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Cage-fluorination during deboronation of *meta*-carboranes†

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Abstract—Reactions of the *meta* carboranes 1,7-RR′-1,7-$C_2B_{10}H_{10}$ (R, R′ = Me; R = Ph, R′ = Me; R, R′ = Ph; R, R′ = 4-FC_6H_4) with tetrabutylammonium fluoride hydrate (TBAFH) in refluxing tetrahydrofuran gave the corresponding *nido*-7,9-RR′-7,9-$C_2B_9H_{10}^-$ salts. The aryl carboranes and TBAFH also yielded salts of the B-fluorinated anions 10-F-7,9-RR′-7,9-$C_2B_9H_9^-$ and 3-F-7,9-RR′-7,9-$C_2B_9H_9^-$. The reaction of 1,7-(4-FC_6H_4)$_2$-1,7-$C_2B_{10}H_{10}$ with TBAFH monitored by ^{19}F NMR showed cage fluorination occurred during deboronation to give 10-F-7,9-(4-FC_6H_4)$_2$-7,9-$C_2B_9H_9^-$. The latter anion rearranged spontaneously to 3-F-7,9-(4-FC_6H_4)$_2$-7,9-$C_2B_9H_9^-$ under the reaction conditions. The ^{11}B, ^{13}C, ^{1}H and ^{19}F NMR spectra of the carboranes have been assigned. © 1997 Published by Elsevier Science Ltd

Keywords: carborane; deboronation; fluorination; fluoride ion; multinuclear NMR; rearrangement.

Many derivatives of the carborane anion 7,9-$C_2B_9H_{12}^-$ have been synthesized from (i) *closo*-1,7-$C_2B_{10}H_{12}$ derivatives by deboronation with nucleophiles [1–5]; (ii) *closo*-1,8-$C_2B_9H_{11}$ derivatives by reaction with nucleophilic anions [6–8]; (iii) *nido*-7,8- and 7,9-$C_2B_9H_{11}^{2-}$ derivatives by reaction with an organic halide [9,10]; and (iv) *nido*-7,8-$C_2B_9H_{12}^-$ derivatives by thermal rearrangement [11].

Cage substitution at boron is known on occasions to accompany the deboronation reactions whereby *closo* carboranes are converted into *nido* anionic systems. For example, deboronation of 1,7-Me_2-1,7-$C_2B_{10}H_{10}$ **1** with alcoholic KOH gives products that appear to depend on delicate control of reaction conditions. From dimethyl-*meta*-carborane and KOH in ethanol in an autoclave at 160°C for 4–9 hours Hawthorne [13] obtained 7,9-Me_2-7,9-$C_2B_9H_{10}^-$ **2** in 86% yield whereas under virtually identical conditions Rudolph [2] reported 3-EtO-7,9-Me_2-7,9-$C_2B_9H_9^-$ in 40% yield. Rudolph also made 3-MeO- and 3-^{i}PrO-7,9-Me_2-7,9-$C_2B_9H_9^-$ anions with methanol and *iso*-propanol respectively in place of ethanol. Complete degradation of the cage took place with *tert*-butyl alcohol.

When 1,7-Ph_2-1,7-$C_2B_{10}H_{10}$ **3** and anhydrous hydrazine were heated in toluene the hydrazinium salt of 7,9-Ph_2-7,9-$C_2B_9H_{10}^-$ **4** was produced.[4] However in neat boiling hydrazine the diphenyl compound was completely degraded, unlike 1-Ph-1,7-$C_2B_{10}H_{11}$ which gave *nido*-7-Ph-7,9-$C_2B_9H_{11}^-$.

Recently we reported the deboronation of *meta* carboranes with tetrabutylammonium fluoride hydrate (TBAFH) in THF [12]. In doing so we failed to detect the simultaneous cage fluorination that may occur when this reagent is used. Here we discuss reactions of the 1,7-disubstituted-*meta*-carboranes, 1,7-RR′-1,7-$C_2B_{10}H_{10}$ (R,R′ = alkyl or aryl) with TBAFH, and report that in certain cases cage B-fluorinated products are formed.

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. External references for the chemical shifts were $SiMe_4$ = 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

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†Dedicated to Prof. Dr Walter Siebert on the occasion of his 60th birthday.

recorded as potassium bromide discs using a Perkin Elmer 1720X FTIR spectrometer.

Tetra-*n*-butylammonium fluoride hydrate (TBAFH), 4-fluoroiodobenzene, iodomethane and tetrahydrofuran (THF) were obtained commercially (Aldrich) and used as received. Commercial TBAFH contained a minor impurity [$\delta(^{11}B)$, -0.4 ppm; $\delta(^{19}F)$, -150.5 ppm] believed to be $^nBu_4NBF_4$. *Meta* carborane, 1,7-$C_2B_{10}H_{12}$, was purified by sublimation under high vacuum. The carboranes, 1,7-Me_2-1,7-$C_2B_{10}H_{10}$,[1] 1,7-Ph_2-1,7-$C_2B_{10}H_{10}$,[13] 1,2-Ph_2-1,2-$C_2B_{10}H_{10}$ [14] and 1-Ph-7-Me-1,7-$C_2B_{10}H_{10}$ [15] were made by reported methods.

General deboronation procedure with TBAFH

To the carborane (10 mmol) in THF (50 cm^3) was added TBAFH (40–60 mmol). The mixture was heated to reflux (bath temperature 70°C). After cooling the contents were poured into 50 cm^3 of distilled water. The precipitate was filtered off, washed with water, dissolved in CH_2Cl_2 (20 cm^3) and re-washed with water (3 x 20 cm^3). The CH_2Cl_2 solution was dried with anhydrous $MgSO_4$, filtered and evaporated to leave the crude tetrabutylammonium salt of the carborane anion.

Reaction of 1,7-Me_2-1,7-$C_2B_{10}H_{10}$ **1** *with TBAFH*

After 15 h the ^{19}F and ^{11}B NMR of the mixture showed the carborane 7,9-Me_2-7,9-$C_2B_9H_{10}^-$ **2**, $HOBF_3^-$ [$\delta(^{19}F) = 143.9$ ppm [16]; *ca* 50% of peak intensity corresponding to removed boron] and an unidentified polyborate [$\delta(^{11}B) = 22.0$ ppm; *ca* 50% of removed boron]. No ^{19}F peak corresponding to a boron-fluorinated carborane anion was seen. The solid was recrystallized from acetonitrile and identified by NMR as the NBu_4^+ salt of **2** (3.63 g, 90%). This compound is stable in acetonitrile solution (see Table 1) but the solid deteriorated rapidly in air at ambient temperature when an IR band developed at 3226 cm^{-1}; m.p. *ca* 78°C; ν_{max} cm^{-1} 2964 s, 2932 s, 2910 s, 2875 s, 2860 s, (alkyl CH stretch); 2543 s, 2514 s, 2500 s, 2479 s (BH stretch); 1471 s, 1458 m, 1381 w, 1261 w, 1169 w, 1057 m, 1017 m, 837 w, 803 w, 737 m, 449 w.

