Deboronation of 9-substituted-*ortho*- and -*meta*-carboranes[1]

Mark A. Fox *, Kenneth Wade

Department of Chemistry, University of Durham, South Road, Durham, DH1 3LE, UK

Abstract

A systematic study has been carried out of deboronation reactions of a series of icosahedral carborane derivatives bearing a variety of substituents on selected (generally antipodal) boron atoms. Reactions of the 9-substituted *meta*-carboranes, $9\text{-}R\text{-}1,7\text{-}C_2B_{10}H_{11}$ (R = OH, 4-MeC$_6$H$_4$, F, Cl, Br, I), with tetrabutylammonium fluoride hydrate (TBAFH) in refluxing THF gave *nido*-carborane salts containing a mixture of 1- and $6\text{-}R\text{-}7,9\text{-}C_2B_9H_{11}^-$ *nido*-anions. Regioselective deboronation occurred with the 9-halo-*meta*-carboranes, $9\text{-}X\text{-}1,7\text{-}C_2B_{10}H_{11}$ (X = F, Cl, Br, I), producing a 2:1 ratio mixture of *nido* $6\text{-}X\text{-}7,9\text{-}C_2B_9H_{11}^-$ and $1\text{-}X\text{-}7,9\text{-}C_2B_9H_{11}^-$. Calculated Mulliken charges at B2 and B3 of some 9-substituted-*meta* carboranes show that these vary in line with observed deboronation rates and product ratios in their reactions with TBAFH. The *ortho*-carborane derivative $9\text{-}I\text{-}1,2\text{-}C_2B_{10}H_{11}$ and TBAFH gave the tetrabutylammonium salt of the *nido* anion $5(6)\text{-}I\text{-}7,8\text{-}C_2B_9H_{11}^-$. The mercurated and thallated *meta* carboranes, $9\text{-}M\text{-}1,7\text{-}C_2B_9H_{11}$ (M = HgOCOCF$_3$ and Tl(OCOCF$_3$)$_2$), with TBAFH underwent boron–metal bond cleavage to yield mainly the *nido* anion $7,9\text{-}C_2B_9H_{12}^-$. Multinuclear (^{11}B, ^{13}C, ^{1}H, ^{19}F) NMR spectra of the carboranes have been recorded and assigned. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ortho-carborane; Meta-carborane; Deboronation; Multinuclear NMR; Nido-carborane anion; Ab initio computations

1. Introduction

Removal of a boron atom from a *closo* carborane $C_2B_{10}H_{12}$ using a strong nucleophile to give a *nido* carborane anion $C_2B_9H_{12}^-$ has been known for more than three decades [1]. These *nido*-anions are precursors to a large number of metallacarborane sandwich compounds and heteroboranes [2]. Strong nucleophiles like ethanolic potassium hydroxide and tetrabutylammonium fluoride hydrate (TBAFH) convert *ortho* carbo-

rane $1,2\text{-}C_2B_{10}H_{12}$ or its alkyl and aryl derivatives $1,2\text{-}R,R'\text{-}1,2\text{-}C_2B_{10}H_{10}$ into the *nido*-anion $7,8\text{-}C_2B_9H_{12}^-$ or derivatives $7,8\text{-}R,R'\text{-}7,8\text{-}C_2B_9H_{10}^-$ [3–7]. Under more forcing conditions *meta* carborane $1,7\text{-}C_2B_{10}H_{12}$ and its alkyl or aryl derivatives $1,7\text{-}R,R'\text{-}1,7\text{-}C_2B_{10}H_{10}$ yield *nido* anions $7,9\text{-}C_2B_9H_{12}^-$ and $7,9\text{-}R,R'\text{-}7,9\text{-}C_2B_9H_{10}^-$, respectively (see Fig. 1, which shows the numbering systems and possible anions formed from deboronation of substituted *ortho* or *meta* carboranes).

The most electropositive boron atom B3 or B6 is removed from *ortho*-carborane $1,2\text{-}C_2B_{10}H_{12}$ to give the *nido* anion $7,8\text{-}C_2B_9H_{12}^-$ whereas the B2 or B3 atom is removed from *meta*-carborane $1,7\text{-}C_2B_{10}H_{12}$ to yield $7,9\text{-}C_2B_9H_{12}^-$ in the deboronation process. For example, deboronation of an 8-substituted *ortho*-carborane is expected to produce a mixture of 1- and 10-substituted-

* Corresponding author. Fax: +44 191 3861127; e-mail: m.a.fox@durham.ac.uk

[1] Dedicated to Professor Brian F.G. Johnson on the occasion of his 60th birthday in recognition of his outstanding contributions to organometallic and cluster chemistry.

nido anions whereas a 9-substituted *ortho*-carborane would give 5- and 6-substituted *nido* anions (enantiomers). These predictions assume no cage rearrangements occur during the process.

Products containing *nido*-anions generated from *ortho* and *meta* carboranes with a substituent at a boron atom reported earlier are shown by Eqs. (a–e). Reactions of the iodocarboranes, $9\text{-}I\text{-}1,2\text{-}C_2B_{10}H_{11}$ and $9\text{-}I\text{-}1,7\text{-}C_2B_{10}H_{11}$, with piperidine gave anions of formulae $B\text{-}I\text{-}7,8\text{-}C_2B_9H_{11}^-$ and $B\text{-}I\text{-}7,9\text{-}C_2B_9H_{11}^-$ but the positions

of the iodine atoms were not determined [8]. Deboronation of several 3-substituted *ortho* carboranes, $3\text{-}R\text{-}1,2\text{-}C_2B_{10}H_{11}$, in alcoholic KOH solution gave either $3\text{-}R\text{-}7,8\text{-}C_2B_9H_{11}^-$ (when R = Ph, Et, NC, NHR) or $7,8\text{-}C_2B_9H_{12}^-$ (when R = OH) or both possible *nido* anions (when R = NH_2) (a) [9–12]. The phenyl carborane $9\text{-}Ph\text{-}1,2\text{-}C_2B_{10}H_{11}$ with KOH gave the $5\text{-}Ph\text{-}7,8\text{-}C_2B_9H_{11}^-$ *nido* anion whereas $9\text{-}F\text{-}1,2\text{-}C_2B_{10}H_{11}$ with NaOH yielded the *nido* anion $5\text{-}F\text{-}7,8\text{-}C_2B_9H_{11}^-$ (b) [13,14].

(e)

