Cage-closing reactions of the *nido*-carborane anion 7,9-C$_2$B$_9$H$_{12}$$^-$ and derivatives; formation of neutral 11-vertex carboranes by acidification †

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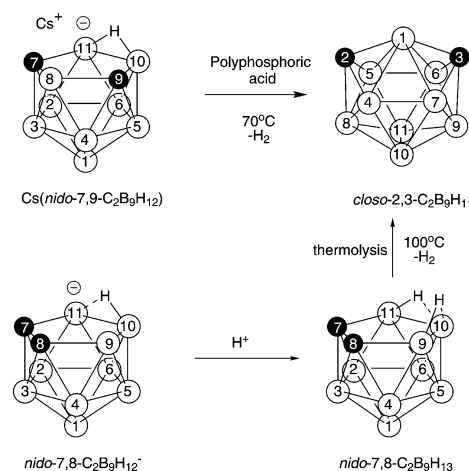*Chemistry Department, Durham University Science Laboratories, South Road, Durham, UK DH1 3LE*

Reactions of the *nido*-carborane salts (Bu$_4$N)(*nido*-7,9-R,R′-7,9-C$_2$B$_9$H$_{10}$) (R,R′ = H; R,R′ = Me; R,R′ = Ph; R = Ph, R′ = Me) with H$_2$SO$_4$ at ambient temperature give the 11-vertex *closo*-carboranes 2,3-R,R′-2,3-C$_2$B$_9$H$_9$ in high yields (R,R′ = H; R,R′ = Me; R,R′ = Ph; R = Ph, R′ = Me). Halogenated derivatives of *closo*-carboranes, 10-X-2,3-C$_2$B$_9$H$_{10}$ (X = Cl, I), are formed from reactions of salts containing 1(6)-X-7,9-C$_2$B$_9$H$_{11}$$^-$ anions with H$_2$SO$_4$, and 4-F-2,3-(*p*-FC$_6$H$_4$)$_2$-2,3-C$_2$B$_9$H$_8$ is formed from (Bu$_4$N)(3-F-7,9-(*p*-FC$_6$H$_4$)$_2$-7,9-C$_2$B$_9$H$_9$) and F$_3$CSO$_3$H. Elimination of the ethoxide and fluoride substituents from the cage occurs during acidification of salts containing 10-OEt-7,9-C$_2$B$_9$H$_{11}$$^-$ and 10-F-7,9-(*p*-FC$_6$H$_4$)$_2$-7,9-C$_2$B$_9$H$_9$$^-$ by F$_3$CSO$_3$H, resulting in the *closo*-carboranes 2,3-C$_2$B$_9$H$_{11}$ and 2,3-(*p*-FC$_6$H$_4$)$_2$-2,3-C$_2$B$_9$H$_9$ as major products respectively. A mixture of *B*-Me-2,3-C$_2$B$_9$H$_{10}$ isomers is obtained from salts containing the 8-Me-7,9-C$_2$B$_9$H$_{11}$$^-$ and 10-Me-7,9-C$_2$B$_9$H$_{11}$$^-$ anions with H$_2$SO$_4$. *B*-Me-2,3-C$_2$B$_9$H$_{10}$ is suggested to be fluxional in solution with 4-Me-2,3-C$_2$B$_9$H$_{10}$ as the major component. Protonation of the fluxional anion 10(11)-*endo*-Me-7,9-C$_2$B$_9$H$_{11}$$^-$ with acetic acid gives a neutral *nido*-carborane 11-Me-2,8-C$_2$B$_9$H$_{12}$ rather than *closo*-*B*-Me-2,3-C$_2$B$_9$H$_{10}$. Molecular geometries of 11-vertex *closo*-carboranes and *B*-methyl-*nido*-carboranes are determined by the combined *ab initio*/GIAO/NMR method at the GIAO-B3LYP/6-311G*//MP2/6-31G* level of theory.