Reaction of 1,7-Ph_2-1,7-$C_2B_{10}H_{10}$ **3** *with TBAFH*

The *meta* carborane was converted into Bu_4N^+ salts of derivatives of the anion 7,9-$C_2B_9H_{12}^-$ by TBAFH during 8 h. The ^{11}B and ^{19}F NMR spectra of the mixture revealed a polyborate [$\delta(^{11}B) = 22.0$ ppm; *ca* 75% peak intensity of removed boron], $HOBF_3^-$ (*ca* 20%) and a ^{19}F resonance at -138.7 ppm [$FB(OH)_3^-$?] [13] along with a mixture of *nido* carboranes. The solid was recrystallized from acetonitrile and identified by its ^{11}B and ^{19}F NMR spectra as a mixture of NBu_4^+ salts of 7,9-Ph_2-7,9-$C_2B_9H_{10}^-$**4**, 10-F-7,9-Ph_2-7,9-$C_2B_9H_9^-$ **5** and 3-F-7,9-Ph_2-7,9-$C_2B_9H_9^-$ **6** in a 1:2:3 ratio (4.53 g); m.p. *ca* 142°C. Found: C, 66.0; H, 10.2; N, 2.4; Calc. for $C_{30}H_{55}B_9NF$ (**5** and **6**): C, 66.0; H, 10.1; N, 2.6%; ν_{max} cm^{-1} 3079 w, 3055 w, 3027 w, 2999 w (aryl CH stretch); 2962 s, 2935 s, 2875 s (alkyl CH stretch); 2544 sbr (BH stretch); 1593 m, 1575 w, 1491 s, 1480 s, 1463 m, 1444 m, 1419 w, 1379 m, 1347 w, 1264 m, 1243 w, 1205 m, 1142 w, 1103 m, 1061 m, 1029 w, 1002 w, 979 w, 914 w, 892 w, 873 w, 852 w, 801 w, 791 w, 759 m, 702 s, 514 w.

Reaction of 1,2-Ph_2-1,2-$C_2B_{10}H_{10}$ **8** *with TBAFH*

The solution was refluxed for 6 h and the initial deep orange colour became pale yellow. The reaction mixture showed $HOBF_3^-$ (*ca* 50% peak intensity of removed boron) and a polyborate [$\delta(^{11}B) = 22.0$ ppm; *ca* 50%] along with 7,8-Ph_2-7,8-$C_2B_9H_{10}^-$ **7** from ^{19}F and ^{11}B NMR. Recrystallization of the white solid after work-up from ethanol gave white crystals characterized as the NBu_4^+ salt of **7** (4.85 g, 92%); m.p. 209°C; Found: C, 67.9; H, 10.6; N, 2.5; Calc. for $C_{30}H_{56}B_9N$: C, 68.3; H, 10.6; N, 2.7%; ν_{max} cm^{-1} 3080 w, 3058 w, 3024 w (aryl CH); 2962 s, 2935 s, 2875 s (alkyl CH); 2526 sbr (BH); 1597 w, 1481 s, 1459 m, 1443 m, 1380 m, 1349 w, 1261 w, 1152 w, 1107 w, 1067 m, 1021 m, 945 w, 928 w, 889 w, 879 w, 801 w, 767 s, 738 w, 699 s, 475 w.

Rearrangement of 7,8-Ph_2-7,8-$C_2B_9H_{10}^-$ **7** *to* 7,9-Ph_2-7,9-$C_2B_9H_{10}^-$ **4**

The salt of **7** (2.00 g; 3.8 mmol) was heated *in vacuo* at 350°C for 15 min. After cooling, most of the solid was dissolved in acetonitrile. The solution was evaporated to leave a sample of 7,9-Ph_2-7,9-$C_2B_9H_{10}^-$ **4** (1.56 g, 78%); m.p. 138°C. This solid deteriorated slowly in air at ambient temperature over several days during which an IR band developed at 3225 cm^{-1}. Found: C, 68.1; H, 10.7; N, 3.1; Calc. for $C_{30}H_{56}B_9N$: C, 68.3; H, 10.6; N, 2.7%. ν_{max} cm^{-1} 3078 w, 3054 w (aryl CH stretch); 2961 s, 2934 s, 2874 s (alkyl CH stretch); 2531 sbr, 2506 s (BH stretch) 1592 m, 1490 s, 1479 s, 1459 m, 1443 m, 1379 m, 1347 w, 1264 m, 1108 w, 1063 w, 1029 w, 874 w, 760 m, 702 s, 513 w.

Reaction of 1-Ph-7-Me-1,7-$C_2B_{10}H_{10}$ **9** *with TBAFH*

After 8 h the ^{11}B NMR of the reaction mixture showed that over 96% of the carborane had given the NBu_4^+ salt of 7-Ph-9-Me-7,9-$C_2B_9H_{10}^-$ **10**, $HOBF_3^-$ (*ca* 45% intensity of removed boron) and polyborate (*ca* 55%). Its ^{19}F NMR spectrum revealed four peaks at -203.4, -206.1, -215.9 and -217.4 ppm in a peak intensity ratio of 4:7:1:1 corresponding to the minor fluorinated carborane anions, **11**, **12**, **13** and

14. After work up the solid (4.04 g) was air sensitive. At ambient temperature in air an IR band developed at 3225 cm^{-1} in 2 h; m.p. *ca* 89°C; ν_{max} cm^{-1} 3048 w (aryl CH); 2961 s, 2932 s, 2910 s, 2875 s, 2860 s (alkyl CH); 2535 sbr, 2493 sbr (BH); 1591 m, 1482 s, 1458 m, 1442 m, 1380 m, 1261 m, 1215 w, 1151 w, 1091 m, 1027 m, 1014 m, 971 w, 881 w, 851 w, 803 m, 761 m, 738 m, 703 m.

Synthesis of 1,7-$(FC_6H_4)_2$-1,7-$C_2B_{10}H_{10}$ **15**

This compound was made by the copper coupling reaction of 1,7-$C_2B_{10}H_{12}$ (5.76 g; 40 mmol) and 4-FC_6H_4I (19.50 g; 88 mmol). The same procedure [14] as had been used for other 1,7-diaryl-1,7-$C_2B_{10}H_{10}$ derivatives was used in the synthesis of **15**. The solid was washed with acetonitrile then crystallized from hexane (8.23 g; 62%); m.p. 154°C. Found: C, 49.7; H, 5.4; Calc. for $C_{14}H_{18}B_{10}F_2$: C, 50.6; H, 5.4%; ν_{max} cm^{-1} 3080 w, 3070 w (aryl CH); 2640 s, 2613 sbr, 2564 s (BH); 1884 w, 1602 m, 1510 s, 1410 m, 1303 w, 1237 s, 1166 s, 1111 m, 1080 m, 1039 w, 1017 m, 875 m, 865 m, 841 s, 811 m, 739 m, 710 w, 553 m, 530 w, 517 m, 492 w, 423 w.

Reaction of 1,7-$(FC_6H_4)_2$-1,7-$C_2B_{10}H_{10}$ **15** *with TBAFH*

(a) *After* 2 *hours*. The reaction mixture in refluxing THF was quenched with cold water after 2 h and the solid (4.70 g) after work-up was recrystallized from hexane. It was identified by its ^{11}B and ^{19}F NMR spectra as a mixture of NBu_4^+ salts of 7,9-(4-$FC_6H_4)_2$-7,9-$C_2B_9H_{10}^-$ **16**, 10-F-7,9-(4-$FC_6H_4)_2$-7,9-$C_2B_9H_9^-$ **17** and 3-F-7,9-(4-$FC_6H_4)_2$-7,9-$C_2B_9H_9^-$ **18** in a 2 : 15 : 1 ratio; m.p. *ca* 99°C; ν_{max} cm^{-1} 3058 w (aryl CH); 2960 s, 2933 s, 2875 s (alkyl CH); 2540 s (BH); 1594 w, 1507 s, 1484 s, 1463 s, 1379 m, 1299 w, 1262 m, 1237 w, 1217 s, 1157 s, 1097 m, 1067 w, 1054 w, 1018 w, 929 w, 863 s, 833 m, 811 m, 755 w, 738 w, 549 w, 535 w, 523 s.