Ratio   1   > 2
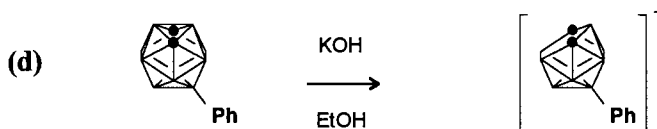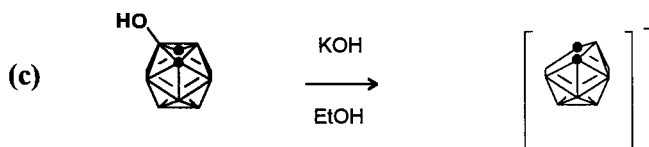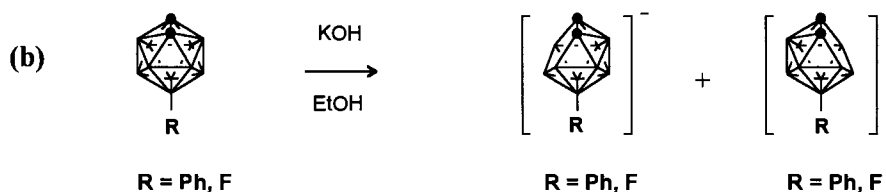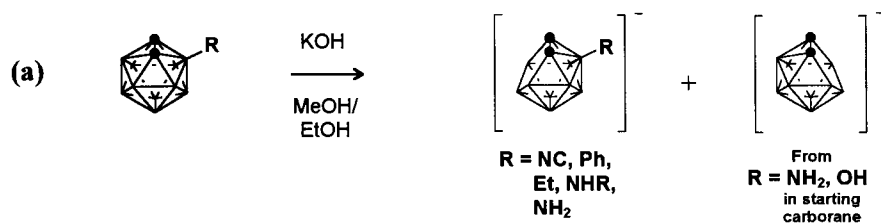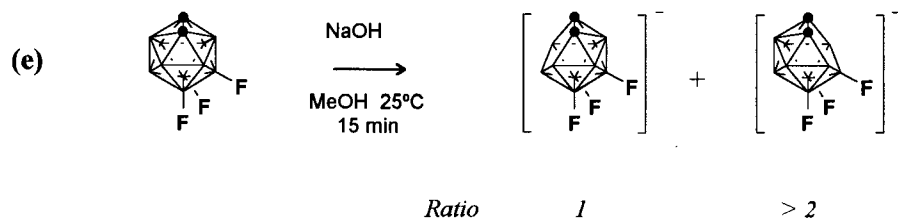
2-Hydroxy-*meta*-carborane gave exclusively the un-substituted *nido*-anion with KOH (c) [12]. Reaction of the *meta* carborane derivative $9\text{-}Ph\text{-}1,7\text{-}C_2B_{10}H_{11}$ with ethanolic KOH gave the $1\text{-}Ph\text{-}7,9\text{-}C_2B_9H_{11}^-$ anion (d) [13]. Deboronation of a 9-substituted *meta* carborane would be expected, but has not been reported, to give two isomeric anions with the substituent at the B1 or B6 position.
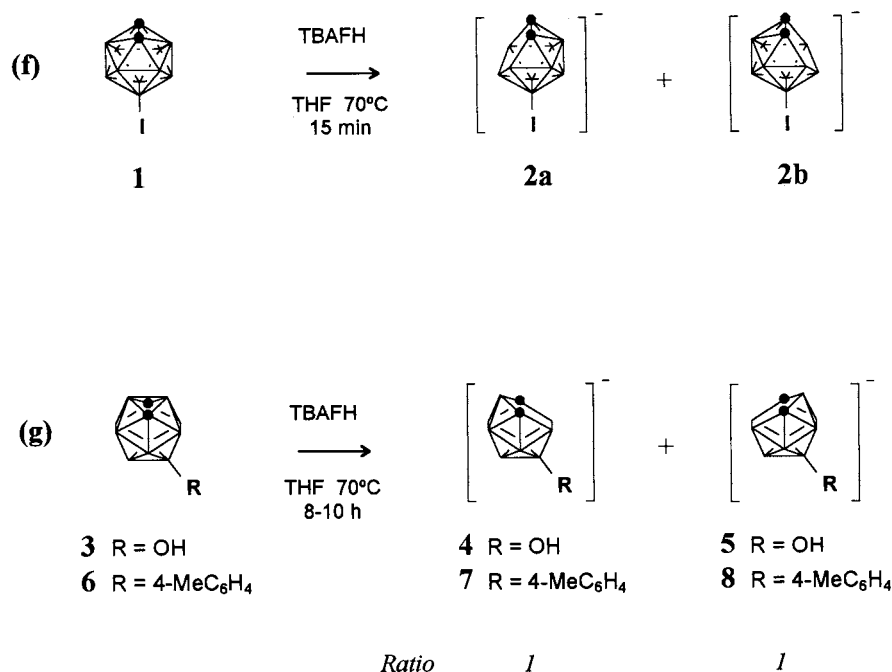
Regioselective deboronation of $8,9,12\text{-}F_3\text{-}1,2\text{-}C_2B_{10}H_9$ with NaOH in methanol at 25°C gave a mixture of *nido* anions $1,5,6\text{-}F_3\text{-}7,8\text{-}C_2B_9H_9^-$ and $5,6,10\text{-}F_3\text{-}7,8\text{-}C_2B_9H_9^-$ (e) [14]. The latter was the dominant isomer based on unassigned ^{19}F- and ^{11}B-NMR data. The ratio of these anions was dependent on the reagent used [15].
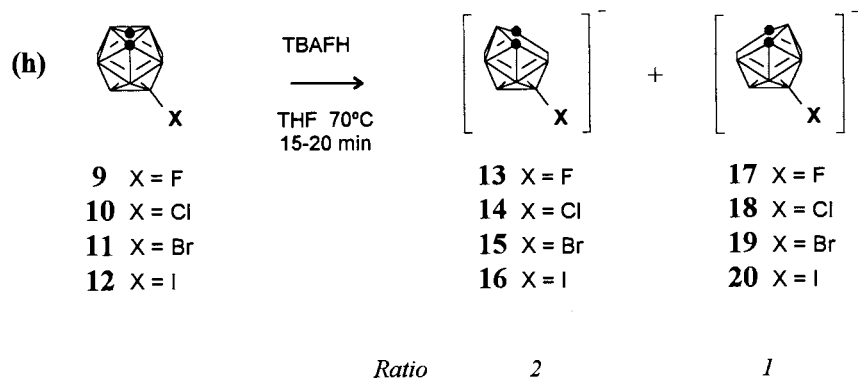
However, there are no NMR or other structural data that confirm the expected position of the substituent in anions reported from deboronation of 9-substituted *ortho* and *meta* carboranes. In view of the incomplete and apparently inconsistent evidence relating to the product identities in such deboronation reactions, we

have carried out systematic studies on a series of 9-sub-stituted *ortho* and *meta* carboranes, identifying pro-ducts by rigorous multinuclear NMR studies including 2D $^{11}B\{^1H\}\text{-}^{11}B\{^1H\}$ COSY and $^{11}B\{^1H\}\text{-}^1H\{^{11}B\}$ cor-relation spectra. We have also calculated the charge distribution in selected carborane derivatives to see whether there were any correlations between charge distributions and sites of attack in deboronation reactions.

2. Results and discussion

The reactions carried out in this study are summa-rized by Eq. (f–j). The boron-substituted *ortho* carbo-rane, $9\text{-}I\text{-}1,2\text{-}C_2B_{10}H_{11}$ **1**, with TBAFH gave the *nido* anion enantiomers $5\text{-}I\text{-}7,8\text{-}C_2B_{10}H_{11}^-$ **2a** and $6\text{-}I\text{-}7,8\text{-}C_2B_{10}H_{11}^-$ **2b** quantitatively (f). Anion **2** is the first 5(6)-substituted derivative of $7,8\text{-}C_2B_9H_{12}^-$ to have as-signed ^{11}B- and ^1H-NMR peaks.

(f)

1   2a   2b

(g)

3 R = OH
6 R = 4-MeC$_6$H$_4$

4 R = OH
7 R = 4-MeC$_6$H$_4$

5 R = OH
8 R = 4-MeC$_6$H$_4$

Ratio   1   1

(h)

9 X = F	**13** X = F	**17** X = F
10 X = Cl	**14** X = Cl	**18** X = Cl
11 X = Br	**15** X = Br	**19** X = Br
12 X = I	**16** X = I	**20** X = I

Ratio 2 1

The hydroxy *meta* carborane 9-HO-1,7-$C_2B_{10}H_{11}$ **3** and excess TBAFH in refluxing THF required over 8 h for quantitative conversion to a 1:1 mixture of the

[10] but, based on the evidence here, the anion 6-Ph-7,9-$C_2B_{10}H_{11}^-$ must also have been formed.

(i)

21 → **22**

(j)

23

22 + **4** + **5**

Ratio 7 2 2
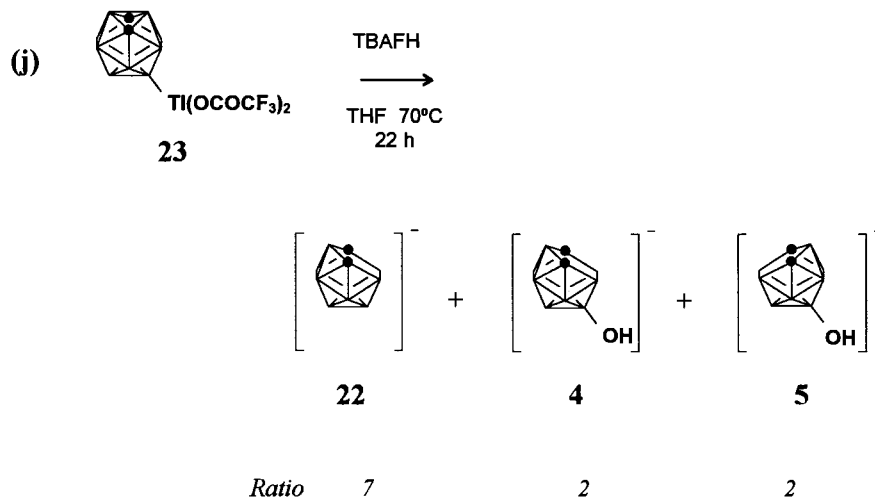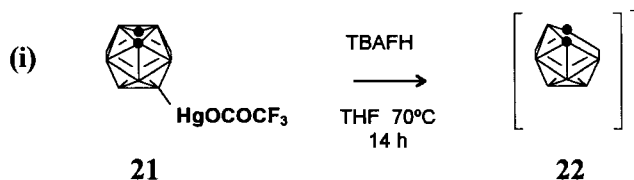
anions 6-HO-7,9-$C_2B_{10}H_{11}^-$ **4** and 1-HO-7,9-$C_2B_{10}H_{11}^-$ **5** (g). Likewise the B-aryl carborane 9-(4-MeC$_6$H$_4$)-1,7-$C_2B_{10}H_{11}$ **6** and TBAFH gave a 1:1 mixture of 6-(4-MeC$_6$H$_4$)-7,9-$C_2B_9H_{11}^-$ **7** and 1-(4-MeC$_6$H$_4$)-7,9-C_2-B$_9$H$_{11}^-$ **8**. Deboronation of 9-Ph-1,7-$C_2B_{10}H_{11}$ to give a *nido* anion 1-Ph-7,9-$C_2B_{10}H_{11}^-$ had been reported