Introduction

Base-induced deboronation of the three isomers of *closo*-C$_2$B$_{10}$H$_{12}$ generates three of the possible isomers of the mono-anions *nido*-C$_2$B$_9$H$_{12}$$^-$, which have long been known to generate the neutral *nido* carboranes C$_2$B$_9$H$_{13}$ on acidification. Two well-characterised isomers 7,8-C$_2$B$_9$H$_{13}$ and 2,9-C$_2$B$_9$H$_{13}$ are formed from their respective mono-anions 7,8-C$_2$B$_9$H$_{12}$$^-$ and 2,9-C$_2$B$_9$H$_{12}$$^-$,[1–3] but the neutral carborane '7,9-C$_2$B$_9$H$_{13}$' produced by protonation of 7,9-C$_2$B$_9$H$_{12}$$^-$ has not been adequately characterised.[4] Since the protonation reactions introduce B–H–B bridges, and not C–H–B bridges, one argument against the existence of 7,9-C$_2$B$_9$H$_{13}$ is the lack of a B–B bond available on the open face to accommodate the second bridging hydrogen.[2]

The 11-vertex *closo*-carborane, 2,3-C$_2$B$_9$H$_{11}$, is formed in 36% yield by the elimination of hydrogen in the reaction of Cs(7,9-C$_2$B$_9$H$_{12}$) with polyphosphoric acid at elevated temperatures (Scheme 1).[4] High yields of the *C*-phenyl derivative 2-Ph-2,3-C$_2$B$_9$H$_{10}$ were obtained from Cs(7-Ph-7,9-C$_2$B$_9$H$_{11}$) by the same method.[4] Acidification of the 7,8-anions 7,8-R,R′-7,8-C$_2$B$_9$H$_{10}$$^-$ results in protonation to generate neutral *nido*-carboranes 7,8-R,R′-7,8-C$_2$B$_9$H$_{11}$, which undergo thermolysis at 100 °C to give C-substituted *closo*-carboranes 2,3-R,R′-2,3-C$_2$B$_9$H$_9$.[5–7]

Boron substituted 11-vertex *closo*-carboranes are limited to those containing hydroxyl and carboranyl groups. Oxidation of 2,3-Me$_2$-2,3-C$_2$B$_9$H$_9$ generates the hydroxy carboranes, 4-HO-2,3-Me$_2$-2,3-C$_2$B$_9$H$_8$ and 4,7-(HO)$_2$-2,3-Me$_2$-2,3-C$_2$B$_9$H$_7$.[8–10] Bromination of the latter compound affords 10-Br-4,7-(HO)$_2$-

2,3-Me$_2$-2,3-C$_2$B$_9$H$_6$.[8] The only boron substituted 11-vertex *closo*-carboranes to be formed by acidification are the two-cage carboranes [11,12] 4-R-2,3-R′$_2$-C$_2$B$_9$H$_8$ (R = carboranyl, R′ = H or Me) generated from Cs(10-R-7,9-R′$_2$-7,9-C$_2$B$_9$H$_8$) and 2-Ph-2,3-C$_2$B$_9$H$_{10}$ from Me$_4$N[PhC$_2$B$_9$H$_{10}$(OH)].[4]

If the substituent in the *nido* anion is at B10 then acid-promoted elimination of the unique hydrogen on the open face, and formation of two B–B bonds between B8 and B10/B11 to form the *closo*-carborane, will place the substituent at B4 (see Scheme 1 for cage numbering), as is found for the neutral two-cage carboranes.[11] The closure appears to be facile – the mechanism has been discussed for the oxidative closure of 7,9-C$_2$B$_9$H$_{11}$$^{2-}$ to give 2,3-C$_2$B$_9$H$_{11}$.[13]

Scheme 1 The reactions of *nido*-7,9-C$_2$B$_9$H$_{12}$$^-$ **1a** and *nido*-7,8-C$_2$B$_9$H$_{12}$$^-$ with acid and the synthesis of *closo*-2,3-C$_2$B$_9$H$_{11}$ **2a** showing the cage numbering. *Exo*-hydrogens are omitted for clarity.