(b) *After* 12 *hours*. The resulting solid after 12 h reflux was recrystallized from hexane and identified by NMR as a mixture of NBu_4^+ salts of **16**, **17** and **18** in a 1 : 1 : 7 ratio (4.76 g) m.p. *ca* 112°C. Found: C, 62.0; H, 9.4; N, 2.3; Calc. for $C_{30}H_{53}B_9NF_3$ (**17** and **18**): C, 61.9; H, 9.1; N, 2.4%. ν_{max} cm^{-1} 3058 w (aryl CH); 2959 s, 2936 s, 2874 s (alkyl CH); 2531 s (BH); 1593 w, 1506 s, 1484 s, 1460 s, 1379 m, 1263 m, 1218 s, 1159 s, 1097 m, 1059 m, 1017 w, 980 w, 927 w, 877 s, 835 m, 802 m, 737 w, 677 w, 561 w, 548 w, 526 s, 473 w, 420 w.

Reaction of 1,7-$(FC_6H_4)_2$-1,7-$C_2B_{10}H_{10}$ *with TBAFH at* 70°*C monitored by* ^{19}*F NMR*

During the reaction of 1,7-$(FC_6H_4)_2$-1,7-$C_2B_{10}H_{10}$ **15** with TBAFH at 70°C, the mixture was monitored by ^{19}F NMR spectroscopy on samples at intervals. After 10 min, the spectrum showed peaks at -138.7 [$FB(OH)_3$?] and -143.9 ($HOBF_3^-$) ppm in addition to peaks corresponding to a 1 : 9 ratio of 7,9-$(FC_6H_4)_2$-7,9-$C_2B_9H_{10}^-$ **16** and 10-F-7,9-$(FC_6H_4)_2$-7,9-$C_2B_9H_9^-$ **17**. At 20 min over 90% of **15** had reacted (Fig. 1(a)). After 45 min the ^{19}F peak corresponding to the starting carborane **15** had disappeared and the peaks of 3-F-7,9-$(FC_6H_4)_2$-7,9-$C_2B_9H_9^-$ **18** appeared. The peak intensity of 7,9-$(FC_6H_4)_2$-7,9-$C_2B_9H_{10}^-$ **16** remained unchanged whereas the peak intensities of **17** decreased while that of **18** increased. After 8 h the ratio of **16**:**17**:**18** was 2 : 1 : 17 (Fig. 1(b)). This was confirmed by ^{11}B NMR where a broad peak at -20 ppm was also present with a peak intensity equivalent to *ca* 90% of removed boron.

RESULTS AND DISCUSSION

The dimethyl-*meta*-carborane, 1,7-Me_2-1,7-$C_2B_{10}H_{10}$ **1**, and excess TBAFH in refluxing THF for 15 h gave the tetrabutylammonium salt of *nido*-7,9-Me_2-7,9-$C_2B_9H_{10}^-$ **2** quantitatively by ^{11}B and ^{19}F NMR spectra of the product mixture. The salt was found to be air-sensitive like other 7,9-$C_2B_9H_{12}^-$ derivatives reported elsewhere.[8, 16] The ^{11}B NMR data for **2** corresponded to that reported by Hawthorne from the deboronation of **1** with ethanolic potassium hydroxide. The products detected along with the salt of anion **2** were $HOBF_3^-$ (*ca* 50% of the boron removed from cage), an unidentified polyborate [$\delta(^{11}B) = 22.0$ ppm; *ca* 50%] and hydrogen. No evidence was obtained of B-fluorinated *nido*-C_2B_9 carboranes among the products. Synthesis of **2** by the TBAFH method is more convenient than by alcoholic KOH as the latter reagent was reported to require an autoclave at 140°C for 4–9 h [1] and may give anions with an alkoxy group substituted at a cage boron [2].

By contrast, cage fluorinated products were the main products obtained when diphenyl-*meta*-carborane was deboronated using TBAFH. 1,7-Ph_2-1,7-$C_2B_{10}H_{10}$ **3** and TBAFH in THF were deduced by ^{11}B and ^{19}F NMR to have given a mixture of 7,9-Ph_2-7,9-$C_2B_9H_{10}^-$ **4**, 10-F-7,9-Ph_2-7,9-$C_2B_9H_9^-$ **5** and 3-F-7,9-Ph_2-$C_2B_9H_9^-$ **6** in a 2 : 1 : 3 ratio after refluxing for 8 h. Other products detected were the fluoroborate $HOBF_3^-$ (*ca* 10% of boron removed from cage), an unidentified polyborate [$\delta(^{11}B) = 22.0$ ppm *ca* 90%] and hydrogen. The mixture of *nido*-carborane anions was characterized by ^{11}B, ^{13}C, ^{19}F, and ^{1}H NMR with the aid of a pure NBu_4^+ salt of anion **4**. The latter sample was obtained by facile thermal isomerization of 7,8-Ph_2-7,8-$C_2B_9H_{10}^-$ **7** at 350°C *in vacuo* for 15 min like the reported [11] thermal isomerization of Cs^+ 7-Ph-7,8-$C_2B_9H_{11}^-$ to Cs^+ 7,9-Ph-7,9-$C_2B_9H_{11}^-$. The anion **7** was made from 1,2-Ph_2-1,2-$C_2B_{10}H_{10}$ **8** with TBAFH.

