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Fluoride-ion deboronation of *p*-fluorophenyl-*ortho*- and -*meta*-carboranes. NMR evidence for the new fluoroborate, $HOBHF_2^-$

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Abstract—The reactions of 1-(4-fluorophenyl)-1,2-dicarbadodecaborane(12) **1** and 1-(4-fluorophenyl)-1,7-dicarbadodecaborane(12) **2** with tetrabutylammonium fluoride hydrate in tetrahydrofuran or acetonitrile have been monitored by ^{19}F and ^{11}B NMR. No carborane intermediates were observed prior to formation of the *nido*- anions 7-(4-FC_6H_4)-7,8-$C_2B_9H_{11}^-$ **3** and 7-(4-FC_6H_4)-7,9-$C_2B_9H_{11}^-$ **4** which each required two molecular proportions of fluoride and, by inference, one of water for complete reaction. The spectra of the initial anionic monoboron product of both reactions showed it to be the new fluoroborate $HOBHF_2^-$ **5**. The B-attached hydrogen atom of the fluoroborate **5** is derived from the starting carborane, since it was retained when $Bu_4NF \cdot (D_2O)_n$ was used, but the *nido*-anions **3** and **4** bonded deuterium at the open face in this experiment. The ^1H, ^{11}B, ^{19}F and ^{13}C NMR spectra of carboranes **1**–**4** have been recorded and assigned. © 1997 Elsevier Science Ltd

Keywords: carborane; deboronation; fluoride ion; multinuclear NMR; mechanism; borate.

Since the 1960s, it has been known [1–5] that the deboronation of *ortho*-carborane, *closo*-1,2-$C_2B_{10}H_{12}$, or its alkyl and aryl derivatives 1,2-R′R″-1,2-$C_2B_{10}H_{10}$, by strong nucleophiles like alkoxides, hydrazine or piperidine forms the *nido*-anion, *nido*-7,8-$C_2B_9H_{12}^-$ or derivatives 7,8-R′R″-7,8-$C_2B_9H_{10}^-$.

These *nido*-anions are precursors to a large number of metallocarborane sandwich compounds as well as a variety of other *nido*- and *closo*-carboranes and heteroboranes [6]. *Meta*-carborane, *closo*-1,7-$C_2B_{10}H_{12}$, and its alkyl or aryl derivatives, 1,7-R′R″-1,7-$C_2B_{10}H_{10}$, require more forcing conditions to give 7,9-$C_2B_9H_{12}^-$ or 7,9-R′R″-7,9-$C_2B_9H_{10}^-$ [2, 3, 7].

Hawthorne determined the products and stoichiometry for deboronation of *ortho*-carborane using potassium hydroxide in ethanol and found that the reaction is first order in both carborane and nucleophile (eq. (1)) [1].

$$C_2B_{10}H_{12} + RO^- + 2\,ROH \rightarrow C_2B_9H_{12}^- + B(OR)_3 + H_2. \quad (1)$$

Deboronation of *ortho*-carborane with piperidine alone gives dipiperidylborane (eq. (2)); in the presence of alcohols trialkylborates are formed (eq. (3)) [4]. In the latter case it is first order in both carborane and piperidine.

$$C_2B_{10}H_{12} + 3HNC_5H_{10} \rightarrow C_5H_{10}NH_2^+C_2B_9H_{12}^- + HB(NC_5H_{10})_2, \quad (2)$$

$$C_2B_{10}H_{12} + HNC_5H_{10} + 3\,ROH \rightarrow C_5H_{10}NH_2^+C_2B_9H_{12}^- + B(OR)_3 + H_2. \quad (3)$$

Onak [8] recently reported the deboronation of *ortho* and *meta* carboranes with "anhydrous" tetrabutylammonium fluoride in THF or acetonitrile; however, the evolution of gas thought to be dihydrogen suggested that traces of water were present. Anionic mono-boron byproducts were detected but not conclusively identified by NMR. These appeared to be different for the *ortho* and *meta* carboranes. Our results described below suggest that the different proportions of reagents used may have given this result, however.

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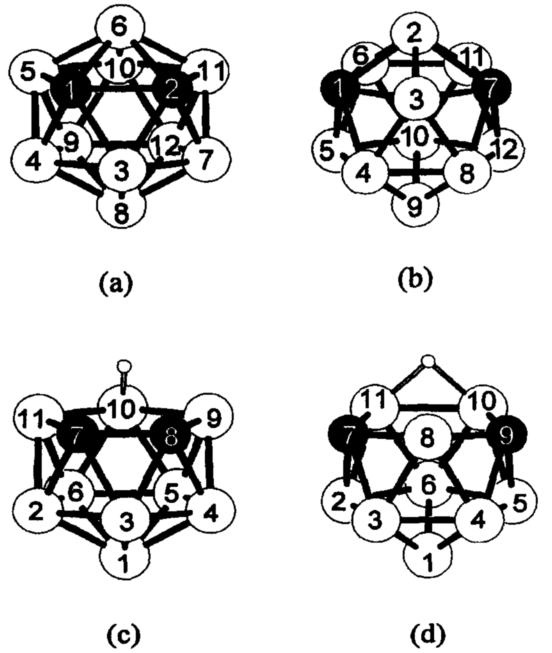
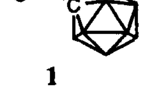


Fig. 1. Structures of carboranes (a) 1,2-$C_2B_{10}H_{12}$, (b) 1,7-$C_2B_{10}H_{12}$, (c) 7,8-$C_2B_9H_{12}^-$ and (d) 7,9-$C_2B_9H_{12}^-$ showing skeletal atom numbering. *Exo* hydrogens are omitted for clarity.