In this paper we report our investigation of the presumed intermediate $C_2B_9H_{13}$ formed on acidification of various salts of $7,9-C_2B_9H_{12}^-$. Conversion to *closo*-$2,3-C_2B_9H_{11}$ occurs in the reaction of $(Bu_4N)(7,9-C_2B_9H_{12})$ with conc. H_2SO_4 at ambient temperature. We apply this simple acidification method using H_2SO_4 or F_3CSO_3H to the many carbon- and boron-substituted derivatives of *nido*-$7,9-C_2B_9H_{12}^-$, obtained by deboronation of *meta*-$C_2B_{10}H_{12}$ derivatives.[3,14–17]

We also discuss the isomeric mixture of *closo*-*B*-Me-$2,3$-$C_2B_9H_{10}$ formed from the acidification of salts containing the known[18] anions 8-Me-$7,9-C_2B_9H_{11}^-$ and 10-Me-$7,9-C_2B_9H_{11}^-$. A unique example of an open $2,8$-C_2B_9 cage, neutral *nido*-7-Me-$2,8$-$C_2B_9H_{12}$, is obtained by acidification of the fluxional anion $10(11)$-*endo*-Me-$7,9-C_2B_9H_{11}^-$.[19–21] This $2,8$-C_2B_9 fragment is found in many *closo*-metallacarboranes with a metal atom occupying the twelfth vertex.[22]

Geometries of the air-sensitive 11-vertex *closo*-carboranes formed in this study were determined by multinuclear NMR spectroscopy and confirmed where possible by the reliable *ab initio*/GIAO/NMR method.[23] In addition 11-vertex geometries of *B*-methyl-*nido*-carboranes (where only the neutral carborane *nido*-11-Me-$2,7$-$C_2B_9H_{12}$ is structurally determined[24]) were deduced by these methods.

Experimental

NMR spectra including 2D ^{11}B–$^{11}B\{^1H\}$ COSY and $^1H\{^{11}B$ selective} were recorded on Varian Unity 300 (299.9 MHz ^1H, 96.2 MHz ^{11}B and 75.4 MHz ^{13}C), Varian Mercury 200 (188.2 MHz ^{19}F) or Varian Inova 500 (160.3 MHz ^{11}B) instruments. ^1H NMR spectra were referenced to residual protio impurity in the solvent (CHD$_2$CN, 1.95; C_6D_5H, 7.15 ppm). ^{13}C NMR spectra were referenced to the solvent resonance (CD$_3$CN, 118.2, 1.3; C_6D_6, 128.0 ppm). ^{11}B and ^{19}F NMR spectra were referenced externally to $Et_2O \cdot BF_3$ in Et_2O $\delta = 0.0$ ppm and neat $CFCl_3$ $\delta = 0.0$ ppm respectively. Boron-11 peak assignments were obtained with the aid of 2D ^{11}B–$^{11}B\{^1H\}$ COSY spectra where possible. Proton peaks corresponding to boron-bound hydrogens were assigned on the basis of selective boron-decoupled proton ($^1H\{^{11}B$ selective}) spectra. Unless otherwise stated, no extraneous resonances due to impurities of any kind were observed in the various NMR spectra of products. Carboranes $7,8-C_2B_9H_{13}$,[25] (Me$_3$NH)(*nido*-$7,9-C_2B_9H_{12}$),[26] (Bu$_4$N)(*nido*-$7,9$-$C_2B_9H_{12}$),[14] (Bu$_4$N)(*nido*-$7,9$-Me$_2$-$7,9$-$C_2B_9H_{10}$),[15] (Bu$_4$N)(*nido*-7-Ph-9-Me-$7,9$-$C_2B_9H_{10}$),[15] (Bu$_4$N)(*nido*-$7,9$-Ph$_2$-$7,9$-$C_2B_9H_{10}$),[15] (Bu$_4$N)[*nido*-10-F-$7,9$-(p-FC$_6$H$_4$)$_2$-$7,9$-$C_2B_9H_9$],[15] (Bu$_4$N)[*nido*-3-F-$7,9$-(p-FC$_6$H$_4$)$_2$-$7,9$-$C_2B_9H_9$],[15] (Bu$_4$N)[*nido*-1-(6-)-Cl-$7,9$-$C_2B_9H_{11}$],[16] (Bu$_4$N)[*nido*-1-(6-)-I-$7,9$-$C_2B_9H_{11}$][16] and (Bu$_4$N)-(*nido*-10-OEt-$7,9$-$C_2B_9H_{11}$)[3,27] were prepared by literature methods. Anhydrous monoglyme and diglyme (both Aldrich) were used as received. Deuterated acetonitrile, CD$_3$CN, was dried over CaH$_2$ and vacuum distilled.