Deboronation of 9-halo-*meta*-carboranes 9-X-1,7-$C_2B_{10}H_{11}$ (**9**, X = F; **10**, X = Cl; **11**, X = Br; **12**, X = I) using TBAFH proved to be rapid (h). The *closo* carboranes were completely deboronated in 15–20 min at 70°C as opposed to 8 h for the hydroxy and aryl
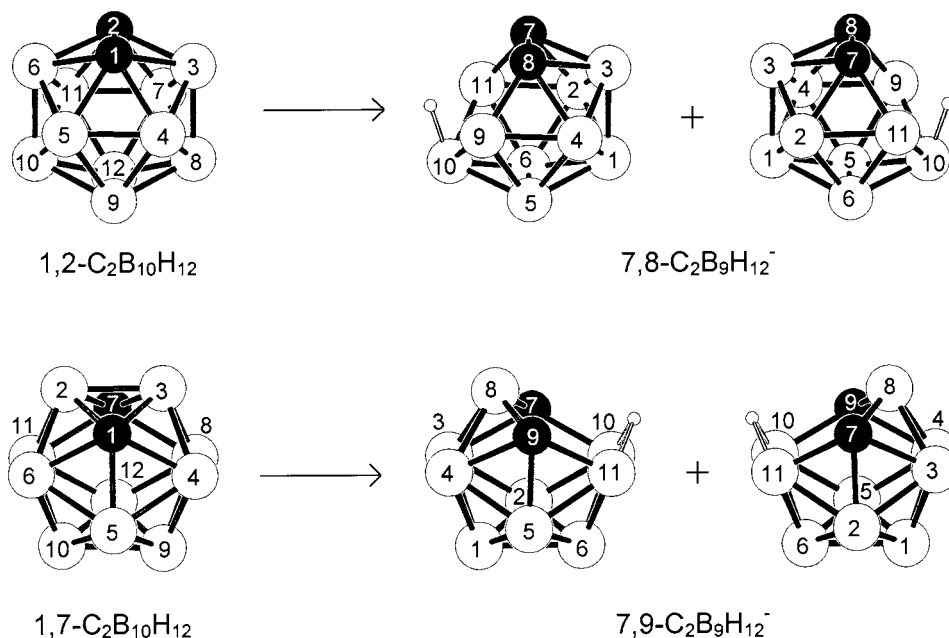
Fig. 1. Conversion of *closo* carboranes 1,2-$C_2B_{10}H_{12}$ and 1,7-$C_2B_{10}H_{12}$ to *nido*-anions 7,8-$C_2B_9H_{12}^-$ and 7,9-$C_2B_9H_{12}^-$, respectively showing skeletal atom numbering. *Exo* hydrogens are omitted for clarity.

carboranes (**3** and **6**). The halogen substituent facilitates the deboronation process as suggested previously [8]. The ratio of the mixture of the *nido* anions 6-X-7,9-$C_2B_{10}H_{11}^-$ (**13**, X = F; **14**, X = Cl; **15**, X = Br; **16**, X = I) and 1-X-7,9-$C_2B_{10}H_{11}^-$ (**17**, X = F; **18**, X = Cl; **19**, X = Br; **20**, X = I) was 2:1 as judged by multinuclear NMR spectroscopy. Thus regioselective deboronation took place with 9-halo-*meta*-carboranes **9**–**12**.

Reaction (i) of the mercury carborane 9-HgOCOCF$_3$-1,7-$C_2B_{10}H_{11}$ **21** with TBAFH in THF at 70°C for 14 h gave only the salt of the *nido*-anion 7,9-$C_2B_9H_{12}^-$ **22**. Under similar conditions (j) the thallium carborane 9-Tl(OCOCF$_3$)$_2$-1,7-$C_2B_{10}H_{11}$ **23** gave a 7:2:2 ratio mixture of anions identified as 7,9-$C_2B_9H_{12}^-$ **22**, 6-HO-7,9-$C_2B_9H_{11}^-$ **4** and 1-HO-7,9-$C_2B_9H_{11}^-$ **5**. The B–Hg and B–Tl bonds were thus cleaved during the reaction with TBAFH.

All tetrabutylammonium salts of the *nido*-anions generated from 9-substituted-*meta*-carboranes here were found to be air-sensitive in the solid state degrading further to boric acid and polyborate residues. These observations are typical of salts containing 7,9-$C_2B_9H_{12}^-$ and related anions [6,7,16].

The compounds made in this study were characterized by IR and detailed NMR spectroscopy. Chemical shift data for the ^{11}B-, ^{13}C-, ^{1}H- and ^{19}F-NMR spectra of all carboranes are given in Table 1. ^{11}B- and ^{1}H-NMR data were assigned by 2D ^{11}B - ^{11}B{^{1}H} COSY and ^{11}B{^{1}H}-^{1}H{^{11}B} correlation spectra. A 2D ^{11}B-^{11}B{^{1}H} COSY spectrum of a 2:1

mixture of the anions **15** and **19** is shown as an example (Fig. 2). The ^{11}B-NMR peaks of 7,9-$C_2B_9H_{12}^-$ **22** at −33.9 and −35.0 ppm were incorrectly assigned to B6 and B1, respectively in the literature [4,17]. Other limited NMR data previously reported [18–20], on the *closo*-carboranes **1**, **10**, **11** and **21** here agree with our findings.

From Table 1, the ^{11}B-, ^{13}C- and ^{1}H-NMR data of carboranes bearing hydroxy or fluorine substituents are shown to be very similar. In the deboronation of C-diphenyl-*meta*-carborane, 1,7-Ph$_2$-1,7-$C_2B_{10}H_{10}$, with TBAFH at 70°C, we obtained a mixture of the anions 10-F-7,9-Ph$_2$-7,9-$C_2B_9H_9^-$, 3-F-7,9-Ph$_2$-7,9-$C_2B_9H_9^-$ and 7,9-Ph$_2$-7,9-$C_2B_9H_{10}^-$ [7]. Under apparently identical conditions, Welch and Weller reported 10-HO-7,9-Ph$_2$-7,9-$C_2B_9H_9^-$ as the major anion [21]. The reported ^{11}B-NMR data of the 10-F and 10-OH anions are similar but there are subtle differences which indicate that either anion could be made from the reaction. The products formed may well depend on the amount of water present.

Antipodal ^{11}B-NMR effects (in which the resonance of a particular cage atom responds to the substituent on the atom opposite) are well known in boranes and heteroboranes [18]. Such effects are observed in the ^{11}B chemical shifts at B2, which is antipodal to the substituted boron atom B9, in the 9-substituted-*meta*-carboranes (see Table 1). We note that antipodal effects also apply to the shifts of the terminal proton at B2. In the halo carboranes **9**–**12** the proton shifts at B2 are 2.39, 2.55, 2.75 and 3.07 ppm, respectively which parallel the trend of the ^{11}B

shifts at B2, -26.7, -22.5, -21.2 and -18.9 ppm. In the 6-halo anions, the ^{11}B and ^{1}H shifts of antipodal B8H show a similar trend; **13** ^{11}B, -9.6 ppm, ^{1}H, 1.71 ppm; **14** -7.2, 1.97; **15** -6.6, 1.97; **16** -5.5, 2.18. In a 1-halo *nido*-anion no antipodal vertex exists in relation to the substituted boron. However a reverse trend in the ^{1}H-NMR shifts of the bridging proton on the 'antipodal' open face is seen; **17** -1.43 ppm; **18** -1.65; **19** -1.87; **20** -2.10.