We have described [9] the fluoride ion deboronation of several *ortho* and *meta* carborane derivatives using tetrabutylammonium fluoride hydrate as a convenient route to *nido* carborane anions. The fluoride ion deboronation of 4-($O_2NC_6H_4$)-1,7-$C_2B_{10}H_{11}$ was followed by ^{19}F and ^{11}B NMR spectroscopy, but accurate determination of the time for complete deboronation was made difficult by the breadth of boron peaks. We detected several mononuclear fluoroborate products and the changes in their ^{19}F and ^{11}B peak intensities during the deboronation process, but in that study were unable to identify them.

We therefore prepared the fluorophenyl derivatives of *ortho* and *meta* carboranes, 1-(4-FC_6H_4)-1,2-$C_2B_{10}H_{11}$ **1** and 1-(4-FC_6H_4)-1,7-$C_2B_{10}H_{11}$ **2** [10,11] in order to use their fluorine "labels" to help monitor the fluoride ion deboronation reactions by ^{19}F NMR spectroscopy. The integrals of the sharp discrete ^{19}F peaks, unlike the broad overlapping ^{11}B peaks, provided semi-quantitative data to observe the progress of the reactions. Here we discuss the stoichiometry and sequence of the fluoride-ion deboronation.



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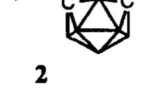

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EXPERIMENTAL

NMR spectra were recorded on a Bruker AC250 (250.1 MHz ^1H, 235.3 MHz ^{19}F, 80.3 MHz ^{11}B and 62.9 MHz ^{13}C) or a Bruker AMX500 (160.5 MHz ^{11}B and 500.1 MHz ^1H) instrument. 2D ^{11}B-$^{11}B\{^1H\}$ COSY, ^{11}B-^1H correlation and $^1H\{^{11}B\}$ spectra were obtained on the Bruker AMX500. Unless otherwise indicated, the lock solvent used was *d*-chloroform. External references for the chemical shifts are $SiMe_4 = 0.00$ ppm for ^1H and ^{13}C, $BF_3 \cdot Et_2O = 0.0$ ppm for ^{11}B and $CFCl_3 = 0.0$ ppm for ^{19}F. Infrared spectra were recorded as potassium bromide discs using a Perkin Elmer 1720X FTIR spectrometer.

Tetra-*n*-butylammonium fluoride hydrate, 4-fluoroiodobenzene, deuterium oxide, d_3-acetonitrile and tetrahydrofuran (THF) were obtained commercially (Aldrich) and used as received. The hygroscopic Bu_4NF hydrate contains a minor impurity believed to be a tetrafluoroborate Bu_4NBF_4 [δ_F −150.5, δ_B −0.4]. The hydrate was assumed to be $Bu_4NF \cdot 3H_2O$ in this study (Found: C, 59.8; H, 13.1; N, 5.9; (Calc.: C, 60.9; H, 13.3; N, 4.4%). *Meta* carborane, 1,7-$C_2B_{10}H_{12}$, was purified by sublimation at 0.01 mmHg. The carborane 1-(4-FC_6H_4)-1,2-$C_2B_{10}H_{11}$ **1** was made by the literature method [10].

Formation of Bu_4NF *containing deuterium oxide*

Tetrabutylammonium fluoride hydrate was heated at 60°C/0.01 mmHg for 2 h to remove as much water as possible. Deuterium oxide was added and after 2 h the excess D_2O was evaporated at 40°C to leave a semi-solid. The IR spectrum of the product $Bu_4NF \cdot xD_2O$ showed a very broad band at 2500–2300 cm^{-1} (O—D stretch) and a band at 1200 (O—D bend) compared with 3500–3200 cm^{-1} (O—H stretch) and 1650 (O—H bend) for the H_2O hydrate.

1-(4-FC_6H_4)-1,7-$C_2B_{10}H_{11}$ (**2**). This compound was made by the copper-coupling reaction [12] of 1,7-$C_2B_{10}H_{12}$ (5.76 g, 0.04 mol) and 4-FC_6H_4I. The same procedure as had been used for other 1-aryl-1,7-$C_2B_{10}H_{11}$ derivatives was used in the synthesis of **2**. Vacuum sublimation with a −78°C cold finger followed by recrystallization from hexane at −30°C gave **2** (4.00 g, 42%); m.p. 65°C ([11] 59–61°C).

