

## Synthesis and Stability of Reactive Salts of Dodecafluoro-*closo*-dodecaborate(2-)

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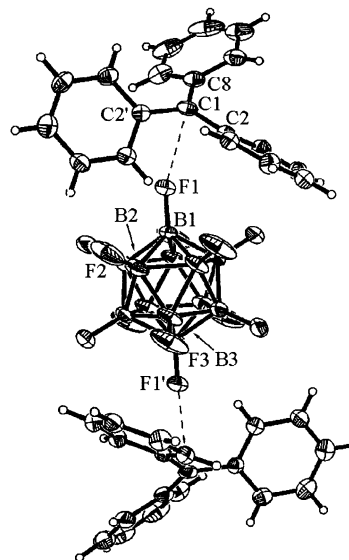
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The  $B_{12}H_{12}^{2-}$  dianion, first prepared in 1960,<sup>1</sup> is the most easily synthesized, the most stable, the most symmetric, and the best studied of the *closo*- $B_nH_n^{2-}$  species.<sup>2</sup> Before the 1990s, the persubstituted derivatives of  $B_{12}H_{12}^{2-}$  were limited to  $B_{12}D_{12}^{2-}$ ,  $B_{12}Cl_{12}^{2-}$ ,  $B_{12}Br_{12}^{2-}$ , and  $B_{12}I_{12}^{2-}$ .<sup>3</sup> Since 1999, Hawthorne and co-workers have reported the synthesis and isolation of salts of  $B_{12}Me_{12}^{2-}$ ,  $B_{12}(OH)_{12}^{2-}$ , and a variety of  $B_{12}(OR)_{12}^{2-}$  and  $B_{12}(OCOR)_{12}^{2-}$  derivatives.<sup>4</sup>

Our interest<sup>5</sup> in highly fluorinated weakly coordinating anions such as 1-R- $CB_{11}F_{11}^-$  prompted us to reinvestigate the synthesis and physicochemical properties of the dodecafluoro-*closo*-dodecaborate(2-) anion,  $B_{12}F_{12}^{2-}$ . Although a dianion would not be expected to be as weakly coordinating as a structurally similar monoanion, there are situations where a weakly coordinating dianion might be suitable for a particular chemical task.<sup>6,7</sup> A species reported<sup>3a</sup> in 1962 to be  $B_{12}F_{12}^{2-}$  was later shown to be the undecafluoromonohydroxy species  $B_{12}F_{11}(OH)^{2-}$ .<sup>3b,c</sup> The first successful synthesis of  $B_{12}F_{12}^{2-}$  was achieved in 1992, when it was reported that the cesium salt could be prepared in 38% yield by heating  $Cs_2B_{12}H_{12}$  in supercritical HF at 550 °C for 5 h.<sup>8</sup> A preliminary report of the structure of  $Cs_2B_{12}F_{12} \cdot H_2O$  was included in that paper.<sup>8</sup> The reported B–F distances are 1.37(1)–1.41(1) Å.

In this paper, we report a significantly lower-temperature synthesis of  $K_2B_{12}F_{12}$  in 72% recrystallized yield. In initial experiments, 20%  $F_2/N_2$  was added to a –70 °C suspension of  $K_2B_{12}H_{12}$  in liquid anhydrous HF (LAHF). After the reaction mixture was stirred at 25 °C for 72 h, it was found that the major products were  $BF_4^-$ ,  $B_{12}F_{12}^{2-}$  (21% based on  $B_{12}H_{12}^{2-}$ ), and a number of dimeric  $B_{24}$  species. To minimize the formation of  $BF_4^-$  and the dimeric species, which presumably results from the oxidative-coupling of one or more  $B_{12}H_{12-x}F_x^{2-}$  species ( $x \leq 3$ ),<sup>9</sup> an alternative synthetic approach was used.<sup>10</sup> The compound  $K_2B_{12}H_{12}$  was stirred in LAHF at 70 °C for 14 h, a procedure known to convert  $B_{12}H_{12}^{2-}$  to  $B_{12}H_8F_4^{2-}$  in high yield.<sup>8</sup> The reaction mixture was then cooled to 25 °C and treated with 20%  $F_2/N_2$  for 72 h [CAUTION: both HF and  $F_2$  are extremely hazardous materials and should only be handled by trained personnel]. Following workup with water and recrystallization from acetonitrile,  $K_2B_{12}F_{12}$  was isolated in 72% yield. The compositional purity of the  $B_{12}F_{12}^{2-}$  anion was determined to be >99.5% from a negative-ion electrospray mass spectrum, which exhibited a grouping of peaks centered at  $m/z$  178.9 (calcd for  $B_{12}F_{12}^{2-}$ , 178.8), and by <sup>11</sup>B and <sup>19</sup>F NMR spectra, which exhibited a single broad resonance at  $\delta$  –17.0 ( $\delta$  0 for external  $BF_3 \cdot OEt_2$ ) and an unresolved multiplet (fwhh = 170 Hz) at  $\delta$  –269.6 ( $\delta$  0 for external  $CFCl_3$ ) which narrowed to a single resonance (fwhh = 27 Hz) upon broad-band <sup>11</sup>B decoupling, respectively.<sup>11</sup>