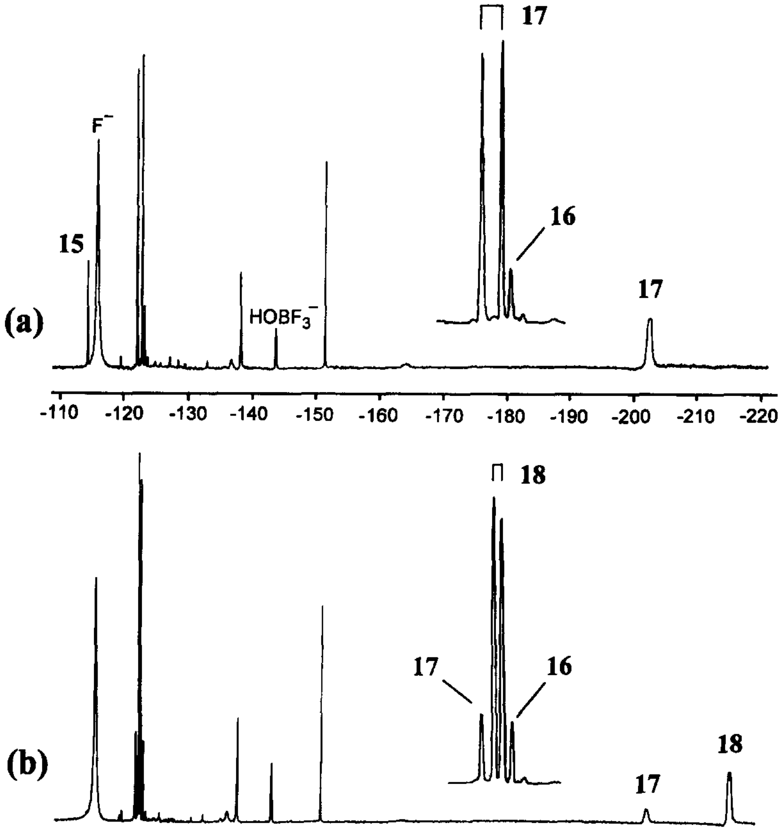
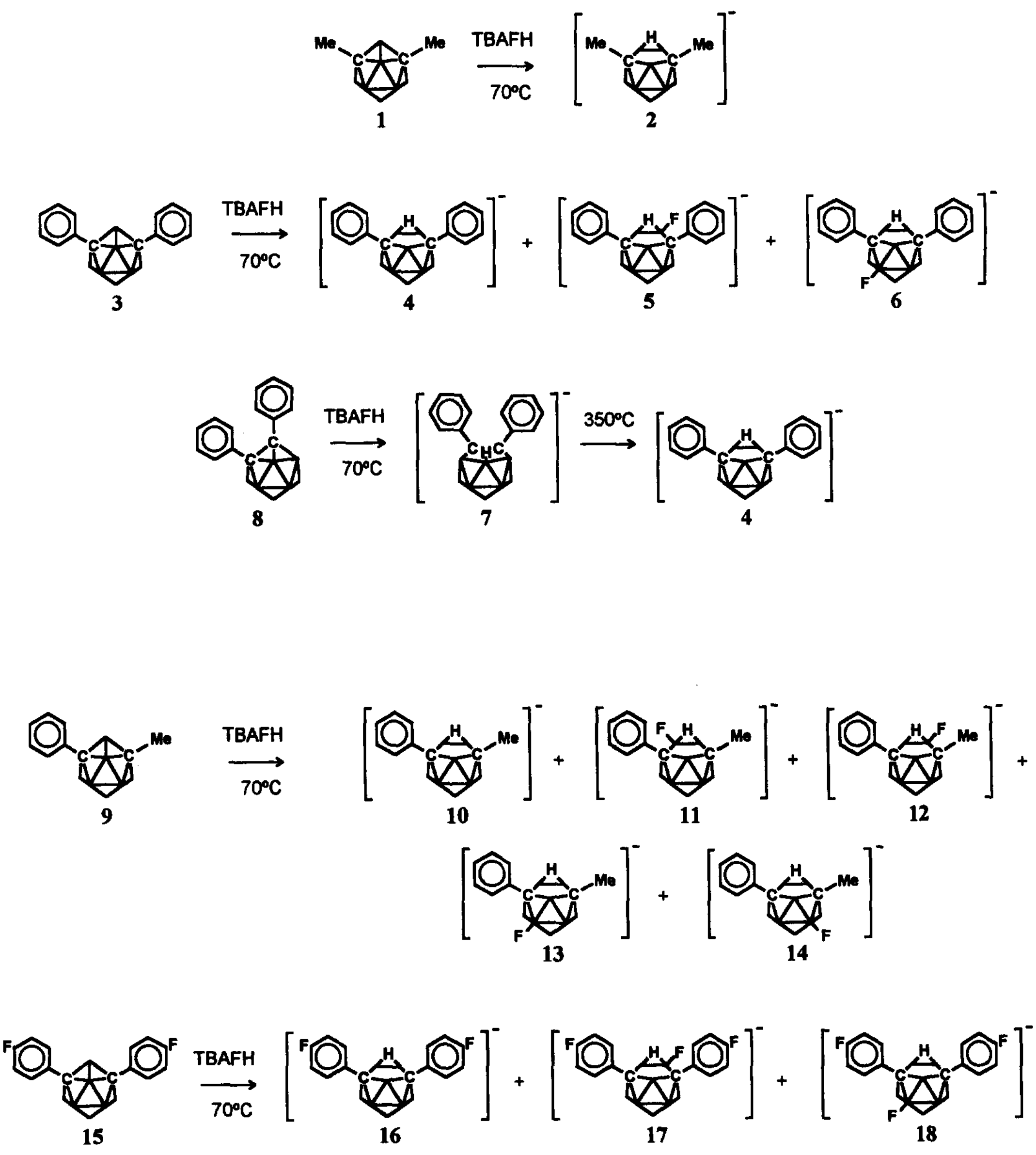


Fig. 1. 235.4 MHz ^{19}F NMR (a) the observed spectrum of the fluoride-ion deboronation of **15** with tetrabutylammonium fluoride hydrate in THF at 1 : 5 ratio after 20 min with expanded spectrum of the −120 ppm region, (b) after 8 h.



With 1-phenyl-7-methyl-*meta*-carborane, deboronation without cage fluorination was the main reaction, though cage fluorinated *nido* carboranes were detected by NMR as minor products. Thus 1-Ph-7-Me-1,7-$C_2B_{10}H_{10}$ **9** with TBAFH gave 7-Ph-9-Me-7,9-$C_2B_9H_{10}^-$ **10** (96% of carborane products), $HOBF_3^-$ (*ca* 45% of removed boron), a polyborate [$\delta(^{11}B) = 22.0$ ppm *ca* 55%] and hydrogen. Four minor carborane anions were observed in the ^{19}F and ^{11}B NMR spectra of the mixture and believed to be 10-, 11-, 3- and 4-F-7-Ph-9-Me-7,9-$C_2B_9H_9^-$ (**11**, **12**, **13** and **14** respectively).

The fluoroaryl labelled aryl carborane 1,7-(4-$FC_6H_4)_2$-1,7-$C_2B_{10}H_{10}$ **15** was made in order to follow the deboronation-fluorination process by ^{19}F NMR. After 20 min, the reaction of **15** with TBAFH in refluxing THF revealed the major product to be 10-F-7,9-(4-$FC_6H_4)_2$-7,9-$C_2B_9H_9^-$ **17** along with the minor products 7,9-(4-$FC_6H_4)_2$-7,9-$C_2B_9H_{10}^-$ **16** and $HOBF_3^-$ when most of the starting carborane had reacted (Fig. 1(a)). After refluxing for 8 h most of the anion **17** had rearranged to 3-F-7,9-(4-$FC_6H_4)_2$-7,9-$C_2B_9H_9^-$ **18** whereas the minor products **16** and $HOBF_3^-$ remained unchanged (Fig. 1(b)).

Our discovery of the cage fluorinations reported here follows our earlier report [12] of the deboronation of various C-substituted *ortho-* and *meta-closo*-carboranes using hydrated tetrabutylammonium fluoride. In that earlier study we used elemental analyses (for C, H and N but not F) and vibrational spectra to characterize the products using ^{11}B and ^{19}F NMR only to follow the course of one particular reaction. Re-examination of these systems using ^{19}F NMR has shown that, although TBAFH can conveniently be used to convert *ortho-* and *meta*-carborane and some of their derivatives into corresponding *nido*-anions $R'R''C_2B_9H_{10}^-$ uncontaminated by cage fluorinated products, the diaryl-*meta*-carboranes $1,7\text{-}Ar_2\text{-}1,7\text{-}C_2B_{10}H_{10}$ (where Ar = 4-$PhOC_6H_4$ or 2-pyridyl) when treated with TBAFH give cage-fluorinated as well as unfluorinated products, and the reaction of TBAFH with the bis(4-nitrophenyl) derivative $1,7\text{-}(4\text{-}O_2NC_6H_4)_2\text{-}1,7\text{-}C_2B_{10}H_{10}$ appears more complex (details unresolved as yet) than we reported in that earlier paper.

We have elsewhere [16] shown that the initial step in the deboronation process, without permanent cage fluorination, involved two parts of fluoride and one of water for one part of carborane to give the fluoroborate $HOBHF_2^-$ as the monoboron product. The fluoroborate then reacted further to give $HOBF_3^-$ (*ca* 50% of boron in $HOBHF_2^-$), a polyborate and hydrogen as observed in the deboronation of **1**, **8** and, to an extent, **9** with TBAFH.