Tetrabutylammonium salt of 7-(4-FC_6H_4)-7,8-$C_2B_9H_{11}^-$ (**3**). A stirred mixture of the *closo* carborane **1** (0.476 g, 2 mmol) and Bu_4NF hydrate (2.52 g, 8 mmol) in THF (20 cm^3) was heated under reflux for 18 h. 45 cm^3 (2 mmol) of a non-condensible gas was produced from this reaction. After cooling, water (100 cm^3) was added and the white precipitate was washed with water. The solid was dissolved in dichloromethane, washed with water, dried over $MgSO_4$ and the solvent vacuum removed. Recrystallization of the solid from ethanol gave the tetrabutylammonium salt of **3** (0.90 g, 96%); m.p. 87°C. Found: C, 59.9; H, 10.9; N, 2.9; Calc. for $C_{24}H_{51}B_9NF$: C, 61.4; H, 10.9;

N, 3.0%. ν_{max} cm^{-1} 3061w, 3037w (aryl CH stretch); 2958s, 2930s, 2872s (alkyl CH stretch); 2523vs,br (BH); 1507s, 1481s, 1456m, 1412w, 1377m, 1234w, 1220s, 1159m, 1149m, 1105w, 1022m, 882m, 835m, 807w, 739m, 531w.

Tetrabutylammonium salt of 7-(4-FC_6H_4)-7,9-$C_2B_9H_{11}^-$ (**4**). The same preparative method as for the synthesis of **3** with the starting carborane **2** instead of **1** produced the tetrabutylammonium salt of **4** (0.86 g, 92%); m.p. 98°C. This compound is stable in acetonitrile solution (see NMR data, Table 1) but the solid deteriorated rapidly in air at ambient temperature where an IR band developed at 3220 cm^{-1}. The IR spectrum was recorded immediately after recrystallization; ν_{max} cm^{-1} 3068w, 3033w, 3020w (aryl CH stretch); 2963s, 2934s, 2875s (alkyl CH); 2529vs,br (BH); 1503s, 1470s, 1383w, 1263w, 1213s, 1156m, 1110m, 1093m, 1059m, 1035m, 1015w, 977w, 925w, 907w, 895w, 877m, 833m, 801m, 738w, 551w, 526w.

General procedure for monitoring deboronation reactions by NMR spectroscopy

Compound **1** or **2** (0.0238 g; 0.1 mmol) was dissolved in THF or CD_3CN (0.4 cm^3) in a 5 mm diameter NMR tube and Bu_4NF hydrate (0.1–0.4 mmol, depending on the desired ratio of reactants) in the same solvent (0.3 cm^3) was added. The open NMR tube was inserted into the Bruker AC250 spectrometer and ^{19}F or ^{11}B NMR spectra were recorded at intervals. Fluorine NMR data of some reactions are reported in the next section.

For the deuterium-labelling experiments the same procedure was carried out with $Bu_4NF \cdot xD_2O$ instead of $Bu_4NF \cdot xH_2O$. The ^{11}B NMR spectra showed no *endo*/bridging hydrogen couplings in the carborane products from **1** and **2** with $Bu_4NF \cdot xD_2O$.

Reaction of $B(OH)_3$ *and* Bu_4NF *hydrate.* A slurry of $B(OH)_3$ (6.5 mg; 0.1 mmol) and THF in an NMR tube was treated with Bu_4NF hydrate (31.5 mg; 0.1 mmol) at ambient temperature. After 5 min the ^{19}F NMR spectrum showed a major peak at δ_F −138.7 ppm (**B**) along with minor peaks at −127 (broad, F^-), −132.6 (**A**), −136.9 (**6**), −143.9 (**7**) and −144.2 (**C**) ppm. Addition of more Bu_4NF and water resulted in an increase in the intensities of the resonances at −136.6 [$(HO)_2BF_2^-$] [16] and −143.9 ppm ($HOBF_3^-$) [16], a decrease in the intensity of the resonance at −138.7 ppm and the disappearance of solid $B(OH)_3$ and the peak at −144.2 ppm.

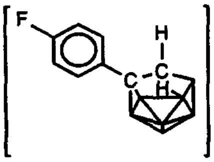
Control experiments of D_2O *and* $Bu_4NF \cdot xD_2O$ *with tetrabutylammonium salts of* 3 *and* 4

The boron NMR spectra of salts of **3** and **4** in THF with D_2O and/or $Bu_4NF \cdot xD_2O$ after 8 h at room temperature showed no evidence of deuterium exchange between D_2O and the *nido* anions.

RESULTS AND DISCUSSION

Formation and characterization of carboranes, 1–4

These carboranes have all been synthesized and characterized previously, **3** and **4** as tetramethylammonium salts [10,11]. New more convenient routes to **2**, **3** and **4** were used here. Carborane **2** was produced by the copper-coupling [12] of *meta* carborane and 4-fluoroiodobenzene instead of by thermal isomerization of **1** [10]. The tetrabutylammonium salts of **3** and **4** were obtained from the fluoride-ion deboronation of **1** and **2** in refluxing THF.



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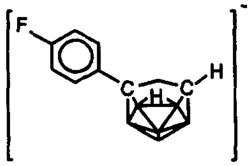

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Detailed multinuclear NMR data of **1**–**4** are reported here as only their ^{19}F NMR data, which are in agreement with our findings, had previously been reported [10,11]. The ^{13}C carboranyl peaks of **3** showed poorly resolved 1 : 1 : 1 : 1 quartets arising from ^{11}B—^{13}C couplings. The B—C couplings are probably associated with the very short C(7)—B(11) and C(8)—B(9) bonds shown in the X-ray crystallographically determined structure of the unsubstituted analogue, 7-C_6H_5-7,8-$C_2B_9H_{11}^-$ [13].