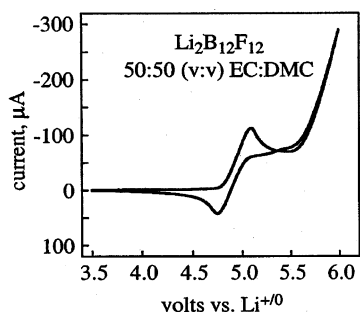
**Figure 1.** Thermal ellipsoid plot of  $[CPh_3]_2[B_{12}F_{12}]$  (50% probability ellipsoids except for hydrogen atoms, which are shown as spheres of arbitrary size). The white, light-gray, and dark-gray ellipsoids are carbon, fluorine, and boron atoms, respectively. Selected distances (Å) and angles (deg): B1–F1, 1.391(4); B2–F2, 1.378(5); B3–F3, 1.382(5); B1–B2, 1.785(6); B1–B3', 1.765(6); B1–B3'', 1.769(6); B2–B3, 1.775(7); B2–B2', 1.761(10); B3–B3', 1.769(6); F1···C1, 3.087(2) Å; B1–F1···C1, 139.0(3)°; C2–C1–C2', 120.0(5)°; C2–C1–C8, 120.0(2)°; F1···C1–C2, 87.0(1)°; F1···C1–C8, 93.1(1)°.

The salt  $K_2B_{12}F_{12}$  was converted to  $[CPh_3]_2[B_{12}F_{12}]$ ,  $[N(n-Bu)_4]_2[B_{12}F_{12}]$ ,  $[NH(n-C_{12}H_{25})_3]_2[B_{12}F_{12}]$ ,  $[NH_4]_2[B_{12}F_{12}]$ , and  $Li_2B_{12}F_{12}$  by metathesis reactions.<sup>10</sup> The  $[NH(n-C_{12}H_{25})_3]_2[B_{12}F_{12}]$  salt is noteworthy because, unlike the other salts, it is soluble in aromatic hydrocarbon solvents. In preliminary work, the reactive salt  $[CPh_3]_2[B_{12}F_{12}]$  has been used to generate compounds containing the reactive cation-like species  $SiMe_2(n-C_{18}H_{37})^+$  and  $AlMe_2^+$ . Given that the putative  $AlMe_2^+$  cation abstracts a fluorine atom from  $B(C_6F_5)_4^-$ ,<sup>12</sup> it is significant that  $B_{12}F_{12}^{2-}$  is stable in the presence of  $AlMe_2^+$ .

Crystals of  $[CPh_3]_2[B_{12}F_{12}]$  suitable for X-ray diffraction<sup>13</sup> were grown from  $CH_2Cl_2$ /hexanes. The structure, shown in Figure 1, consists of the icosahedral  $B_{12}F_{12}^{2-}$  dianion weakly interacting with the two  $CPh_3^+$  cations via two symmetry-related  $BF \cdots C$  contacts. Only three boron atoms and three fluorine atoms are unique. The B–F distances in the  $B_{12}F_{12}^{2-}$  anion are the same to within  $\pm 3\sigma$  as the lower-belt and antipodal B–F distances in 1-Et- $CB_{11}F_{11}^-$  and 1- $CH_2Ph$ - $CB_{11}F_{11}^-$ .<sup>5a,b</sup> The most important structural feature is the  $F1 \cdots C1$  distance of 3.087(2) Å, which is only 0.08 Å shorter than the 3.17 Å sum of van der Waals radii for carbon and fluorine.<sup>14</sup> Furthermore, the  $F1 \cdots C1$  distance in  $[CPh_3]_2[B_{12}F_{12}]$  is far

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**Figure 2.** Cyclic voltammogram of a 0.064 M ethylene carbonate:dimethyl carbonate (50:50 v:v) solution of  $\text{Li}_2\text{B}_{12}\text{F}_{12}$  ( $\Delta E_p = 240$  mV, Pt working and counter electrodes, lithium foil reference electrode, no supporting electrolyte). The quasi-reversible  $\text{B}_{12}\text{F}_{12}^{1-2-}$   $E_{1/2}$  value is 4.9 V. There was no reduction wave more positive than 0 V. The sharp rise in current at potentials more positive than 5.5 V is due to solvent oxidation.