The carborane anion **17** and an unidentified polyborate were obtained as the major products by quenching the reaction of $1,7\text{-}(4\text{-}FC_6H_4)_2\text{-}1,7\text{-}C_2B_{10}H_{10}$ **15** and TBAFH with cold water as soon as all the starting carborane **15** had reacted. Here the fluoroborate $HOBF_3^-$ was not produced thus, by inference, $HOBHF_2^-$ was not formed. The initial step of the deboronation with cage fluorination seems to include B—F bond formation on the open face but not the intermediate $HOBHF_2^-$.

Rearrangement from the initially formed 10-F isomer to the apparently more stable 3-F isomer may well involve a flip of B(8) over the open face (Fig. 2). The B(8) atom of the 10-F isomer migrates to occupy the missing vertex of the icosahedron to form the 3-F isomer. Investigations into other *nido*-$C_2B_9H_{12}^-$ rearrangements also proposed vertex flips of this kind.[10] The factors responsible for the conversion have not been determined. From our results the reported formation of $3\text{-}RO\text{-}7,9\text{-}Me_2\text{-}7,9\text{-}C_2B_9H_9^-$ anions from $1,7\text{-}Me_2\text{-}1,7\text{-}C_2B_{10}H_{10}$ with KOH/ROH probably involves the intermediate $10\text{-}RO\text{-}7,9\text{-}Me_2\text{-}7,9\text{-}C_2B_9H_9^-$.

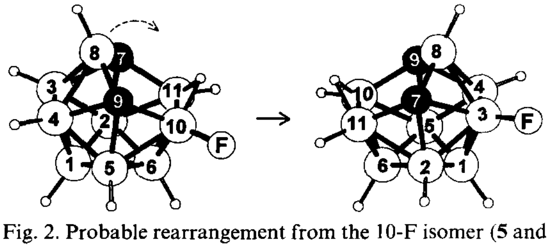


Fig. 2. Probable rearrangement from the 10-F isomer (**5** and **17**) to the 3-F isomer (**6** and **18**). The aryl substituents on cage carbons are omitted for clarity.

Details of the ^{11}B, ^{13}C, ^1H and ^{19}F NMR data of the carboranes studied in the present work are given in Table 1. ^{11}B and ^1H NMR data produced in this work have been assigned by a combination of 2D ^{11}B-$^{11}B\{^1H\}$ COSY and $^{11}B\{^1H\}$-$^1H\{^{11}B\}$correlation spectra and comparison with NMR data of closely related species. ^{13}C and ^1H assignments of the aryl groups were aided by $^{13}C\{^1H\}$-^1H correlation spectra. The limited NMR data reported [17–21] agree with our findings. ^{19}F chemical shifts and $^1J_{BF}$ coupling constants of fluorine atoms attached to cage borons, like the fluorinated salts here, are typically found in the regions of −177.8 to −274.0 ppm and 42 to 64 Hz respectively [5, 22].

CONCLUSIONS

Tetrabutylammonium fluoride hydrate (TBAFH) in refluxing tetrahydrofuran is a convenient reagent by which to convert neutral *closo*-carboranes $R'R''C_2B_{10}H_{10}$ into *nido*-carborane anions $R'R''C_2B_9H_{10}^-$, though its use is not without risk of simultaneous conversion of a cage BH unit into a BF unit, forming anionic products $R'R''C_2B_9H_9F^-$. When used with the parent carboranes 1,2- and $1,7\text{-}C_2B_{10}H_{12}$, with diphenyl-*ortho*-carborane $1,2\text{-}Ph_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ and with dimethyl-*meta*-carborane, $1,7\text{-}Me_2\text{-}1,7\text{-}C_2B_{10}H_{10}$, TBAFH in refluxing THF afforded unfluorinated products $R_2C_2B_9H_{10}^-$ (R = H, Me or Ph). However, some cage fluorination occurred with 1-phenyl-7-methyl-*meta*-carborane and with the diaryl-*meta*-carboranes $1,7\text{-}Ar_2\text{-}1,7\text{-}C_2B_{10}H_{10}$ (Ar = Ph or 4-FC_6H_4) the main products were the fluorinated anions $Ar_2C_2B_9H_9F^-$ in which the BF unit occupied initially the 10 but later the 3 position. Reexamination of the products of reactions between TBAFH in refluxing THF and other diaryl derivatives of *meta*-carborane, $1,7\text{-}Ar_2\text{-}1,7\text{-}C_2B_{10}H_{10}$ (Ar = 4-$PhOC_6H_4$ or 2-pyridyl) reported on previously by us [12] shows that these too had suffered cage fluorination. We conclude that cage fluorination should be considered to be highly likely when TBAFH is used for deboronation of these and other C,C′-diaryl-*meta*-carboranes, and may also occur in reactions involving C-aryl-C′-alkyl-*meta*-carboranes.

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Table 1. ^{11}B, ^{13}C, ^{1}H and ^{19}F NMR data for carboranes **1**–**10** and **15**–**18**

