>/*c* (no. 14) *a* = 12.39(2), *b* = 33.367(12), *c* = 13.790(5) Å, β = 97.13(2)°, *V* = 5659(7) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.785 g cm<sup>–3</sup>, *F*(000) = 3040, μ(Mo–Kα) = 0.248 mm<sup>–1</sup>. 19448 data were recorded and merged to give 8392 unique (*R*<sub>int</sub> = 0.1365). The structure was solved *via* direct methods (SHELX-93).<sup>14</sup> An absorption correction was applied using DIFABS.<sup>15</sup> The final *R*, *R*<sub>w</sub> indices [*I* > 2σ(*I*)] were 0.067, 0.099 for 911 parameters (non-hydrogen atoms anisotropic, hydrogen atoms in idealised positions, C–H = 0.96 Å, with *U*<sub>iso</sub> tied to *U*<sub>eq</sub> of the parent atoms). CCDC 182/1028.

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