Some ^{11}B chemical shifts of **1**–**4** can be assigned on the assumption that the shifts of the boron atoms neighbouring the cage carbon with the fluorophenyl group attached are significantly changed with respect to shifts of the related unsubstituted carboranes 1,2-$C_2B_{10}H_{12}$, 1,7-$C_2B_{10}H_{12}$, 7,8-$C_2B_9H_{12}^-$ and 7,9-$C_2B_9H_{12}^-$ [5,14]. The ^{11}B and ^1H assignments of **1** are consistent with those for 1-phenyl-*ortho*-carborane, 1-C_6H_5-1,2-$C_2B_{10}H_{11}$ [15].

Times of conversion in the fluoride ion deboronation of 1 *and* 2

The deboronation of **1** (0.143 M) with Bu_4NF hydrate (0.143–0.571 M) in acetonitrile or THF was monitored by ^{19}F NMR spectroscopy. The ^{19}F peak at −112.6 ppm for **1** decreased while the peak at −120.5 ppm corresponding to **3** increased during the process (see Fig. 2). No other ^{19}F peaks were observed which might be attributed to carborane intermediates.

The fluoride ion deboronation of **1** was followed using various molar ratios of fluoride ion : carborane (0.143 M) i.e. 1 : 1, 2 : 1, 3 : 1 and 4 : 1. Complete conversion of **1** into **3** was achieved with a ratio of 2 : 1 or higher. The reaction of 1 : 1 ratio left one-third of **1** unreacted after two weeks.

For the *meta* carborane **2** deboronation occurred much more slowly. A 4 : 1 fluoride : carborane ratio

Table 1. ^{19}F, ^{11}B, ^{13}C and ^{1}H NMR data for carboranes **1–4**

	δ(^{19}F)(ppm)[a]	δ(^{11}B)(ppm)[b]	δ(^{13}C{^{1}H})(ppm)[c]	δ(^{1}H{^{11}B})(ppm)[d]
1	−112.6	−1.3 (1B, d, 149; B9), −3.8 (1B, d, 148; B12), −8.4 (2B, d, 151; B8,10), −10.1 (2B, d, 165; B4,5), −10.8 (2B, d, 143; B3,6), −12.1 (2B, d, 164; B7,11)	163.5 (d, $^{1}J_{CF}$ 252 Hz; *para* phenyl CF), 129.8 (d, $^{4}J_{CF}$ 9; *ortho* phenyl C), 129.3 (s; *ipso* phenyl C), 115.8 (d, $^{3}J_{CF}$ 22; *meta* phenyl C), 75.8 (s; C1), 60.7 (s; C2)	7.51 (2H, dd, $^{3}J_{HH}$ = 8.7, $^{4}J_{HF}$ = 4.8; *ortho* phenyl CH), 6.94 (2H, dd, $^{3}J_{HH}$, $^{3}J_{HF}$ = 8.6; *meta* phenyl CH], 3.95 (1H, s; C2H), 2.52 (2H, s; B3,6H), 2.38 (2H, s; B4,5H), 2.35 (1H, s; B9H), 2.23 (3H, s; B8,10,12H), 2.19 (2H, s; B7,11H)
2	−114.3	−3.3 (1B, d, 162; B5), −8.1 (1B, d, 155; B12), −9.8 (4B, d, 156; B4,6,9,10), −12.8 (2B, d, 167; B8, 11), −14.5 (2B, d, 181; B2,3)	162.8 (d, $^{1}J_{CF}$ 250; CF), 131.1 (s; *ipso*), 129.6 (d, $^{4}J_{CF}$ 7; *ortho*), 115.2 (d, $^{3}J_{CF}$ 22; *meta*), 77.2 (C1), 55.1 (C2);	7.41 (2H, dd, $^{3}J_{HH}$ 8.6, $^{4}J_{HF}$ 4.9; *ortho*), 6.94 (2H, dd, $^{3}J_{HH}$, $^{3}J_{HF}$ = 8.6; *meta*), 3.07 (1H, s, C7H), 2.86 (2H, s, B2H and B3H), 2.56 (1H, s, B5H), 2.40 (3H, s; B12,9,10H), 2.20 (2H, s; B8, 11H), 2.13 (2H, s; B4,6H).
3	−120.5	−7.9 (1B, d, 138; B11), −9.5 (1B, d, 130; B9), −12.8 (1B, d, 155; B3), −16.6 (1B, d, 134; B5), −17.1 (1B, d, 150; B6), −18.8 (1B, d, 155; B2), −21.5 (1B, d, 147; B4), −31.8 [1B, dd, 148, ^{1}J(BHμ) 50; B10], −34.9 (1B, d, 138; B1)	160.3 (d, $^{1}J_{CF}$ 241; CF), 141.6 (s; *ipso*), 128.0 (s, *ortho*), 113.6 (d, $^{3}J_{CF}$ 20; *meta*), 61.2 (brq, $^{1}J_{BC}$ 22; C7), 45.4 (brq, $^{1}J_{BC}$ 24; C8)	7.33 (dd, 2H, $^{3}J_{HH}$ 8.6 Hz, $^{4}J_{HF}$ 5.5 Hz, *ortho*), 6.99 (2H, dd, $^{3}J_{HH}$, $^{3}J_{HF}$ 8.7; *meta*), 2.33 (1H, s; C8H), 2.24 (1H, s; B9H), 2.20 (1H, s; B11H), 1.95 (1H, s; B3H), 1.86 (1H, s; B2H), 1.42 (3H, s; B4,5,6H), 0.83 (1H, s; B1H), 0.33 (1H, s; B10H), −2.30 (1H, s; Hμ).
4	−122.0	−0.7 (1B, d, 147; B2), −3.2 (1B, d, 130; B8), −4.5 (1B, d, 147; B5), −17.2 (1B, d, 147; B3), −20.8 (2B, *d*; B4, 11), −21.5 [1B, dd, 145, ^{1}J(BHμ) 50; B10], −32.1 (1B, d, 138; B1), −34.7 (1B, d, 138; B6)	159.9 (d, $^{1}J_{CF}$ 242; CF), 144.6 (s; *ipso*), 129.5 (s; *ortho*), 113.2 (d, $^{3}J_{CF}$ 22; *meta*), 52.6 (s, C7), 31.4 (s, C9)	7.51 (2H, dd, $^{3}J_{HH}$ 8.6, $^{4}J_{HH}$ 5.7; *ortho*), 6.96 (2H, dd, $^{3}J_{HH}$, $^{3}J_{HF}$ 8.6; *meta*), 2.56 (1H, s; B2H), 2.37 (1H, s; B8H), 2.24 (1H, s; B5H), 1.67 (2H, s; B10, 11H), 1.5[e] (2H, m; B3H, C9H), 1.19 (1H, s; B4H), 0.82 (1H, s; B1H), 0.22 (1H, s; B6H), −1.76 (1H, s; Hμ)