	$\delta(^{11}B)$(ppm)[a]	$\delta(^{13}C\{^1H\})$(ppm)[b]	$\delta(^1H\{^{11}B\})$(ppm)[c]	$\delta(^{19}F)$(ppm)[d]
1[e]	−7.1 (2B, d, 162; B5,12), −9.7 (6B, d, 164[f]; B4,6,8,11,9,10), −11.8 (2B, d, 177; B2,3)	71.3 (s; C1,7), 24.4 (s; CH_3)	2.76 (2H, s; B2,3H), 2.20 (6H, s; B4,6,8,11,9,10H), 2.05 (2H, s; B5,12H), 1.70 (6H, s; CH_3)	
2[g]	−0.1 (1B, d, 133; B8), −2.8 (1B, d, 146; B2,5), −16.8 (2B, d, 143; B3,4), −20.5 (2B, dd, 130, $J_{BH\mu}$ = 48; B10,11), −32.5 (1B, d, 137; B1), −34.8 (1B, d, 138; B6)	42.3 (s; C7,9), 25.5 (s; CH_3)	2.09 (1H, s; B8H), 2.07 (2H, s; B2,5H), 1.41 (6H, s; CH_3), 1.32[f,h] (2H, B10, 11H), 0.97 (2H, s; B3,4H), 0.50 (1H, s; B1H), 0.00 (1H, s; B6H), −1.88 (t, $^2J_{HH}$ = 12; Hμ)	
3[e]	−5.2 (2B, d, 154; B5,12), −9.7 (6B, d, 156[f]; B4,6,8,11,9,10), −12.5 (2B, d, 178; B2,3)	135.2 (s; *ipso* phenyl C), 128.7 (s; *meta*), 128.4 (s; *para*), 127.8 (s; *ortho*), 78.2 (C1,7)	7.54 (4H, d, $^3J_{HH}$ = 8; *ortho* phenyl CH), 7.33 (4H, m; *meta*), 7.31 (2H, m; *para*), 3.31 (2H, s; B2,3H), 2.69 (2H, s; B9,10H), 2.63 (4H, s; B4,6,8,11H), 2.34 (2H, s; B5,12H)	
4[g]	−1.6 (3B, d, 138[f]; B2,5,8), −17.7 (2B, d, 147; B3,4), −20.5 (2B, dd, 138, $J_{BH\mu}$ = 41; B10,11), −31.0 (1B, d, 138; B1), −35.1 (1B, d, 138; B6)	148.2 (s; *ipso*), 128.4 (s; *ortho*), 127.0 (s; *meta*), 123.9 (s; *para*), 53.3 (s; C7,9)	7.42 (4H, d, $^3J_{HH}$ = 8; *ortho*), 7.11 (4H, dd, $^3J_{HH}$ = 7.5[f]; *meta*), 7.00 (1H, t, $^3J_{HH}$ = 7; *para*), 2.73 (1H, s; B8H), 2.60 (2H, s; B2,5H), 1.81 (2H, d, $^2J_{HH}$ = 12; B10,11H), 1.45 (2H, s; B3,4H), 0.93 (1H, s; B1H), 0.32 (1H, s; B6H), −1.19 (1H, t, $^2J_{HH}$ = 12; Hμ)	
5[g]	1.4 (1B, s; B10), −1.0 (1B, d, 141; B2), −2.9 (2B, d, 138[f]; B8,B5), −17.6 (1B, d, 146; B4), −22.9 (1B, dd, 150[f], $J_{BH\mu}$ = 50[f]; B11), −24.6 (1B, d, 151; B3), −34.0 (1B, d, 141; B1), −35.9 (1B, d, 140; B6)	148.4 (s, *ipso*[i]), 145.4 (s, *ipso*), 129.7 (s; *ortho*), 128.6 (s; *ortho*[i]), 127.3 (s; *meta*), 127.1 (s; *meta*[i]), 124.6 (s; *para*), 124.1 (s; *para*[i]), 53.5 (s; C7), 48.3 (s; C9)	7.46 (2H, d, $^3J_{HH}$ = 8; *ortho*), 7.42 (2H, d, $^3J_{HH}$ = 8; *ortho*[i]), 7.19 (2H, dd, $^3J_{HH}$ = 7.5; *meta*), 7.13 (2H, dd, $^3J_{HH}$ = 7.5; *meta*[i]), 7.06 (1H, t, $^3J_{HH}$ = 7; *para*), 7.02 (1H, t, $^3J_{HH}$ = 7; *para*[i]), 2.80 (1H, s; B2H), 2.68 (1H, s; B5H), 2.55 (s, B8H), 2.05 (1H, d, $^2J_{HH}$ = 13.5[f]; B11H), 1.50 (1H, s; B4H), 1.09 (1H, s; B3H), 0.77 (1H, s; B1H), 0.63 (1H, dd, $^2J_{HF}$ = 24.5, $^2J_{HH}$ = 13.5; Hμ), 0.48 (1H, s; B6H)	−202.1 (brs; BF)
6[g]	1.6 (1B, s; B3), −1.5 (1B, *d*; B5), −3.0 (1B, *d*; B8), −4.2 (1B, *d*; B2), −19.9 (1B, *d*; B4), −20.6 (1B, *dd*; B11), −26.3 (1B, dd, 150[f], $J_{BH\mu}$ = 50[f]; B10), −32.5 (1B, 140, d; B1), −38.5 (1B, 141, d; B6)	148.3 (s; *ipso*), 145.3 (s; *ipso*[i]), 128.8 (s; *ortho*[i]), 128.5 (s; *ortho*), 127.2 (s; *meta*[i]), 127.1 (s; *meta*), 124.2 (s; *para*[i]), 124.0 (s; *para*), 54.9 (s; C9), 49.1 (s; C7)	7.48 (2H, d, $^3J_{HH}$ = 8.4; *ortho*[i]), 7.39 (2H, d, $^3J_{HH}$ = 8.4; *ortho*), 7.18 (2H, dd, $^3J_{HH}$ = 7.5[f]; *meta*[i]), 7.12 (2H, dd, $^3J_{HH}$ = 7.5[f]; *meta*), 7.06 (1H, t, $^3J_{HH}$ = 7; *para*[g]), 7.01 (1H, t, $^3J_{HH}$ = 7; *para*), 2.86 (1H, s; B8H), 2.72 (1H, s; B5H), 2.66 (1H, s; B2H), 1.72 (1H, d; B11H), 1.46 (2H, s; B4,10H), 1.23 (1H, s; B1H), 0.24 (1H, s; B6H), −1.30 (1H, t, $^2J_{HH}$ = 12; Hμ)	−215.2 (q, $^1J_{BF}$ = 55; BF)
7[g]	−7.3 (2B, d, 135; B9,11), −13.5 (1B, d, 156; B3), −15.7 (2B, d, 135; B5,6), −18.0 (2B, d, 148; B2,4), −32.3 (1B, dd, 141, $J_{BH\mu}$ = 50; B10), −34.7 (1B, d, 140; B1)	141.8 (s; *ipso*), 131.7 (s; *ortho*), 126.4 (s; *meta*), 125.3 (s; *para*), 68.5 (q, J_{BC} = 21[f]; C7,8)	7.27 (4H, d, $^3J_{HH}$ = 8.0; *ortho*), 7.02 (4H, m; *meta*), 7.00 (2H, m; *para*), 2.60 (1H, s; B3H), 2.14 (2H, s; B9,11H), 1.57 (1H, s; B2,4H), 1.33 (2H, s; B5,6H), 0.74 (1H, s; B1H), 0.23 (1H, brs; B10H), −1.75 (1H, d, $^2J_{HH}$ = 5.5 Hz; Hμ)	
8[e]	0.7 (2B, d, 147; B9,12), −6.0 (4B, d, 161[f]; 4,5,7,11), −7.2 (2B, *d*; B8,10), −8.2 (2B, d, 168[f]; B3,6)	130.6 (s; *ortho*), 130.5 (s; *ipso*), 130.1 (s; *para*), 128.2 (s; *meta*), 85.2 (s; C1,2)	7.46 (2H, d, $^3J_{HH}$ = 8; *ortho*), 7.24 (1H, t, $^3J_{HH}$ = 7.2; *para*), 7.15 (2H, t, $^3J_{HH}$ = 7.5[f]; *meta*), 3.27 (2H, s; B3,6H), 2.55 (6H, s; B4,5,7,11,9,12H), 2.37 (2H, s; B8,10H)	
9[e]	−4.3 (1B, d, 160; B5), −7.1 (1B, d, 163; B12), −9.4 (6B, d, 152[f]; B4,6,8,11,9,10), −11.7 (2B, d, 178; B2,3)	135.2 (s; *ipso* C), 128.6 (s; *meta*), 128.3 (s; *para*), 127.8 (s; *ortho*), 78.8 (s; C1), 70.7 (s; C7), 24.7 (s; CH_3)	7.33 (2H, d, $^3J_{HH}$ = 8; *ortho*), 7.16 (3H, m; *meta,para*), 3.10 (2H, s; B2,3H), 2.57 (3H, s; B9,10,12H), 2.47 (1H, s; B5H), 2.40 (2H, s; B4,6H), 2.27 (2H, s; B8,11H), 1.83 (3H, s; CH_3)	