CAUTION: Benzene is a suspected carcinogen and exposure should be minimised. The reactions described here must be performed with suitable containment. The alternative toluene cannot be separated from *closo*-$C_2B_9H_{11}$ on sublimation. Toluene also undergoes sulfonation[28] giving organic impurities which cannot be separated from the desired *closo*-carborane product.

Synthesis of $2,3-C_2B_9H_{11}$ 2a

Under nitrogen, a vigorously stirred and cooled (0 °C ice bath) suspension of (Bu$_4$N)(*nido*-$7,9$-$C_2B_9H_{12}$) **1a** (3.75 g, 10 mmol) in benzene (100 ml) was treated with conc. H_2SO_4 (100 ml). After the solid had dissolved and gas evolution ceased (2 h), the benzene layer was separated and dried (MgSO$_4$). Benzene was removed under reduced pressure to give a residue. Sublimation of the residue at 50 °C/0.1 mmHg gave a white air-sensitive solid *closo*-$2,3$-$C_2B_9H_{11}$ **2a** (0.98 g, 74%). The adduct 10-

(D$_3$CCN)-$2,3$-$C_2B_9H_{11}$ **3** was formed by addition of dry CD$_3$CN to a sample of pure $2,3$-$C_2B_9H_{11}$ in an NMR tube.

Syntheses of 2-R-3-R′-$2,3$-$C_2B_9H_9$ (R,R′ = Me 2b, Ph 2c; R = Ph, R′ = Me 2d)

Under nitrogen at 0 °C (ice bath), a stirred suspension of (Bu$_4$N)(*nido*-$7,9$-Me$_2$-$7,9$-$C_2B_9H_{10}$) **1b** (0.81 g, 2 mmol) in benzene (25 ml) was treated with conc. H_2SO_4 (30 ml). After the solid had dissolved and gas evolution ceased (1 h), the benzene layer was separated. After drying (MgSO$_4$), benzene was removed under reduced pressure. Sublimation of the residue at 50 °C/0.1 mmHg gave *closo*-$2,3$-Me$_2$-$2,3$-$C_2B_9H_9$ **2b** (0.27 g, 83%). Similar yields were obtained for *closo*-$2,3$-Ph$_2$-$2,3$-$C_2B_9H_9$ **2c** and *closo*-2-Ph-3-Me-$2,3$-$C_2B_9H_9$ **2d** and from (Bu$_4$N)(*nido*-$7,9$-Ph$_2$-$7,9$-$C_2B_9H_{10}$) **1c** and (Bu$_4$N)(*nido*-7-Ph-9-Me-$7,9$-$C_2B_9H_{10}$) **1d** respectively. The diphenyl derivative **1c** required heating to 40 °C for complete conversion.