[a] 235 MHz ^{19}F in CD$_3$CN at 25°C.

[b] 164 MHz ^{11}B in CD$_3$CN at 25°C (relative intensity, peak pattern, *J*/Hz, assignments), ^{1}J(BH) coupling constants are reported unless otherwise stated.

[c] 63 MHz ^{13}C{^{1}H} in CDCl$_3$ at 25°C for **1** and **2** and in CD$_3$CN at 25°C for **3** and **4** (peak pattern, *J*/Hz, assignments). The shifts of the cation (Bu$_4$N$^+$) in **3** and **4** salts are 58.2 (s; NCH$_2$), 23.2 (s; CH$_2$C$_2$H$_5$), 19.2 (s; CH$_2$CH$_3$) and 12.7 (s; CH$_3$).

[d] 500 MHz ^{1}H{^{11}B} in CDCl$_3$ at 25°C for **1** and **2** and in CD$_3$CN at 25°C for **3** and **4** (relative intensity, peak pattern, *J*/Hz; assignments). The shifts of the cation (Bu$_4$N$^+$) in **3** and **4** salts are 3.05 (8H, m; NCH$_2$), 1.58 (8H, m; C*H*$_2$C$_2$H$_5$), 1.34 (8H, tq, $^{3}J_{HH}$ = 7.3; C*H*$_2$CH$_3$) and 0.95 (12H, t, ^{3}J(HH) 7.3 Hz; CH$_3$).

[e] Obscured by a cation peak.

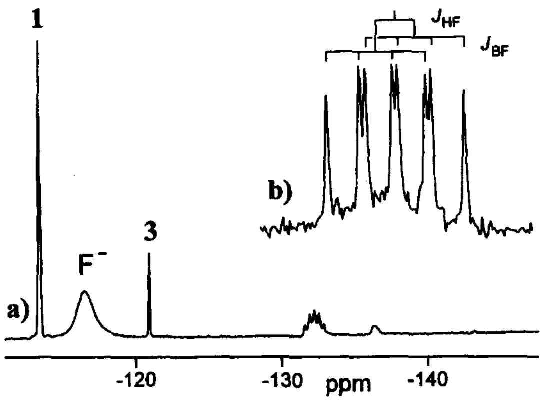

Fig. 2. 235.4 MHz ^{19}F NMR spectra (a) the observed spectrum of the fluoride-ion deboronation of **1** with tetrabutylammonium fluoride hydrate in THF at 1 : 1 ratio after 2 min, (b) expanded spectrum of $HOBHF_2^-$ **5**.

Table 2. Times of conversion in fluoride ion deboronation reactions of **1** and **2** at 25°C. (Carborane concentration initially at 0.143 M.)

Carborane : fluoride ratio	50% conversion[a]	100% conversion[a]
Carborane **1**		
1 : 1	24 h	[b]
1 : 2	34 min	3 days
1 : 3	25 min	5 h
1 : 4	12 min	3 h
Carborane **2**		
1 : 4	4 h	[c]

[a] Time taken for 50% or 100% of the starting carborane, **1** or **2**, to convert to the deboronated carborane, **3** or **4**.
[b] 68% conversion after 12 days.
[c] 88% conversion after 12 days.

took two weeks for *ca.* 90% conversion of **2** into **4**. The preparative reactions we reported previously [9] as being essentially complete after 3.5 h at 25°C were carried out in more concentrated solutions.