Table 1. *Continued*

	$\delta(^{11}B)$(ppm)[a]	$\delta(^{13}C\{^1H\})$(ppm)[b]	$\delta(^1H\{^{11}B\})$(ppm)[c]	$\delta(^{19}F)$(ppm)[d]
10[g]	−0.7 (2B, d, 138[f]; B2,8), −3.7 (1B, d, 138; B5), −16.9 (1B, d, 146[f]; B3), −17.7 (1B, d, 147[f]; B4), −19.9 (1B, dd, 130, $J_{BH\mu} = 33$; B11), −21.4 (1B, dd, 130, $J_{BH\mu} = 45$; B10), −31.7 (1B, d, 138; B1), −35.1 (1B, d, 138; B6)	148.8 (s; *ipso*), 128.4 (s; *ortho*), 127.0 (s; *meta*), 123.6 (s; *para*), 53.1 (s; C7), 43.3 (s; C9), 25.3 (s; CH_3)	7.38 (2H, d, $^3J_{HH} = 7.5$; *ortho*), 7.08 (2H, t, $^3J_{HH} = 7$[f]; *meta*), 6.96 (1H, t, $^3J_{HH} = 6.5$; *para*), 2.45 (1H, s; B8H), 2.41 (1H, s; B2H), 2.32 (1H, s; B5H), 1.70[h] (4H; B10H,CH_3), 1.53[f,h] (1H, *d*; B11H), 1.33 (1H, s; B4H), 1.15 (1H, s; B3H), 0.76 (1H, s; B1H), 0.20 (1H, s; B6H), −1.51 (1H, t, $^2J_{HH} = 12$; Hμ)	
15[e]	−4.9 (2B, d, 153; B5,12), −9.4 (6B, d, 156[f]; B4,6,8,11,9,10), −12.2 (2B, d, 178; B2,3)	162.9 (d, $^1J_{CF} = 249$; *para*), 131.0 (s; *ipso*), 129.6 (d, $^4J_{CF} = 7.5$; *ortho*), 115.2 (d, $^3J_{CF} = 22$; *meta*), 77.5 (s; C1,7)	7.44 (4H, dd, $^3J_{HH} = 8.75$, $^4J_{HF} = 5.0$; *ortho*), 6.95 (4H, dd, $^3J_{HH}$, $^3J_{HF} = 8.5$[f]; *meta*), 3.25 (2H, s; B2,3H), 2.64 (2H, s; B9, 10H), 2.60 (4H, s; B4,6,8,11H), 2.32 (2H, s; B5,12H)	−113.4 (s, CF)
16[g]	−1.6 (3B, *d*; B2,5,8), −17.3 (2B, *d*; B3,4), −20.4 (2B, *dd*; B10,11), −30.8 (1B, *d*; B1), −34.9 (1B, *d*; B6)	160.2 (d, $^1J_{CF} = 240$; *para*), 143.4 (s; *ipso*), 129.9 (d, $^4J_{CF} = 8$; *ortho*), 113.4 (d, $^3J_{CF} = 21$; *meta*), 53.1 (s; C7,9)	7.42 (4H, dd, $^3J_{HH} = 8.75$, $^4J_{HF} = 5.0$; *ortho*), 6.87 (4H, dd, $^3J_{HH}$, $^3J_{HF} = 8.75$; *meta*), 2.73 (1H, s; B8H), 2.60 (2H, s; B2,5H), 1.81 (2H, d, $^2J_{HH} = 12$; B10,11H), 1.45 (2H, s; B3, 4H), 0.93 (1H, s; B1H), 0.32 (1H, s; B6H), −1.19 (1H, t, $^2J_{HH} = 12$; Hμ)	−123.2 (s; CF)
17[g]	1.3 (1B, s; B10), −1.0 (1B, d, 141; B2), −2.7 (2B, d, 138[f]; B8, B5), −17.4 (1B, d, 146; B4), −22.8 (1B, dd, 150[f], $J_{BH\mu} = 50$[f]; B11), −24.5 (1B, d, 151; B3), −34.0 (1B, d, 141; B1), −35.9 (1B, d, 140; B6)	160.6 (d, $^1J_{CF} = 240$; *para*), 160.3 (d, $^1J_{CF} = 240$; *para*[i]), 143.6 (s; *ipso*[i]), 140.4 (s; *ipso*), 131.2 (d, $^4J_{CF} = 8$; *ortho*), 130.1 (d, $^4J_{CF} = 8$; *ortho*[i]), 113.8 (d, $^3J_{CF} = 21$[f]; *meta*), 113.5 (d, $^3J_{CF} = 21$[f]; *meta*[i]), 51.8 (s; C7), 47.0 (s; C9)	7.48 (2H, dd, $^3J_{HH} = 8.75$, $^4J_{HF} = 5.0$; *ortho*), 7.44 (2H, dd, $^3J_{HH} = 8.75$, $^4J_{HF} = 5.0$; *ortho*[i]), 6.95 (2H, t, $^3J_{HH}$, $^3J_{HF} = 8.75$[f]; *meta*), 6.88 (2H, t, $^3J_{HH}$, $^3J_{HF} = 8.75$[f]; *meta*[i]), 2.81 (1H, s; B2H), 2.70 (1H, s; B5H), 2.57 (s, B8H), 2.05 (1H, d, $^2J_{HH} = 13.5$[f]; B11H), 1.50 (1H, s; B4H), 1.11 (1H, s; B3H), 0.76 (1H, s; B1H), 0.62 (1H, dd, $^2J_{HF} = 24.5$, $^2J_{HH} = 13.5$; Hμ), 0.48 (1H, s; B6H)	−122.1 (1F, s; CF), −122.9 (1F, s, CF), −202.7 (1F, brs, BF)
18[g]	1.6 (1B, s; B3), −1.6 (1B, *d*; B5), −2.9 (1B, *d*; B8), −3.9 (1B, *d*; B2), −19.7 (1B, *d*; B4), −20.5 (1B, *dd*; B11), −25.1 (1B, dd, 150[f], $J_{BH\mu} = 50$[f]; B10), −32.5 (1B, d, 140; B1), −38.4 (1B, d, 141; B6)	160.7 (d, $^1J_{CF} = 240$; *para*[i]), 160.3 (d, $^1J_{CF} = 240$; *para*), 143.5 (s; *ipso*), 140.4 (s; *ipso*[i]), 130.4 (d, $^4J_{CF} = 8$; *ortho*[i]), 130.0 (d, $^4J_{CF} = 8$; *ortho*), 113.7 (d, $^3J_{CF} = 21$[f]; *meta*[i]), 113.5 (d, $^3J_{CF} = 21$[f]; *meta*), 53.2 (s; C9), 47.8 (s; C7)	7.48 (2H, dd, $^3J_{HH} = 8.75$, $^4J_{HF} = 5.0$; *ortho*[i]), 7.39 (2H, dd, $^3J_{HH} = 8.75$, $^4J_{HF} = 5.0$; *ortho*), 6.94 (2H, t, $^3J_{HH}$, $^3J_{HF} = 8.5$[f]; *meta*), 6.87 (2H, t, $^3J_{HH}$, $^3J_{HF} = 8.5$[f]; *meta*[i]), 2.90 (1H, s; B8H), 2.68 (1H, s; B5H), 2.64 (1H, s; B2H), 1.73 (1H, d; B11H), 1.47 (2H, s; B4,10H), 1.22 (1H, s; B1H), 0.25 (1H, s; B6H), −1.33 (1H, t, $^2J_{HH} = 12$; Hμ)	−122.6 (1F, s; CF), −122.9 (1F, s; CF), −216.5 (1F, q, $^1J_{BF} = 56$; BF)

[a] 164 MHz ^{11}B at 25°C (relative intensity, peak pattern, *J*(Hz); assignments), $^1J_{BHt}$ coupling constants are reported unless otherwise stated.

[b] 63 MHz $^{13}C\{^1H\}$ at 25°C (peak pattern, *J*(Hz); assignments).

[c] 500 MHz $^1H\{^{11}B\}$ at 25°C (relative intensity, peak pattern, *J*(Hz); assignments).