Syntheses of 10-X-$2,3$-$C_2B_9H_{10}$ (X = Cl 2e, I 2f)

Under nitrogen at 0 °C (ice bath), a 1 : 2 mixture of (Bu$_4$N)(*nido*-1-Cl-$7,9$-$C_2B_9H_{10}$) **1e** and (Bu$_4$N)(*nido*-6-Cl-$7,9$-$C_2B_9H_{10}$) **1g** (0.82 g, 2 mmol) suspended in benzene (25 ml) was treated with conc. H_2SO_4 (30 ml). After the solid had dissolved and gas evolution ceased, the benzene layer was separated. After drying (MgSO$_4$), benzene was removed under reduced pressure. The residue (0.3 g) was dissolved in benzene-d_6 and a sample of the solution was shown by NMR spectroscopy to contain *closo*-10-Cl-$2,3$-$C_2B_9H_{10}$ **2e** of high purity – estimated to be 95% on the basis of its ^1H and ^{13}C NMR spectra where the proton and carbon peaks corresponding to a Bu$_4$N$^+$ group are also present. Attempts to purify the halogenated carborane by sublimation or crystallisation proved unsuccessful.

From the related iodide salts (Bu$_4$N)(*nido*-1-I-$7,9$-$C_2B_9H_{10}$) **1f** and (Bu$_4$N)(*nido*-6-I-$7,9$-$C_2B_9H_{10}$) **1h** using the same procedure, 10-I-$2,3$-$C_2B_9H_{10}$ **2f** was obtained in similar purity. NMR data for 10-I-$2,3$-$C_2B_9H_{10}$: δ_B (C_6D_6) -3.1 (d, B5,6), -4.3 (d, B4,7), -7.3 (d, B11), -7.3 (d, B8,9), -12.8 (d, B1), -18.2 (s, B10); δ_H 4.84 (C2,3H), 3.45 (B11H), 3.09 (B4,7H), 2.51 (B8,9H), 2.28 (B5,6H), 0.03 (B1H).

Synthesis of 4-F-$2,3$-(p-FC$_6$H$_4$)$_2$-$2,3$-$C_2B_9H_8$ 2i

Under nitrogen at 0 °C (ice bath), a vigorously stirred suspension of (Bu$_4$N)[*nido*-3-F-$7,9$-(p-FC$_6$H$_4$)$_2$-$7,9$-$C_2B_9H_8$] **1i** (1.16 g, 2 mmol) in benzene (20 ml) was treated with F_3CSO_3H (10 ml). After the solid had dissolved and gas evolution ceased (2 h), the benzene layer was separated. After drying (MgSO$_4$), benzene was removed under reduced pressure. The residual oil (0.55 g, 81%) was identified as 4-F-$2,3$-(p-FC$_6$H$_4$)$_2$-$2,3$-$C_2B_9H_8$ **2i** by multinuclear NMR spectroscopy. Like **2e** and **2f**, the purity of the oil **2i** was at least 90% with the same impurity observed in its proton and carbon NMR spectra. ^{19}F NMR: observed δ_F (C_6D_6) -112.2 (m, FC$_6$H$_4$), -161.4 (broad singlet, BF); calculated δ_F -95.7 (FC$_6$H$_4$), -96.2 (FC$_6$H$_4$), -153.5 (BF).

Acidification of 10-F-$7,9$-(p-FC$_6$H$_4$)$_2$-$7,9$-$C_2B_9H_9^-$ 1j

Under nitrogen at 0 °C (ice bath), a suspension of (Bu$_4$N)-[*nido*-10-F-$7,9$-(p-FC$_6$H$_4$)$_2$-$7,9$-$C_2B_9H_8$] **1j** (1.16 g, 2 mmol) in benzene (20 ml) was treated with F_3CSO_3H (10 ml). After the solid had dissolved, the benzene layer was separated. After drying (MgSO$_4$), benzene was removed under reduced pressure. Vacuum sublimation of the residue gave an off-white air-sensitive solid, $2,3$-(p-FC$_6$H$_4$)$_2$-$2,3$-$C_2B_9H_9$ (0.46 g, 72%) **2j**. ^{19}F NMR: observed δ_F (C_6D_6) -112.2 (FC$_6$H$_4$); calculated δ_F -96.2 (FC$_6$H$_4$).

Acidification of 10-EtO-$7,9$-$C_2B_9H_{11}^-$ 1k

Under nitrogen at 0 °C (ice bath), a stirred suspension of (Bu$_4$N)(*nido*-10-EtO-$7,9$-$C_2B_9H_{11}$) **1k** (0.42 g, 1 mmol) in

benzene (20 ml) was treated with 10 ml of F_3CSO_3H (or conc. H_2SO_4). ^{11}B NMR spectroscopy on an aliquot of the benzene solution revealed only $2,3-C_2B_9H_{11}$ **2a**.