The B3 atom was suggested to have a lower electron density than the B6 atom by the influence of the F8 atom in 8,9,12-trifluoro-*ortho*-carborane as the reason for its regioselective deboronation [14]. Calculated electron densities of the trifluorocarborane with its geometry optimized [22] at the STO3G level support this theory; Mulliken charges at B3 and B6 are 0.106 and 0.086, respectively.

In the case of 9-substituted-*meta*-carboranes deboronated here by TBAFH, only the halocarboranes **9–12** show regioselective deboronation. Mulliken charges of B2 and B3 calculated from ab initio optimized geometries of the parent *meta*-carborane $C_2B_{10}H_{12}$, **3**, the anion 9-O-1,7-$C_2B_{10}H_{11}^-$, **6**, **9**, **10** and **11** are listed in Table 2. In every substituted carborane the B2 atom has a lower electron density than B3. If the B3 atom is preferentially removed by TBAFH then the 6-isomer *nido*-anion would dominate as discovered here for the halocarboranes **9–12**. In the reaction of the aryl carborane **6** with TBAFH, the 1:1 ratio mixture produced and the slow deboronation rate (compared to the halocarboranes) are expected from the calculated charges. Mulliken charges of the aryl compound **6** at B2 and B3 are comparable to the parent *meta* carborane and are lower than the charges at B3 found for the hydroxy carborane **3** and the halocarboranes **9–11**.

The calculated charges at B2 and B3 of the hydroxy carborane **3** do not explain the following observations, (a) the 1:1 ratio mixture produced; and (b) the much slower rate of deboronation (compared to the halocarboranes) in the reaction of **3** with TBAFH. As the reaction took place in a strongly basic medium the carborane **3** probably existed as the *closo* carborane anion 9-O-1,7-$C_2B_{10}H_{11}^-$ with the hydroxy proton removed [12]. Calculated Mulliken charges of this anion at B3 are comparable with *meta* carborane and the aryl carborane so in view of the slow rate of deboronation the hydroxy carborane **3** may be present as the anion in the reaction mixture. The charges at B2 and B3 of the anion 9-O-1,7-$C_2B_{10}H_{11}^-$ however do not support the 1:1 product ratio observed from the deboronation of **3**.

During the reported deboronation of 1,7-Ph$_2$-1,7-$C_2B_{10}H_{10}$ with TBAFH, the 10-F-7,9-Ph$_2$-7,9-$C_2B_9H_9^-$ anion spontaneously rearranged to 3-F-7,9-Ph$_2$-7,9-

$C_2B_9H_9^-$ [7]. Calculated energies for the 10- and 3-F-7,9-$C_2B_9H_{11}^-$ *nido*-anions as models showed the 3-isomer to be 6.4 kJ mol^{-1} more stable than the 10-isomer in accord with the conversion observed [23].

If cage rearrangement between the two fluoro *nido* anions, **13** and **17**, occurred during the deboronation then a 1:1 ratio mixture was expected as the difference in energy is only 0.3 kJ mol^{-1}. The conversion between anions during the reaction of the fluorocarborane **9** with TBAFH is therefore ruled out on the basis of the 2:1 ratio observed even when left refluxing overnight. On the other hand, the hydroxy anions **4** and **5** may rearrange during the long reaction time. They are only 1.4 kJ mol^{-1} apart in energy and would result in an ca. 1:1 ratio mixture as observed.

The ratio of deboronation products from 8,9,12-F$_3$-1,2-$C_2B_{10}H_9$ (e) has been reported to depend on the reagent used [15]. Here the chloro carborane **10** gave 2:1 ratio mixtures of *nido*-anions **14** and **18** with alcoholic KOH and piperidine whereas no reaction took place with diethylamine. We believe the varying product ratios observed in reaction (e) with different reagents is due to the fluorine substituent (i.e. F8) next to one of the boron atoms (i.e. B3) to be removed. In 9-chloro-*meta*-carborane **10** there is no substituent near the borons to be removed so the product ratio is unaffected by different reagents.
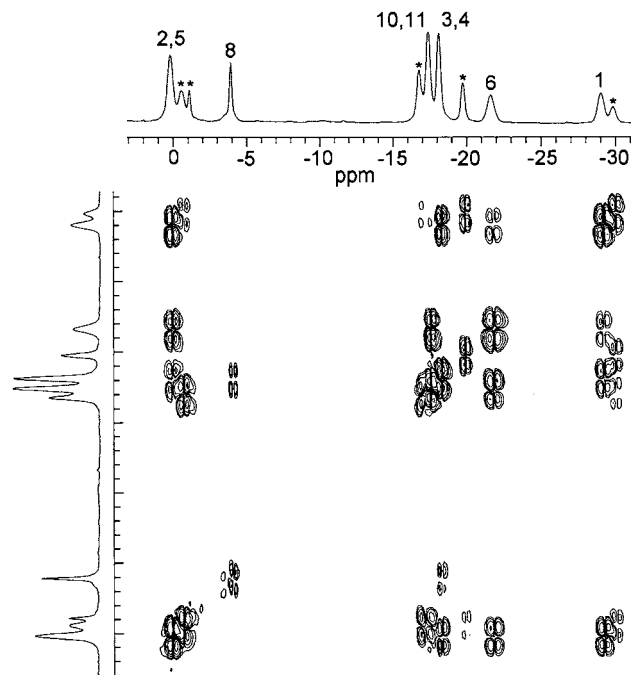

Fig. 2. 160.46 MHz 2D ^{11}B-$^{11}B\{^1H\}$ phase sensitive, double quantum filtered COSY NMR spectrum of a 2:1 ratio mixture of 6-Br-7,9-$C_2B_9H_{11}^-$ **15** and 1-Br-7,9-$C_2B_9H_{11}^-$ **19**. Assignments of peaks with asterisks arising from **19** are shown in Table 1.