[d] 235 MHz ^{19}F at 25°C (relative intensity, peak pattern, *J*(Hz); assignments).

[e] In $CDCl_3$.

[f] Values are uncertain due to overlapping or poorly resolved peaks.

[g] As $^nBu_4N^+$ salt in CD_3CN at 25°C, NMR data for the cation $^nBu_4N^+$ ^{13}C; 58.2 (s; NCH_2), 23.2 (s; $CH_2C_2H_5$), 19.2 (s; CH_2CH_3) and 12.7 (s; CH_3); ^1H; 3.05 (8H, m; NCH_2), 1.58 (8H, m; $CH_2C_2H_5$), 1.34 (8H, tq, $^3J_{HH} = 7.3$; CH_2CH_3) and 0.95 (12H, t, $^3J_{HH}$ 7.3 Hz; CH_3).

[h] Obscured by cation peak.

[i] Of the aryl group attached to C7.

REFERENCES

1. M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owen, S. G. Schwerin, F. N. Tebbe and P. A. Wegner, *J. Am. Chem. Soc.* 1968, **90,** 862.
2. W. R. Pretzer, D. A. Thompson and R. W. Rudolph, *Inorg. Chem.* 1975, **14,** 2571.
3. L. I. Zakharkin and V. N. Kalinin, *J. Gen. Chem. USSR,* (*Engl. Transl*) 1965, **35,** 1693; L. I. Zakharkin and V. N. Kalinin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* 1967, 462; P. M. Garrett, T. A. George and M. F. Hawthorne, *Inorg. Chem.* 1969, **8,** 2008.
4. V. I. Stanko and V. A. Brattsev, *J. Gen. Chem. USSR,* (*Engl. Transl*) 1967, **37,** 486; V. I. Stanko and V. A. Brattsev, *J. Gen. Chem. USSR,* (*Engl. Transl*) 1968, **38,** 636.
5. H. Tomita, H. Luu and T. Onak, *Inorg. Chem.* 1991, **30,** 812.
6. V. Chowdhry, W. R. Pretzer, D. N. Rai and R. W. Rudolph, *J. Am. Chem. Soc.* 1973, **95,** 4560.
7. M. F. Hawthorne and D. A. Owen, *J. Am. Chem. Soc.* 1968, **90,** 5912; D. A. Owen and M. F. Hawthorne, *J. Am. Chem. Soc.* 1969, **91,** 6002; G. D. Mercer and F. R. Scholer, *Inorg. Chem.* 1974, **13,** 2256; L. J. Todd, A. R. Siedle, F. Sato, A. R. Garber, F. R. Scholer and G. D. Mercer, *Inorg. Chem.* 1975, **14,** 1249.
8. J. D. Hewes, M. Thompson and M. F. Hawthorne, *Organometallics* 1985, **4,** 13.
9. V. A. Brattsev, S. P. Knyazev and V. I. Stanko, *J. Gen. Chem. USSR,* (*Engl. Transl*) 1975, **45,** 1173; Yu. T. Struchkov, M. Yu. Antipin, V. I. Stanko, V. A. Brattsev, N. I. Kirillova and S. P. Knyazev, *J. Organometal. Chem.* 1977, **141,** 133; S. P. Knyazev, V. A. Brattsev and V. I. Stanko, *J. Gen. Chem. USSR,* (*Engl. Transl*) 1977, **47,** 2627; L. I. Zakharkin, G. G. Zhigareva, V. A. Antonovich and Yu. T. Struchkov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* 1984, 1534.
10. S. P. Knyazev, V. A. Brattsev and V. I. Stanko, *Dokl. Akad. Nauk SSSR,* (*Engl. Transl*) 1977, **234,** 323; L. I. Zakharkin, G. G. Zhigareva, V. A. Antonovich, A. I. Yanovskii and Yu. T. Struchkov, *J. Gen. Chem. USSR,* (*Engl. Transl*) 1986, **56,** 1823.
11. P. M. Garrett, F. N. Tebbe and M. F. Hawthorne, *J. Am. Chem. Soc.* 1964, **86,** 5016.
12. M. A. Fox, W. R. Gill, P. L. Herbertson, J. A. H. MacBride, K. Wade and H. M. Colquhoun, *Polyhedron* 1996, **15,** 565.
13. R. Coult, M. A. Fox, W. R. Gill, P. L. Herbertson, J. A. H. MacBride and K. Wade, *J. Organometal. Chem.* 1993, **462,** 19.
14. V. I. Stanko, V. V. Kopylov and A. I. Klimova, *J. Gen. Chem. USSR,* (*Engl. Transl*) 1965, **35,** 1437; M. M. Fein, J. Bobinski, N. Mayes, N. Schwartz and M. S. Cohen, *Inorg. Chem.* 1963, **2,** 1111.
15. L. I. Zakharkin and A. V. Kazantsev, *J. Gen. Chem. USSR,* (*Engl. Transl*) 1967, **37,** 1149.
16. M. A. Fox, J. A. H. MacBride and K. Wade. *Polyhedron* 1997, **16,** 2499.
17. Ref. 1. For the Me_3NH^+ salt of **2** in $(CD_3)_2CO$; ^{11}B; 3.7 (128), 4.3 (131), 17.5 (133), 19.1 (124), 32.7 (136): ^1H; 1.42 (CMe).
18. J. Cowie, D. J. Donohue, N. L. Douek and A. J. Welch, *Acta Cryst.* 1993, **C49,** 710. For the Et_3NH^+ salt of **7,** solvent unknown; ^{11}B; −6.5 (2B), −12.8 (1B), −14.8 (2B), −17.3 (2B), −31.5 ($J_{BH\mu}$ = 50, 1B), −33.8 (1B).
19. L. I. Zakharkin, V. N. Kalinin, E. G. Rhys and V. A. Antonovich, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* 1980, 1446. For **3** ^{13}C(THF); 135.31 (*ipso*), 128.94, 128.55, 127.90, 78.8 (cage C). For **8** ^{13}C(THF); 126.99, 126.08, 119.98, 85.8 (cage C).
20. Ref. 8. For the Me_3NH^+ salt of **10,** ^{11}B (THF); −1.3 (2B), −3.9 (1B), −17.3 (2B), −20.2 (1B), −21.8 (1B), −31.9 (1B), −35.1 (1B): ^1H ($(CD_3)_2CO$); 7.14 (d,2H), 6.72 (m, 3H), 1.77 (s, 3H).
21. L. J. Todd, A. R. Siedle, G. M. Bodner, S. B. Kahl and J. P. Hickey, *J. Magn. Reson.* 1976, **23,** 301. For **1** in $(CD_3)_2CO$ ^{11}B; 7.2 (B5,12), 9.9 (B4,6,8,11,9,10), 11.7 (B2,3), ^{13}C; 72.1 (C1,7), 36.4 (CH_3). For **3** in $(CD_3)_2CO$, ^{13}C; 79.3 (C1,7).
22. V. N. Lebedev, M. V. Galakhov, V. I. Bakhmutov and L. I. Zakharkin, *Organometal. Chem. USSR* 1989, **2,** 493; L. I. Zakharkin, V. N. Kalinin, B. A. Kvasov and E. I. Fedin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* 1968, 2415; V. N. Lebedev, E. V. Balagurova, A. V. Polyakov, A. I. Yanovsky, Yu. T. Struchkov and L. I. Zakharkin, *J. Organometal. Chem.* 1990, **385,** 307. The reported chemical shifts are referenced to CF_3CO_2H, $\delta(CFCl_3) = \delta(CF_3CO_2H) - 75.0$ ppm.