Synthesis of $11-Me-2,7-C_2B_9H_{12}$ 4

Under nitrogen, a stirred solution of $7,8-C_2B_9H_{13}$ (12.3 g, 0.064 mol) in a 1 : 1 mixture of diethyl ether and benzene (400 ml) was treated dropwise with BuLi (64 ml of 2.5 M in hexanes, 0.16 mol). An aliquot of the solution was then examined by ^{11}B NMR spectroscopy to ensure complete conversion to $Li_2C_2B_9H_{11}$[29] and the solvents were removed under reduced pressure. The oily residue was dissolved in 300 ml of THF and cooled to 0 °C. MeI (8 ml, 0.256 mol) was added dropwise to the solution.

Working at 0 °C, an aliquot of the THF solution was transferred into a Youngs' NMR tube, THF was removed under reduced pressure, and CD_3CN added to the residue to record multinuclear NMR spectra for the anion $11-Me-2,7-C_2B_9H_{11}^-$ **5**.

At 0 °C THF was removed under reduced pressure and the residue was treated with heptane (200 ml) and acetic acid (200 ml). The solution was allowed to warm to room temperature and water (400 ml) was added. The heptane layer was separated and washed with distilled water (4 × 200 ml). The organic layer was dried ($MgSO_4$), and the heptane removed under reduced pressure. The oily residue was distilled at 80 °C/0.01 mmHg to give 6.5 g (68% yield) of $11-Me-2,7-C_2B_9H_{12}$ **4** as a clear oil which solidified on cooling to −30 °C.

Synthesis of $8-Me-7,9-C_2B_9H_{11}^-$ 1l

A sample of $11-Me-2,7-C_2B_9H_{12}$ **4** (1.5 g, 0.1 mol) in diethyl ether (30 ml) was treated with neat Me_3N (3 ml) and the resulting precipitate isolated by filtration. The air-sensitive white solid $(Me_3NH)(8-Me-7,9-C_2B_9H_{11})$ **1l** (1.85 g, 89%) was washed with water (5ml) then diethyl ether (2 × 10ml) and finally dried *in vacuo*.

Synthesis of $9-Me-7,8-C_2B_9H_{11}^-$ 6

A THF (10 ml) solution of $11-Me-2,7-C_2B_9H_{12}$ **4** (1.5 g, 0.1 mol) was added to a stirred suspension of NaH (1.5 g, excess) in THF (25 ml). The solution was filtered and THF was removed under reduced pressure to leave a semi-solid. This residue was treated with H_2O (25 ml) and then a saturated solution of Me_3NHCl in water (25ml) to give a yellow oil. The oil was separated from the aqueous layer, and triturated with anhydrous diethyl ether to give an off-white solid. The hygroscopic but air-stable solid $(Me_3NH)(9-Me-7,8-C_2B_9H_{11})$ **6** (1.62 g, 78%) was dried *in vacuo*.

Synthesis of $10-Me-7,9-C_2B_9H_{11}^-$ 1m

Under nitrogen $(Me_3NH)(7,9-C_2B_9H_{12})$ (3.87 g, 0.02 mol) was dissolved in 1 : 1 mixture of diethyl ether and benzene (100 ml). BuLi (20 ml of 2.5 M in hexanes, 0.05 mol) was added dropwise with stirring. An aliquot of the solution was examined by ^{11}B NMR and shown to contain $Li_2C_2B_9H_{11}$.[29] The solvents were then removed under reduced pressure. The oily residue was dissolved in THF (100 ml) and cooled to 0 °C before MeI (2.5 ml, 0.08 mol) was added dropwise.