Table 1
^{11}B, ^{13}C, ^{1}H and ^{19}F NMR data for carboranes **1–23**

	$\delta(^{11}\text{B})$ (ppm)[a]	$\delta(^{13}\text{C}\{^{1}\text{H}\})$ (ppm)[b]	$\delta(^{1}\text{H}\{^{11}\text{B}\})$ (ppm)[c]	$\delta(^{19}\text{F})$ (ppm)
1[e]	−1.1 (1B, d, 151; B12), −7.7 (2B, d, 156; B8,10), −13.0 (2B, d, 160[f]; B4,5), −13.5 (2B, d, 165[f]; B7,11), −14.8 (2B, d, 165[f]; B3,6), −16.7 (1B, s; B9)	54.9 (C1), 50.7 (C2)	3.90 (1H, s; C2H), 3.70 (1H, s; C1H), 2.74 (1H, s; B12H), 2.62 (2H, s; B4, 5H), 2.57 (2H, s; B8, 10H), 2.40 (2H, s; B7, 11H), 2.22 (2H, s; B3, 6H)	
2[g]	−9.2 (1B, d, 130; B9), −10.4 (1B, d, 130; B11), −15.9 (1B, d, 130; B6), −17.0 (1B, d, 146; B3), −20.8 (1B, d; B2), −21.2 (1B, d; B4), −24.4 (1B, s; B5), −30.1 (1B, dd, 138, $^{1}J_{\text{BH}\mu}$ = 57; B10), −35.3 (1B, d, 147; B1)	43.3 (1:1:1:1 brq, $^{1}J_{\text{CB}}$ = 35; C8), 40.2 (1:1:1:1 brq, $^{1}J_{\text{CB}}$ = 34; C7)	2.21 (1H, s; B9H), 1.97 (3H, s; C7,8,B11H), 1.70 (1H, s; B3H), 1.64[h] (2H, s; B4,6H), 1.25[h] (1H, s; B2H), 0.85 (1H, s; B1H), 0.58 (1H, s; B10H), −2.60 (1H, d, $^{2}J_{\text{HH}}$ = 7.5; Hμ)	
3[e]	8.7 (1B, s; B9), −8.0 (2B, d, 160; B5,12), −11.6 (1B, d, 148; B10), −14.8 (2B, d, 162; B4,8), −16.8 (2B, d, 165; B6,11), −20.3 (1B, d, 181; B3), −26.9 (1B, d, 181; B2)	44.4	2.73 (2H, s; C1,7H), 2.45 (3H, s; B3,5,12H), 2.31 (3H, s; B2,4,8H), 2.20 (1H, s; B10H), 2.00 (2H, s; B6, 11H)[i]	
4[g]	−2.7 (2B, d; B2,5), −9.2 (2B, s; B6), −10.3 (1B, d, 135; B8), −22.5 (4B, d+dd; B3,4,10,11), −34.0 (1B, d; B1)	30.4	2.58 (2H, s; B2, 5H), 1.70 (1H, s; B8H), 1.57[h] (2H; B10, 11H), 1.20 (2H, s; C7, 9H), 1.00 (2H, s; B3, 4H), 0.62 (1H, s; B1H), −1.99 (1H, dt, $^{2}J_{\text{HH}}$ = 12; Hμ)[i]	
5[g]	−2.7 (1B, s; B1), −4.0 (1B, d; B8), −4.7 (2B, d; B2,5), −20.5 (2B, d, 141; B3,4), −24.1 (2B, dd, 140, $^{1}J_{\text{BH}\mu}$ = 50; B10, 11), −34.5 (1B, d; B6)	28.3	2.47 (2H, s; B2, 5H), 2.03 (1H, s; B8H), 1.42 (4H, s+d, $^{2}J_{\text{HH}}$ = 12; B3,4,10, 11H), 1.12 (2H, s; C7, 9H), 0.35 (1H, s; B6H), −1.47 (1H, t, $^{2}J_{\text{HH}}$ = 12; Hμ)[i]	
6[e]	0.5 (1B, s; B9), −6.5 (2B, d, 149; B5, 12), −9.6 (1B, d, 160; B10), −13.1 (2B, d, 167[f]; B4, 8), −13.9 (2B, d, 164[f]; B6, 11), −17.5 (1B, d, 180; B3), −20.0 (1B, d, 181; B2)	137.0 (para CMe), 133.1 (ortho C), 128.4 (meta C), 54.1 (C1,7), 21.1 (Me)[j]	7.46 (2H, d, 7; ortho CH), 7.14 (2H, d, 7; meta CH), 2.99 (2H, s; C1, 7H), 2.71 (1H, s; B3H), 2.63 (1H, s; B2H), 2.58 (2H, s; B5, 12H), 2.44 (2H, s; B4, 8H), 2.36 (4H, s; B10H, Me), 2.29 (2H, s; B6, 11H)	
7[g]	−3.2 (2B, d; B2, 5), −6.5 (1B, d, 135; B8), −20.8 (4B, d+dd; B3, 4, 10, 11), −24.0 (1B, s; B6), −32.1 (1B, d; B1)	133.7[k] (ortho C), 127.8 (para C), 126.9 (meta C), 32.4 (C7, 9), 19.9 (Me)[j]	7.35[k] (2H, d, 7.5; ortho CH), 6.87[k] (2H, d, 7.5; meta CH), 2.51 (2H, s; B2, 5H), 2.08[k] (3H, s; Me), 2.05 (1H, s; B8H), 1.58[h] (2H; B10, 11H), 1.29[h] (2H; C7, 9H), 1.16 (2H, s; B3, 4H), 0.78 (1H, s; B1H), −1.90 (1H, dt, $^{2}J_{\text{HH}}$ = 12; Hμ)	
8[g]	−3.0 (2B, d; B2, 5), −4.1 (1B, d; B8), −19.6 (2B, d, 135[f]; B3, 4), −22.1 (3B, s+dd, 138, $^{1}J_{\text{BH}\mu}$ = 48; B1, 10, 11), −32.8 (1B, d; B6)	134.4[k] (ortho C), 127.8 (para C), 126.9 (meta C), 32.4 (C7, 9), 19.9 (Me)[j]	7.53[k] (2H, d, 7.5; ortho CH), 6.94[k] (2H, d, 7.5; meta CH), 2.45 (2H, s; B2, 5H), 2.21 (1H, s; B8H), 2.13[k] (3H, s; Me), 1.58[h] (2H; B10, 11H), 1.35 (2H, s; B3, 4H), 1.29[h] (2H; C7, 9H), 0.39 (1H, s; B6H), −1.77 (1H, t, $^{2}J_{\text{HH}}$ = 12; Hμ)	
9[e]	10.3 (1B, s; B9), −8.4 (2B, d, 159; B5, 12), −12.4 (1B, d, 146; B10), −15.3 (2B, d, 162; B4, 8), −17.0 (2B, d, 170; B6, 11), −20.6 (1B, d, 185; B3), −26.7 (1B, d, 183; B2)	44.1	2.77 (2H, s; C1,7H), 2.51 (3H, s; B3, 5, 12H), 2.39 (3H, s; B2, 4, 8H), 2.25 (1H, s; B10H), 2.03 (2H, s; B6, 11H)	−207.3 (1:1:1:1 brq, $^{1}J_{\text{BF}}$ = 62)

Table 1
(Continued)