longer than the related  $\text{BF}_3 \cdots \text{C}$  distances in  $[\text{CPh}_2(p\text{-OMe-C}_6\text{H}_4)]\text{-}[\text{BF}_4]$  and  $[\text{CPh}(p\text{-OMe-C}_6\text{H}_4)_2][\text{BF}_4]$ , 2.68 and 2.58 Å, respectively.<sup>15</sup>

The  $\text{BF}_3 \cdots \text{C}$  distances demonstrate that  $\text{B}_{12}\text{F}_{12}^{2-}$  is considerably less basic than  $\text{BF}_4^-$  despite the higher negative charge. To further probe the applicability of  $\text{B}_{12}\text{F}_{12}^{2-}$  as a weakly coordinating anion, we examined its thermal, chemical, and electrochemical stability. A thermogravimetric analysis of  $\text{Li}_2\text{B}_{12}\text{F}_{12}$  revealed no mass loss up to 450 °C (heating/cooling at 10 °C/min). The sample was recovered unchanged as judged by  $^{19}\text{F}$  NMR spectroscopy. In contrast, crystalline  $\text{LiPF}_6$  decomposes at 70 °C.<sup>16</sup> None of the salts we examined appeared to be shock sensitive. A thermogravimetric-mass spectral analysis of  $[\text{NH}_4]_2[\text{B}_{12}\text{F}_{12}]$  revealed no mass loss and no mass spectral evidence for the evolution of  $\text{NH}_3$  up to 480 °C (heating/cooling at 20 °C/min). The sample was recovered unchanged as judged by  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectroscopy. In contrast, crystalline  $[\text{NH}_4]_2[\text{B}_{12}\text{H}_{12}]$  decomposes at 310 °C.<sup>17</sup>

The  $\text{B}_{12}\text{H}_{12}^{2-}$  anion is known to react with 38% sulfuric acid.<sup>4c</sup> In contrast, the lithium salt of  $\text{B}_{12}\text{F}_{12}^{2-}$  was stable in 98% sulfuric acid and in 70% nitric acid for at least 24 h. Even more remarkable is the observation that the  $\text{B}_{12}\text{F}_{12}^{2-}$  anion was unchanged after treatment with aqueous 3 M KOH for 10 days. Note that the related fluoroanion 1-H-CB $_{11}\text{F}_{11}^-$  is converted to mono- and dihydroxy derivatives in 3 M NaOH after only 24 h<sup>5c</sup> and  $\text{C}_2\text{H}_2\text{B}_{10}\text{F}_{10}$  is rapidly hydrolyzed even in pH 7 water.<sup>18</sup>

With regard to redox stability,  $\text{B}_{12}\text{F}_{12}^{2-}$  did not react with 10 equiv of aqueous  $\text{Ce}^{4+}$  (hours) or with metallic sodium in THF (1 day). In contrast, 1-H-CB $_{11}\text{F}_{11}^-$  reacts with sodium in THF to form 1,10-H $_2$ -CB $_{11}\text{F}_{10}^-$ , among other products. In a 50:50 (v:v) mixture of ethylene carbonate and dimethyl carbonate,  $\text{B}_{12}\text{F}_{12}^{2-}$  was not reduced at 0 V versus  $\text{Li}^{+/0}$  and underwent a quasi-reversible oxidation at 4.9 V versus  $\text{Li}^{+/0}$  (ca. 1.9–2.0 V versus NHE), as shown in Figure 2 ( $\Delta E_p = 240$  mV). Under these conditions, 1-Me-CB $_{11}\text{F}_{11}^-$  was not oxidized prior to the onset of solvent oxidation (5.5 V versus  $\text{Li}^{+/0}$ ). For comparison, the  $\text{B}_{12}\text{Me}_{12}^{1-2-}$  and  $\text{CB}_{11}\text{Me}_{12}^{0/1-}$   $E_{1/2}$  values are 0.4 and 1.6 V (versus NHE), respectively.<sup>20</sup> The fact that the oxidation of  $\text{B}_{12}\text{F}_{12}^{2-}$  may be reversible suggests that salts of the radical monoanion  $\text{B}_{12}\text{F}_{12}^{\cdot-}$  might

be isolable. Note that the radicals  $\text{B}_{12}\text{Me}_{12}^{1-}$  and  $\text{CB}_{11}\text{Me}_{12}^{1-}$  have been isolated.

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**Supporting Information Available:** Synthetic details and selected NMR spectral data for new compounds and tables of X-ray parameters and results for  $[\text{CPh}_3]_2[\text{B}_{12}\text{F}_{12}]$  (PDF and CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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