Working at 0 °C, a sample of the THF solution was taken into a Youngs' NMR tube and the solvent was removed under reduced pressure. CD_3CN was added to the residue to obtain multinuclear NMR data for the anion *nido*-$10-endo-Me-7,9-C_2B_9H_{11}^-$ **1n**.

The solution was allowed to warm to room temperature over 2 h and the solvents were removed under reduced pressure. The oily residue was slowly treated with Me_3NHCl in water. The resulting oil was separated from the aqueous layer, and triturated with diethyl ether to give an air-sensitive off-white solid of $(Me_3NH)(10-Me-7,9-C_2B_9H_{11})$ **1m** (1.95 g, 47%).

Synthesis of $7-Me-2,8-C_2B_9H_{12}$ 7

A solution containing a 4 : 1 mixture of $K^+(nido-7,9-C_2B_9H_{12})$ and $K^+(nido-10-OEt-7,9-C_2B_9H_{12})$ from the deboronation[3] of $1,7-C_2B_{10}H_{12}$ with KOH in ethanol was subjected to azeotropic distillation with toluene using a Dean–Stark apparatus to remove water and ethanol, precipitating the carborane salts. The resulting solid was filtered and dried *in vacuo*. A solution of this white solid (0.3 g) in THF (30 ml) was refluxed with an excess of NaH (1 g) for 12 h. The resulting solution was filtered, and an aliquot of the filtrate was examined by ^{11}B NMR spectroscopy and shown to contain $Na_2C_2B_9H_{11}$.[29] The filtrate was cooled to −80 °C and MeI (2 ml, 0.064 mol) was added. The temperature was raised to 0 °C and THF was removed under reduced pressure, finally leaving the residue *in vacuo* at 0 °C for 5 h. At 0 °C the oily residue was dissolved in diethyl ether (10 ml) and slowly treated with HCl in diethyl ether (10 ml of 2 M solution). An aliquot was removed and the solvents removed under reduced pressure to give an oil which was dissolved in benzene-d_6 for NMR spectroscopy. Detailed NMR studies on this sample showed neutral carborane $7-Me-2,8-C_2B_9H_{12}$ **7** along with minor organic impurities. Attempts to purify the carborane by sublimation resulted in isolation of *arachno*-$1,3-C_2B_7H_{13}$ **8**.[4] See ESI† for detailed NMR data for **8**.

Syntheses of $B-Me-2,3-C_2B_9H_{10}$ isomers 2l–n

Under nitrogen a stirred suspension of $(Me_3NH)(8-Me-7,9-C_2B_9H_{11})$ **1l** (2.08 g, 10 mmol) in benzene (30 ml) was slowly treated with conc. H_2SO_4 (10 ml) and stirred for 1 h. The benzene layer was separated then dried ($MgSO_4$) and the solvents were removed under reduced pressure. The oily residue was distilled at 50 °C/0.01 mmHg to give a clear air-sensitive oil (1.08 g, 74%) identified by NMR as a 10 : 3 : 1 mixture of $4-Me-2,3-C_2B_9H_{10}$ **2l**, $1-Me-2,3-C_2B_9H_{10}$ **2m** and $8-Me-2,3-C_2B_9H_{10}$ **2n**.

The same mixture of *closo*-$B-Me-2,3-C_2B_9H_{10}$ isomers was obtained using an identical procedure with $(Me_3NH)-(10-Me-7,9-C_2B_9H_{11})$ **1m** instead of $(Me_3NH)(8-Me-7,9-C_2B_9H_{11})$ **1l**.

Reduction of $4-F-2,3-(p-FC_6H_4)_2-2,3-C_2B_9H_8$ 2i by $NaBH_4$

An excess of $NaBH_4$ (0.5 g, 13 mmol) was added to a solution of $4-F-2,3-(p-FC_6H_4)_2-2,3-C_2B_9H_8$ **2i** (0.4 g, 1.1 mmol) in dry diglyme (20 ml). The solution was slowly heated to 70 °C and maintained at this temperature for 2 h. A sample of the solution was shown to contain the known anion $10-F-7,9-(p-FC_6H_4)_2-7,9-C_2B_9H_8^-$ **1j** by ^{11}B and ^{19}F NMR spectroscopy.[15]