	$\delta(^{11}B)$ (ppm)[a]	$\delta(^{13}C\{^1H\})$ (ppm)[b]	$\delta(^1H\{^{11}B\})$ (ppm)[c]	$\delta(^{19}F)$ (ppm)
10[e]	1.0 (1B, s; B9), −6.4 (2B, d, 164; B5, 12), −9.8 (1B, d, 146[f]; B10), −13.2 (2B, d, 167; B4, 8), −14.8 (2B, d, 163; B6, 11), −18.5 (1B, d, 182; B3), −22.5 (1B, d, 181; B2)	53.1	2.96 (2H, s; C1,7H), 2.61 (1H, s; B3,5,12H), 2.55 (1H, s; B2H), 2.48 (2H, s; B4, 8H), 2.34 (1H, s; B10H), 2.17 (2H, s; B6, 11H)	
11[e]	−6.1 (2B, d, 153[f]; B5, 12), −6.3 (1B, s; B9), −9.3 (1B, d, 152; B10), −12.8 (2B, d, 170[f]; B4, 8), −14.1 (2B, d, 170[f]; B6, 11), −17.9 (1B, d, 183; B3), −21.2 (1B, d, 183; B2)	54.4	3.00 (2H, s; C1,7H), 2.75 (1H, s; B2H), 2.67 (2H, s; B5, 12H), 2.59 (1H, s; B2H), 2.55 (2H, s; B4, 8H), 2.43 (1H, s; B10H), 2.22 (2H, s; B6, 11H)	
12[e]	−5.6 (2B, d, 168; B5, 12), −8.4 (1B, d, 154; B10), −12.0 (2B, d, 174[f]; B4,8), −12.9 (2B, d, 171[f]; B6, 11), −16.9 (1B, d, 183; B3), −18.9 (1B, d, 183; B2), −23.6 (1B, s; B9)	56.2	3.07 (3H, s; C1,7,B2H), 2.69 (3H, s; B3,5,12H), 2.58 (2H, s; B4,8H), 2.47 (1H, s; B10H), 2.24 (2H, s; B6,11H)	
13[g]	−3.1 (2B, d; B2,5), −5.2 (1B, s; B6), −9.6 (1B, d, 135; B8), −22.8 (2B, d; B3,4), −23.4 (2B, dd; B10,11), −34.9 (1B, d; B1)	29.5	2.67 (2H, s; B2, 5H), 1.71 (1H, s; B8H), 1.60 (2H, d, $^2J_{HH}$ = 12; B10, 11H), 1.26 (2H, s; C7, 9H), 1.02[h] (2H, brq, $^2J_{HF}$ = 47; s; B3, 4H), 0.71 (1H, s; B1H), −1.91 (1H, dt, $^2J_{HF}$ = 12, $^2J_{HH}$ = 7; Hμ)	−247.0 (1:1:1:1 brq, $^1J_{BF}$ = 47)
14[g]	−2.4 (2B, d, 149[h]; B2,5), −7.2 (1B, d, 135; B8), −18.0 (1B, s; B6), −20.6 (2B, dd; B10, 11), −21.2 (2B, d; B3, 4), −32.1 (1B, d; B1)	32.0	2.55 (2H, s; B2,5H), 1.79 (1H, s; B8H), 1.60[h] (2H; B10, 11H), 1.28[h] (2H, s; C7, 9H), 1.01[h] (2H, s; B3,4H), 0.76 (1H, s; B1H), −1.70 (1H, t, $^2J_{HH}$ = 12; Hμ)	
15[g]	−2.5 (2B, d, 146[f]; B2, 5), −6.6 (1B, d, 130; B8), −20.8 (2B, dd; B10, 11), −20.8 (2B, d; B3,4), −24.3 (1B, d; B6), −31.7 (1B, d; B1)	32.5	2.70 (2H, s; B2, 5H), 1.97 (1H, s; B8H), 1.73 (2H, d, $^2J_{HH}$ = 12; B10, 11H),1.35[h] (2H, s; C7, 9H), 1.08 (2H, s; B3, 4H), 0.93[h] (1H, s; B1H), −1.61 (1H, t, $^2J_{HH}$ = 12; Hμ)	
16[g]	−2.4 (2B, d, 152[f]; B2, 5), −5.5 (1B, d, 136; B8), −19.1 (2B, dd, $^1J_{BH\mu}$ = 58; B10, 11), −20.1 (2B, d; B3,4), −30.8 (1B, d; B1), −39.6 (1B, s; B6)	33.4	2.75 (2H, s; B2, 5H), 2.18 (1H, s; B8H), 1.80 (2H, d, $^2J_{HH}$ = 12; B10, 11H), 1.40[h] (2H, s; C7, 9H), 1.16 (2H, s; B3, 4H), 1.04[h] (1H, s; B1H), −1.44 (1H, t, $^2J_{HH}$ = 12; Hμ)	
17[g]	0.3 (1B, s; B1), −4.1 (1B, d; B8), −5.0 (2B, d, 177; B2,5), −21.4 (2B, d, 135; B3, 4), −24.5 (2B, dd, $^1J_{BH\mu}$ = 50; B10,11), −35.2 (1B, d; B6)	26.8	2.54 (2H, s; B2, 5H), 2.03 (1H, s; B8H), 1.47 (2H, d, $^2J_{HH}$ = 12; B10, 11H), 1.17 (2H, s; C7, 9H), 1.08 (2H, s; B3, 4H), 0.45 (1H, s; B6H), −1.43 (1H, t, $^2J_{HH}$ = 12; Hμ)	−263.6 (1:1:1:1 brq, $^1J_{BF}$ = 44)
18[g]	−3.6 (2B, d; B2,5), −3.8 (1B, d; B8), −13.6 (1B, s; B1), −19.7 (2B, d, 147; B3,4), −22.9 (2B, dd, 134, $^1J_{BH\mu}$ = 47; B10, 11), −32.9 (1B, d; B6)	32.0	2.44 (2H, s; B2, 5H), 1.97 (1H, s; B8H), 1.51 (2H, d, $^2J_{HH}$ = 12; B10, 11H), 1.48 (2H, s; B3, 4H), 1.19 (2H, s; C7, 9H), 0.52 (1H, s; B6H), −1.65 (1H, t, $^2J_{HH}$ = 12; Hμ)	
19[g]	−3.2 (2B, d; B2,5), −3.7 (1B, d; B8), −19.5 (2B, d; B3,4), −19.9 (1B, s; B1), −22.5 (2B, dd, 138, $^1J_{BH\mu}$ = 49; B10, 11), −32.5 (1B, d; B6)	32.5	2.55 (2H, s; B2, 5H), 2.05 (1H, s; B8H), 1.50 (2H, s+d, $^2J_{HH}$ = 12; B3, 4, 10, 11H), 1.26[h] (4H, s; C7, 9H), 0.55 (1H, s; B6H), −1.87 (1H, t, $^2J_{HH}$ = 12; Hμ)	

Table 1
(Continued)

	$\delta(^{11}B)$ (ppm)[a]	$\delta(^{13}C\{^1H\})$ (ppm)[b]	$\delta(^1H\{^{11}B\})$ (ppm)[c]	$\delta(^{19}F)$ (ppm)
20[g]	−2.4 (2B, d; B2,5), −3.7 (1B, d; B8), −19.5 (2B, d; B3,4), −22.5 (2B, dd, 151, $^1J_{BH\mu}$ = 47; B10, 11), −31.9 (1B, d; B6), −35.2 (1B, s; B1)	33.4	2.57 (2H, s; B2, 5H), 2.00 (1H, s; B8H), 1.55[h] (2H, s; B3, 4H), 1.52 (2H, d, $^2J_{HH}$ = 12; B10, 11H), 1.30[h] (2H, s; C7, 9H), 0.65 (1H, s; B6H), −2.10 (1H, t, $^2J_{HH}$ = 12; Hμ)	
21[e]	−5.1 (2B, d, 162; B5,12), −8.8 (1B, d; B10), −9.1 (1B, s+d $^1J_{BHg}$ = 2747; B9), −11.6 (5B, d, 167[f]; B4,6,8,11), −13.7 (1B, d; B3[k]), −15.4 (1B, d, 181; B2[k])	156.1 (q, $^3J_{CF}$ = 38; CO), 114.3 (q, $^1J_{CF}$ = 288; CF$_3$), 52.5 (s+d, $^3J_{CHg}$ = 126; C1,7)	3.11 (2H, s; C1,7H), 2.73 (1H, s; B2H), 2.62 (1H, s; B3H), 2.28 (6H, s; B4, 5, 6, 8, 11, 12H), 2.11 (1H, s; B10H)	−74.7
22[g]	−4.1 (2B, d, 147; B2,5), −5.5 (1B, d, 136; B8), −21.1 (2B, d, 143; B3, 4), −22.3 (2B, dd, 135, $^1J_{BH\mu}$ = 53; B10, 11), −33.9 (1B, d, 140; B1), −35.0 (1B, d, 134; B6)	31.8	2.18 (2H, s; B2, 5H), 2.01 (1H, s; B8H), 1.42 (2H, d, $^2J_{HH}$ = 12; B10, 11H), 1.17 (2H, s; C7, 9H), 1.08 (2H, s; B3, 4H), 0.66 (1H, s; B6H), 0.09 (1H, s; B1H), −2.34 (1H, t, $^2J_{HH}$ = 12; Hμ)	
23[l]	−2.4 (1B, d, $^1J_{BTl}$ = 11,062; B9), −6.0 (2B, d; B5,12), −12.8 (6B, d; B2, 3, 4, 6, 8, 11)	−166.1 (q, $^3J_{CF}$ = 37; CO), 124.3 (q, $^1J_{CF}$ = 289; CF$_3$), 63.7 (d, $^3J_{CTl}$ = 442; C1,7)	3.98 (2H, s; C1, 7H), 2.80 (4H, s; B2, 3, 5, 12H), 2.32 (4H, s; B4, 6, 8, 11H), 2.19 (1H, s; B10H)	−74.2
	9.5 (1B, d; B10)			

[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{^{1}H} at 25°C (peak pattern, J/Hz; assignments).
[c] 500 MHz ^{1}H{^{11}B} at 25°C (relative intensity, peak pattern, J/Hz; assignments).
[d] 235 MHz ^{19}F at 25°C (peak pattern, J/Hz; assignments).
[e] In CDCl$_3$.
[f] Values are uncertain due to overlapping or poorly resolved peaks.
[g] As ^{n}Bu$_4$N$^+$ salt in CD$_3$CN at 25°C, NMR data for the cation ^{n}Bu$_4$N$^+$ ^{13}C; 58.2 (s; NCH$_2$), 23.2 (s; CH$_2$C$_2$H$_5$), 19.2 (s; CH$_2$C$_2$H$_5$) and 12.7 (s; CH$_3$); ^{1}H; 3.05 (8H, m; NCH$_2$), 1.58 (8H, m; CH$_2$C$_2$H$_5$), 1.34 (8H, tq, $^3J_{HH}$ = 7.3; CH$_2$CH$_3$) and 0.95 (12H, t, $^3J_{HH}$ = 7.3 Hz; CH$_3$).
[h] Obscured by cation peak.
[i] OH proton peak not observed.
[j] Peak of aryl carbon attached to a carboranyl boron not seen.
[k] Assignment uncertain.
[l] In (CD$_3$)$_2$CO.