Identification of fluoroborates 5–9

The ^{19}F peaks at −136.9, −143.9 and −150.9 ppm from the deboronation were identified as $(HO)_2BF_2^-$ **6**, $HOBF_3^-$ **7** and BF_4^- **8** respectively by comparison with their reported ^{19}F chemical shifts [16,17]. The literature values are for aqueous solutions but these ions show only very small solvent effects to which minor differences from our observations in acetonitrile or tetrahydrofuran solutions are attributable.

In the present study, a further fluoroborate anion was observed by ^{19}F NMR as a doublet of 1 : 1 : 1 : 1 quartets at −132.3 ppm and by ^{11}B as a doublet of triplets at 2.5 ppm, indicating the presence of the HBF_2 unit, presumably in the form of $HOBHF_2^-$ **5**.

Another fluoroborate peak, a doublet of 1 : 1 : 1 : 1 quartets, was seen at −136.3 ppm in the ^{19}F spectrum with the same ^{19}F values as the fluoroborate deduced by Onak [8] to be HBF_3^- from the "anhydrous" fluoride ion deboronation of *meta* carborane; HBF_3^- has been identified previously from H^- (as NaH) and BF_3 but no NMR data were available [18].

Peaks in the ^{19}F NMR spectrum at −132.6 (**A**), −138.7 (**B**) and −144.2 ppm (**C**), which could be new fluoroborates, were observed during the deboronation reactions of **1** and **2**. The ^{19}F NMR spectrum of a mixture of boric acid and tetrabutylammonium fluoride in THF at 25°C showed a major peak at −138.7 ppm (**B**) along with these minor peaks at −132.6 and −144.2. It is likely that these fluoroborates arise from secondary reaction of $B(OH)_3$ and fluoride ion. The resonance **B** may be $B(OH)_3F^-$ which, interestingly, appeared not to have been detected in previous studies of aqueous solutions of boric acid and potassium fluoride [17–20].

Monitoring of the reaction of 1-(4-FC_6H_4)-1,2-$C_2B_{10}H_{11}$ 1 *with fluoride ion*

At 1 : 1 *ratio*. Both the reaction profile (Fig. 3) and the peak intensity data (Table 3) of the reaction between carborane **1** and fluoride ion at ambient temperature demonstrated the changes in the fluoroborate peaks with time. The integrals of the fluoride ion peaks at *ca.* −117 ppm were not recorded, as peaks with variable broadening usually give unreliable measurements. The broadening of the peak at −117 ppm was by hydrogen bonding [19,20] of fluoride ion with a species, possibly a boroxole, formed during the deboronation process.

The initially formed major and minor fluoroborates were thus $HOBHF_2^-$ **5** and $(HO)_2BF_2^-$ **6** respectively.

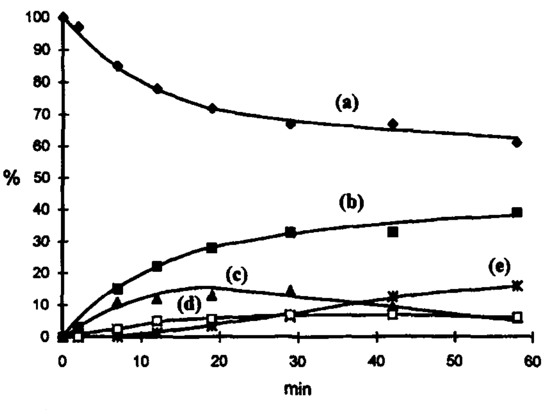

Fig. 3. Reaction profile of the fluoride-ion deboronation of **1** (1 : 1 ratio). 100% represents the total amount of carboranes **1** and **3**. The fluoroborates are shown in relative molar quantities e.g. the peak intensities for **5** are halved. Curve (a) with closed diamonds represent carborane **1**, (b) closed squares, carborane **3**, (c) closed triangles, $HOBHF_2^-$ **5**, (d) open squares, $(HO)_2BF_2^-$ **6**, (e) crosses, $HOBF_3^-$ **7**.

Table 3. ^{19}F and ^{11}B NMR data for fluoroborates **5–9** and **A–D**

	Fluoroborate	δ(^{19}F)(ppm)[a]	δ(^{11}B)(ppm)[b]
5	$[HOBHF_2]^-$	−132.3 [*J*(HF) 85, *J*(BF) 76]	2.5 [*J*(BH) 125, *J*(BF) 75]
6	$[(HO)_2BF_2]^-$	−136.9 [*J*(BF) 29]	2.1 [*J*(BF) 30]
7	$[HOBF_3]^-$	−143.9 [*J*(BF) 16]	1.2 [*J*(BF) 16]
8	$[BF_4]^-$	−150.5	−0.4
9	$[HBF_3]^-$	−136.3 [*J*(HF) 92, *J*(BF) 71]	[c]
A		−132.6	[d]
B	$[FB(OH)_3]^-$?	−138.7 [*J*(BF) 10]	1.5
C		−144.2 [*J*(BF) 12]	0.5[e]
D		−149.4 [*J*(BF) 8]	−0.3[e]

[a] 235 MHz ^{19}F in CD_3CN at 25°C (*J*/Hz).