Table 2
Calculated Mulliken charges at B2 and B3 atoms in *closo-meta*-carboranes (from STO3G optimized geometries)

Level		Parent	3	6[a]	9	10	11	anion of 3
HF/STO3G	B2	0.102	0.097	0.101	0.097	0.102	0.102	0.094
	B3	0.102	0.104	0.102	0.104	0.105	0.105	0.102

[a] H instead of Me group.

2.1. Summary

Nucleophilic deboronation of neutral *ortho*- and *meta-closo*-carboranes 1,2- and 1,7-$C_2B_{10}H_{12}$ has long been known to generate *nido* carborane anionic products $C_2B_9H_{12}^-$ whose skeletal structures could be understood if the boron atom removed were one of the two boron atoms originally connected to both carbon atoms in the *closo* parent, i.e. in the 3 or 6 positions in the case of *ortho* carborane, or the 2 or 3 positions in the case of *meta* carborane. These boron atoms were those calculated to bear the greatest positive charge in the *closo* parent and so represented the preferred sites of attack by nucleophiles. We have studied the deboronation, by tetrabutylammonium fluoride hydrate (TBAFH), of neutral *closo* carboranes bearing a halogen atom or a hydroxy or aryl group as a substituent on a cage boron atom remote from the cage carbon atoms of *ortho* and *meta* carboranes. The sites occupied by the substituents in the anionic *nido* products, $C_2B_9H_{11}X^-$, of these reactions have been identified by detailed multinuclear NMR studies and shown to be those expected assuming that no drastic rearrangement reactions have occurred during deboronation. However reactions with TBAFH convert neutral *meta closo* carboranes bearing mercury or thallium trifluoroacetate residues on their cage boron atoms into unsubstituted *nido* anions 7,9-$C_2B_9H_{12}^-$, by cleavage of their mercury–boron or thallium–boron bonds.

Reactions of a 9-halogeno-*meta*-carborane, i.e. a carborane bearing a halogen atom on a boron atom opposite to (antipodal to) one of the likely sites of nucleophilic attack, yields predominantly one *nido* anion, that corresponding to removal of the BH unit not opposite to the boron bearing the halogen atom. However, 9-hydroxy and 9-aryl *meta* carboranes $C_2B_{10}H_{11}X$ afford the mixtures of *nido* anionic products $C_2B_9H_{11}X^-$ expected by nucleophilic deboronation at either the two or three positions. A halogen substituent therefore appears to facilitate deboronation even when it is opposite to (antipodal to) the boron atom to be removed. We have calculated Mulliken charges (generated from optimized geometries) for these halogenated *closo* carboranes, and shown that the boron atom removed remains the one bear-

ing the highest positive charge and so presumably the preferred site for nucleophilic attack. We conclude that the identity of the deboronated (*nido*-carborane) product, and indeed the likely rate of deboronation, can be predicted from charge calculations using the optimized geometries of *closo* ortho- or *meta*-carborane derivatives $C_2B_{10}H_{11}X$ bearing halogen substituents (X) on the boron atoms, or indeed on *closo para*-carborane derivatives $C_2B_{10}H_{11}X$ bearing halogen atoms on boron atoms.

3. Experimental

All reactions were manipulated under air in a well-ventilated fume hood. NMR spectra were recorded on a Bruker AC250 (250.1 MHz ^{1}H, 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 ^{1}H) instrument. 2D ^{11}B-^{11}B{^{1}H} COSY, [11]B-^{1}H and [13]C-^{1}H correlation and [1]H{[11]B} spectra were obtained on the Bruker AMX500. External references for the chemical shifts were $SiMe_4 = 0.00$ ppm for ^{1}H 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. Ab initio computations were carried out at the HF/STO3G level using a PC version of GAMESS on an IBM-compatible PC. All optimized geometries here were obtained without symmetry constraints.

Tetra-*n*-butylammonium fluoride hydrate (TBAFH) and tetrahydrofuran (THF) were obtained commercially (Aldrich) and used as received. *Ortho*-carborane, 1,2-$C_2B_{10}H_{12}$, and *meta*-carborane, 1,7-$C_2B_{10}H_{12}$, were purified by sublimation under high vacuum. The carboranes, 9-I-1,2-$C_2B_{10}H_{11}$ **1**, [25] 9-HO-1,7-$C_2B_{10}H_{11}$ **3**, [20], [26–28] 9-(4-MeC_6H_4)-1,7-$C_2B_{10}H_{11}$ **6**, [24,29] 9-F-1,7-$C_2B_{10}H_{11}$ **9**, [26,27,30] 9-Cl-1,7-$C_2B_{10}H_{11}$ **10**, [31] 9-Br-1,7-$C_2B_{10}H_{11}$ **11**, [26] 9-I-1,7-$C_2B_{10}H_{11}$ **12**, [25] 9-Hg(OCOCF_3)-1,7-$C_2B_{10}H_{11}$ **21** [20,26] and 9-Tl(OCOCF_3)$_2$-1,7-$C_2B_{10}H_{11}$ **23** [20,26,27] were made from the corresponding parent *closo*-carborane $C_2B_{10}H_{12}$ by reported methods [25–31].

IR data: **3**: ν_{max} cm^{-1} 3275 m (OH stretch); 3061 m (carboranyl CH stretch); 2598 sbr (BH stretch);

1684 w, 1363 w, 1191 sbr, 1137 s, 1064 m, 1012 s, 977 m, 717 m; **6**: 3065 s (carboranyl CH); 3048 w, 3023 w (aryl CH stretch); 2988 w, 2925 w, 2872 w (alkyl CH stretch); 2634 s, 2604 s, 2598 s, 2573 s (BH); 1918 w, 1610 m, 1511 m, 1232 s, 1210 m, 1192 m, 1157 m, 1105 m, 1069 m, 1031 s, 1024 m, 990 m, 947 m, 870 s; **9**: 3069 m (carboranyl CH); 2607 sbr (BH); 1387 m, 1257 s, 1217 sbr, 1160 s, 1105 w, 1065 m, 1012 s, 977 s, 729 m, 715 m; **21**: [32] 3071 m, 3031 w (carboranyl CH); 2605 sbr (BH); 1665 sbr (CO stretch); 1413 m, 1187 sbr, 1151 sbr, 843 m, 728 s; **23**: 3039 s (carboranyl CH); 2638 s, 2614 s, 2595 s (BH); 1669 sbr (CO), 1436 s, 1165 sbr, 1132 sbr, 839 s, 806 s, 749 m, 725 s.

3.1. General deboronation procedure with TBAFH [5–7]

To the carborane (5 mmol) in THF (30 ml) was added TBAFH (25 mmol). The mixture was heated to reflux (bath temperature 70°C). The progress of the reaction was monitored by the IR spectrum of the solution using KBr plates. Reaction was considered to be complete when the *closo* carborane BH stretching band at ca. 2600 cm^{-1} had completely disappeared and been replaced by the *nido* BH band at ca. 2530 cm^{-1}. After cooling, the contents were poured into 50 ml of distilled water. The precipitate was filtered off, washed with water, dissolved in CH_2Cl_2 (20 ml) and re-washed with water (3 × 20 ml). The CH_2Cl_2 solution was dried with anhydrous $MgSO_4$, filtered and evaporated to leave the crude tetrabutylammonium salt of the *nido*-carborane anion.

3.2. Reaction of 9-I-1,2-$C_2B_{10}H_{11}$ **1** with TBAFH

After 15 min of reaction time the solid was recrystallized from ethanol and identified by NMR as the NBu$_4^+$ salt of 5-I-7,8-$C_2B_9H_{11}^-$ **2** (2.36 g, 94%); m.p. 90°C; Found: C, 43.0; H, 9.7; N, 2.8; Anal. Calc. for $C_{18}H_{47}B_9NI$: C, 43.1; H, 9.4; N, 2.8%. ν_{max} cm^{-1} 3034 w; 2962 s, 2933 s, 2875 s (alkyl CH stretch); 2535 sbr (BH stretch); 1469 s, 1381 m, 1169 m, 1083 m, 1032 m, 1064 m, 1020 m, 881 m, 735 m.

3.3. Reaction of 9-HO-1,7-$C_2B_{10}H_{11}$ **3** with TBAFH

The solution was refluxed for 10 h for complete deboronation of **3**. After work up the semi-solid was recrystallized from propan-2-ol to produce a solid identified by multinuclear NMR spectroscopy as a mixture of NBu$_4^+$ salts of 6-HO-7,9-$C_2B_9H_{11}^-$ **4** and 1-HO-7,9-$C_2B_9H_{11}^-$ **5** in a 1:1 ratio (1.43 g, 73%). This solid deteriorated slowly in air at ambient temperature, and an IR band developed at 3260 cm^{-1}; ν_{max} cm^{-1} 3357 mbr (OH stretch); 3030 w; 2964 s, 2940 m, 2877 m (alkyl CH); 2529 sbr (BH); 1591 mbr, 1465 s, 1419s, 1382 m, 1303 s, 1214 m, 1149 m, 1112 s, 1068 m, 1029 m, 915 m, 817 m, 779 m.

3.4. Reaction of 9-(4-MeC_6H_4)-1,7-$C_2B_{10}H_{11}$ **6** with TBAFH

After 8 h refluxing the resulting white solid was recrystallized from propan-2-ol to produce a solid identified by NMR as a mixture of NBu$_4^+$ salts of 6-(4-MeC_6H_4)-7,9-$C_2B_9H_{11}^-$ **7** and 1-(4-MeC_6H_4)-7,9-$C_2B_9H_{11}^-$ **8** in a 1:1 ratio (1.65 g, 71%). This mixture was air-sensitive, and an IR band developed at 3230 cm^{-1} over several days; ν_{max} cm^{-1} 3025 w; 2962 m, 2934 m, 2875 m (alkyl CH); 2529 sbr (BH); 1613 m, 1514 m, 1508 m, 1482 s, 1459 s, 1403 s, 1379 s, 1369 s, 1349 s, 1261 s, 1182 s, 1151 m, 1111s, 1080 s, 1055 s, 1034 s, 1023 s, 881 m, 869 m, 817 s, 803 s, 735 s, 685 m.

3.5. Reaction of 9-F-1,7-$C_2B_{10}H_{11}$ **9** with TBAFH

^{19}F NMR spectroscopy of the mixture showed the reaction required only 15 min refluxing for complete deboronation of **9** (3 mmol used). After work up the solid was recrystallized from propan-2-ol to produce a solid identified by NMR as a mixture of NBu$_4^+$ salts of 6-F-7,9-$C_2B_9H_{11}^-$ **13** and 1-F-7,9-$C_2B_9H_{11}^-$ **17** in a 2:1 ratio (0.72 g, 73%). This solid deteriorated rapidly in air at ambient temperature, and an IR band developed at 3227 cm^{-1} in 4–6 h; ν_{max} cm^{-1} 3020 w; 2964 s, 2935 m, 2876 m (alkyl CH); 2525 sbr (BH); 1471 s, 1383 m, 1185 m, 1148 m, 1111 s, 1063 m, 1031 m, 1013 m.

3.6. Reaction of 9-Cl-1,7-$C_2B_{10}H_{11}$ **10** with TBAFH

The reaction required 20 min refluxing for complete deboronation of **10** (twofold scale used). The solid was recrystallized from propan-2-ol to produce white crystals identified as a mixture of NBu$_4^+$ salts of 6-Cl-7,9-$C_2B_9H_{11}^-$ **14** and 1-Cl-7,9-$C_2B_9H_{11}^-$ **18** in a 2:1 ratio (3.36 g, 82%). This solid deteriorated slowly in air at ambient temperature when an IR band at 3225 cm^{-1} developed in 2–3 days; ν_{max} cm^{-1} 3034 w; 2964 s, 2935 m, 2876 m (alkyl CH); 2543 sbr (BH); 1471 s, 1430 m, 1383 s, 1111 m, 883 m, 793 m, 737 m.

3.7. Reaction of 9-Cl-1,7-$C_2B_{10}H_{11}$ **10** with KOH

A stirred solution of 10 mmol of the carborane **10** and 40 mmol of KOH in 100 ml of ethanol was refluxed for 2 h. Ethanol was removed under vacuum

leaving a white semi-solid. The residue was dissolved in 100 ml of distilled water and an aqueous solution of 18-crown-6 (25 mmol) was added to give a white precipitate. The solid was filtered, washed with distilled water and recrystallized from an acetonitrile-ethanol mixture to give a 2:1 mixture of K (18-C-6)$^+$ salts of **14** and **18** identified by multinuclear NMR spectroscopy.

3.8. Reaction of 9-Cl-1,7-$C_2B_{10}H_{11}$ **10** with piperidine

5 mmol of the carborane was dissolved in 30 ml of neat piperidine and heated at 50°C for 1 h. The reaction was judged to be complete by the disappearance of the *closo* B–H stretch peak at ca. 2600 cm^{-1} in the IR of the reaction mixture. The piperidine was removed under vacuum leaving a semi-solid. A portion of the residue was dissolved in d_3-acetonitrile and investigated by ^{11}B- and ^{1}H-NMR spectroscopy. The solid was identified from NMR as a 2:1 mixture of piperidinium salts of 6-Cl-7,9-$C_2B_9H_{11}^-$ **14** and 1-Cl-7,9-$C_2B_9H_{11}^-$ **18**.

3.9. Reaction of 9-Cl-1,7-$C_2B_{10}H_{11}$ **10** with diethylamine

The chloro carborane (5 mmol) was dissolved in 50 ml of neat diethylamine and refluxed at 120°C for 2 weeks. Negligible change in the reaction mixture was shown by IR and ^{11}B-NMR spectroscopy.

3.10. Reaction of 9-Br-1,7-$C_2B_{10}H_{11}$ **11** with TBAFH

The deboronation reaction of **11** was complete in 20 min. Recrystallization of the crude solid from propan-2-ol gave white crystals identified by NMR (see Fig. 2) as a mixture of NBu$_4^+$ salts of 6-Br-7,9-$C_2B_9H_{11}^-$ **15** and 1-Br-7,9-$C_2B_9H_{11}^-$ **19** in a 2:1 ratio (1.82 g, 80%). This mixture was found to be air-sensi-tive when an IR band at 3233 cm^{-1} developed on exposure to air during 2–3 h; v_{max} cm^{-1} 3026 w; 2961 s, 2933 s, 2874 s (alkyl CH); 2538 sbr (BH); 1469 s, 1381 m, 1134 m, 1109 s, 1055 m, 1032 m, 898 m, 876 m, 851 m, 733 m.

3.11. Reaction of 9-I-1,7-$C_2B_{10}H_{11}$ **12** with TBAFH

Complete deboronation of **12** took 20 min of reaction time. The crude solid was recrystallized from propan-2-ol to give a white solid identified by NMR as a mixture of NBu$_4^+$ salts of 6-I-7,9-$C_2B_9H_{11}^-$ **16** and 1-I-7,9-$C_2B_9H_{11}^-$ **20** in a 2:1 ratio (2.13 g, 85%). This mixture was found to be slightly air-sensitive when an IR band at 3230 cm^{-1} developed on exposure to air during 2–3 weeks; Found: C, 41.9; H, 9.2; N, 2.6; Anal. Calc. for $C_{18}H_{47}B_9NI$: C, 43.1; H,

9.4; N, 2.8%. v_{max} cm^{-1} 3018 w; 2963 s, 2933 m, 2875 m (alkyl CH); 2546 sbr, 2523 s, 2505 s (BH); 1471 s, 1470m, 1380 m, 1169 m, 1109 s, 1056 m, 1031 m, 912 m, 898 m, 872 m, 844 m, 798 m, 733 m.

3.12. Reaction of 9-Hg($OCOCF_3$)-1,7-$C_2B_{10}H_{11}$ **21** with TBAFH

After 14 h refluxing the resulting semi-solid was recrystallized from a 1:1 ethanol: propan-2-ol mixture to produce a solid identified by NMR as NBu$_4^+$ 7,9-$C_2B_9H_{12}^-$ **22** [5] (0.96 g, 51%).

3.13. Reaction of 9-Tl($OCOCF_3$)$_2$-1,7-$C_2B_{10}H_{11}$ **23** with TBAFH

After 22 h refluxing, the crude solid was recrystallized from propan-2-ol to produce a solid (1.36 g) identified by NMR as a mixture of NBu$_4^+$ 7,9-$C_2B_9H_{12}^-$ **22**, 6-HO-7,9-$C_2B_9H_{11}^-$ **4** and 1-HO-7,9-$C_2B_9H_{11}^-$ **5** in a 7:2:2 ratio. An insoluble solid from the work up was found to contain 91.9% Tl and is believed to be TlF (Anal. Calc. 91.5% Tl).

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