[b] 80 MHz ^{11}B in CD_3CN at 25°C (*J*/Hz).

[c] Obscured by other borate peaks, reported [8] as 1.5 (140, J_{BF} 71).

[d] Obscured by other borate peaks.

[e] Other peaks may be obscured by other borate peaks.

The initial step involved two molecular proportions of fluoride and one of water for one part of carborane **1** to give the *nido* carborane anion **3** and $HOBHF_2^-$ **5** (eq. (4)). A secondary reaction then took place between **5** and water to give **6** and hydrogen (eq. (5)).

$$\underset{\mathbf{1}}{RC_2B_{10}H_{11}} + 2F^- + H_2O \rightarrow \underset{\mathbf{2}}{RC_2B_9H_{11}^-} + \underset{\mathbf{5}}{HOBHF_2^-}, \quad (4)$$

$$\underset{\mathbf{5}}{HOBHF_2^-} + H_2O \rightarrow \underset{\mathbf{6}}{(HO)_2BF_2^-} + H_2. \quad (5)$$

Gas evolution was at a maximum between 20 and 40 min and the non-condensible gas was presumed to be hydrogen. During that period the resonance at the 20 ppm region was seen as a broad peak in the ^{11}B NMR spectrum expected for an unidentified species containing at least one trigonal boron attached to three oxygens as in boric acid, $B(OH)_3$, or boroxoles $(OBOH)_3$ etc. The decline in the amount of $HOBHF_2^-$ **5** matched the increase in the amount of $HOBF_3^-$ **7** in the same period (see Fig. 3 and Table 4). From these observations $HOBHF_2^-$ gave $(HO)_2BF_2^-$ **6** and hydrogen with water as in step (5) followed by the conversion of **6** into $HOBF_3^-$ **7** and a boroxole polyborate. The peak of the fluoroborate $HOBF_3^-$ **7** slowly decreased in the absence of fluoride ion (see Table 4) to give a peak at −150.5 ppm corresponding to BF_4^- **8**.

The polyborate and the fluorine-containing products **A**, **B**, **C** and **D** formed during the deboronation, but significantly not in the initial stages, were not identified. Species **A**, **B** and **C** were also formed from boric acid and fluoride as described earlier. As they are products of later reactions of the borates initially formed, and as fluoro-monoborate-polyborate systems are known to be complex [17–20] we did not study them further in the present work.

At 4 : 1 *ratio.* Reaction data (Table 5) show similar changes in the fluoroborates as for the 1 : 1 ratio except in the later stages where $HOBF_3^-$ **7** remained as the major fluoroborate product. The excess fluoride ion appeared to prevent the conversion of $HOBF_3^-$ **7** into BF_4^- **8**. Approximately one part of $HOBF_3^-$ **7** and two parts of H_2 were formed from two parts of the carborane **1** and three parts of fluoride. If the polyborate formed is derived from triboric acid $B_3O_3(OH)_3$ as seems likely, the overall reaction can be represented by eq. (6).

$$6\,\underset{\mathbf{1}}{RC_2B_{10}H_{11}} + 9F^- + 9H_2O \rightarrow 6\,\underset{\mathbf{2}}{RC_2B_9H_{11}^-} + 3\,\underset{\mathbf{7}}{HOBF_3^-} + 6H_2 + B_3O_3(OH)_3 \quad (6)$$

Monitoring of the reaction of 1-(4-FC_6H_4)-1,7-$C_2B_{10}H_{11}$ **2** *with fluoride ion reaction at* 4 : 1 *ratio*

At the initial stage in the deboronation of **2** the major fluoroborate produced was $(HO)_2BF_2^-$. Other fluoroborates present were $HOBHF_2^-$, HBF_3^- **9** and $HOBF_3^-$ and these products became dominant after a few minutes (see Table 6). The steps for the deboronation of **1** seem to apply for **2** along with an additional step (7) and thus the overall eq. (8) from steps (4) and (7). The carboranes **2** or **4**, unlike **1** and **3**, may play a part in step (7).

$$HOBHF_2^- + F^- \rightarrow HBF_3^- + OH^-, \quad (7)$$

$$\underset{\mathbf{2}}{RC_2B_{10}H_{11}} + 3F^- + H_2O \rightarrow \underset{\mathbf{4}}{RC_2B_9H_{11}^-} + \underset{\mathbf{9}}{HBF_3^-} + OH^-. \quad (8)$$

The amount of fluoride ion used was found to be slightly higher for the deboronation of **2** (2.3 : 1) com-

Table 4. Deboronation of 1-p-fluorophenyl-*ortho*-carborane at 25°C. Relative ^{19}F peak intensities using a 1 : 1 fluoride : carborane **1** ratio

Species[a]	**1**	**3**	**5**	**6**	**7**	**8**	**A**	**B**	**C**	**D**	Total[b]
2 min	97	3	6	0.5							6.5
7 min	85	15	22	5	1						28
12 min	78	22	24	10	4		2	1			41
19 min	72	28	26	11	11		3	2			53
29 min	67	33	29	13	21		4	3			70
42 min	67	33	19	14	38		6	5	1		83
58 min	61	39	12	12	48		5	7	1		85
201 min	54	46		5	80			16	6		107
26 h	46	54			54			11	40		105
5 days	36	64			5	69		8	9	10	100
12 days	32	68				97		7	2	3	109

[a] Species **9** is observed in trace amounts.
[b] Total ^{19}F peak intensities of all fluoroborates.

Table 5. Deboronation of 1-p-fluorophenyl-*ortho*-carborane at 25°C. Relative ^{19}F peak intensities using a 4 : 1 fluoride : carborane **1** ratio

Species[a]	**1**	**3**	**5**	**6**	**7**	**A**	**B**	**C**	Total
2 min	80	20	20	8	1	2	1		32
7 min	56	44	42	17	10	3	3		75
15 min	48	52	43	21	25	3	5		97
25 min	36	64	31	24	44	8	7		114
35 min	22	78	22	25	59	8	10		124
45 min	18	82	14	23	77	8	9		131
104 min	4	96		15	142	3	11	1	172
204 min		100		9	156	1	10	3	179
6 days		100		7	162		10	3	182

[a] Species **8** and **D** are not observed, **9** observed in trace amounts.

Table 6. Deboronation of 1-p-fluorophenyl-*meta*-carborane at 25°C. Relative ^{19}F peak intensities using a 4 : 1 fluoride : carborane **2** ratio

Species[a]	**2**	**4**	**5**	**6**	**7**	**9**	**A**	**B**	**C**	Total
2 min	96	4	0.5	5	1	2				8.5
6 min	93	7	5	6	3	3				17
15 min	89	11	9	8	7	4		0.5		28.5
25 min	86	14	11	9	14	5		1		40
35 min	81	19	12	8	20	7		1		48
50 min	74	26	16	10	32	9	1	1		69
160 min	59	41	2	10	102	10	2	4		130
12 h	39	61		5	167	12	1	9	4	198
3 days	22	78		3	187	15		13	11	229
12 days	12	88		1	171	13		16	12	213

[a] Species **8** and **D** are not observed.

pared to **1** (1.8 : 1). The difference lies in the additional step in the formation of HBF$_3^-$ where a higher fluoride ion : carborane ratio is involved *cf.* eqs (6) and (8). Fluoroborates produced from the fluoride ion deboronation of **2** were the same as those from the deboronation of **1**, except that a substantial amount of HBF$_3^-$ was formed in the former case. These observations suggest a common deboronation mechanism for *ortho* and *meta* carboranes. We do not exclude the possibility of HF (present as HF_2^- if there is excess fluoride) being involved in the system, e.g. HF and H_2O instead of F^- and OH^- in step (7).

Labelling experiments with deuterium oxide

Experiments with deuterium oxide instead of water in the fluoride ion deboronation were carried out to check whether the B—H bond from the carborane was retained in the fluoroborates, $(HO)HBF_2^-$ and HBF_3^-. The ^{19}F peak patterns expected from $(DO)HBF_2^-$ and HBF_3^- in the deboronation reactions of **1** and **2** with D_2O were seen. The carboranes were identified as **3** and **4** but with deuterium atoms in place of the *endo*/bridging hydrogens. A deuterium-bridged carborane has been reported [21] from facile D_2O exchange with the potassium salt of $7,8\text{-}C_2B_9H_{12}^-$ but control reactions of D_2O with tetrabutylammonium salts **3** and **4** showed no exchange. From these observations, steps (9) and (10) were deduced.

$$RC_2B_{10}H_{11} + 2F^- + D_2O \rightarrow \mu\text{-D-}RC_2B_9H_{10}^- + (DO)HBF_2^-, \quad (9)$$

$$RC_2B_{10}H_{11} + 3F^- + D_2O \rightarrow \mu\text{-D-}RC_2B_9H_{10}^- + HBF_3^- + OD^-. \quad (10)$$

Comparison with "anhydrous" fluoride ion deboronation of ortho- *and* meta-*carborane*

When little water is present in the F^- deboronation of *ortho* carborane we would expect the likely step to be eq. (6) and the fluoroborate $HOBF_3^-$ **7** to be formed. For *meta*-carborane where the amount of water is minimal the preferred step would be eq. (8) and the fluoroborate product, HBF_3^- **9**. The fluoroborates **7** and **9** have indeed been reported from the "anhydrous" fluoride ion deboronation of *ortho*- and *meta*-carborane respectively [8]. The ratio of fluoroborate products of *meta* carborane deboronation, unlike its *ortho* analogue, appear to depend on the amount of water present.

CONCLUSION

This study has shown that the *ortho* and *meta* carboranes, **1** and **2**, when undergoing deboronation by fluoride ion, require two parts of fluoride and one of water to give their respective *nido*-carborane anions, **3** and **4**, and the fluoroborate anion $HOBHF_2^-$. Other fluoroborates and hydrogen have been detected from secondary reactions during the deboronation.

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22.7 to 23.3 and BF_4^- 15.2 to 16.3. Our ^{19}F chemical shift for C_6F_6 in THF is -166.2 ppm.

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