Reduction of $Me-2,3-C_2B_9H_{10}$ isomers 2l–n by $NaBH_4$

Under nitrogen, a stirred slurry of $NaBH_4$ in dry DME (40 ml) was treated dropwise with a solution of $B-Me-2,3-C_2B_9H_{10}$ **2l–n** (0.73 g, 5 mmol) in dry DME (10 ml). After gas evolution had ceased (1 h), the DME was removed under reduced pressure. Water was added to the residue followed by a saturated aqueous solution of Bu_4NBr. The resulting precipitate was filtered off and dried *in vacuo*. The white solid (1.31 g, 67%) was identified by NMR spectroscopy as being the Bu_4N^+ salts of a 16 : 5 : 2 : 1 ratio mixture of 10-, 8-, 3- and $2-Me-7,9-C_2B_9H_{11}^-$ anions (**1m**, **1l**, **1o**, **1p** respectively). Limited observed NMR data for **1p** δ_H 0.02 (B–Me), −2.40 (Hμ). Calculated δ_B 2.2 (B2), −4.7 (B5), −7.5 (B8), −20.6 (B3), −22.7 (B4), −24.0 (B11), −25.6 (B10), −34.3 (B1), −36.3 (B6); δ_H 2.83 (B5H), 2.55 (B8H), 1.86 (B10H), 1.76 (B11H), 1.67 (B3H), 1.62 (B4H), 1.15 (B1H), 1.02 (C7H), 0.95 (C9H), 0.70 (B6H), 0.17 (CH_3), −2.43 (Hμ). The other possible isomers 6- and $1-Me-7,9-C_2B_9H_{11}^-$ have calculated δ_H values of −0.03 and 0.21 for B–Me and −2.20 and −2.02 for Hμ respectively.

Computational section

All *ab initio* computations were carried out with the Gaussian 94 and 98 packages.[30,31] The geometries discussed here were optimised at the HF/6-31G* level with no symmetry constraints. Frequency calculations were computed on these optimised geometries at the HF/6-31G* level for imaginary frequencies. For 8-F-2,3-$C_2B_9H_{10}$ **XIII**, an imaginary frequency was unexpectedly found at this level but at the B3LYP/6-31G*// B3LYP/6-31G* level no imaginary frequency was found. Optimisation of these geometries was then carried out at the computationally intensive MP2/6-31G* level and NMR shifts calculated at the GIAO-B3LYP/6-311G* level. Theoretical [11]B chemical shifts at the GIAO-B3LYP/6-311G*//MP2/6-31G* level listed in Table 1 and Table 2 have been referenced to B_2H_6 (16.6 ppm [32]) and converted to the usual $BF_3 \cdot OEt_2$ scale: $\delta(^{11}B)$ = 102.83 − $\sigma(^{11}B)$. The ^{13}C and ^{1}H chemical shifts were referenced to $SiMe_4$: $\delta(^{13}C)$ = 184.81 − $\sigma(^{13}C)$; $\delta(^{1}H)$ = 32.28 − $\sigma(^{1}H)$. Theoretical ^{19}F chemical shifts at the GIAO-B3LYP/6-311G*// MP2/6-31G* level have been referenced to HF (214 ppm) and converted to the usual $CFCl_3$ scale: $\delta(^{19}F)$ = 185.4 − $\sigma(^{19}F)$.[33] Relative energies (Table 3) were computed at the MP2/6-31G* level with ZPE (calculated at HF/6-31G*) corrections scaled by 0.89. Where appropriate, the non-hydrogen atoms of experimental and calculated geometries were compared using the *ofit* command of XP,[34] which produces a r.m.s. deviation or misfit value.

See ESI† for .xyz files containing Cartesian coordinates of MP2-optimized geometries of **I** to **XXXVII**.

Results and discussion

No reaction occurs on adding acetic acid to a suspension of $(Bu_4N)(nido$-7,9-$C_2B_9H_{12})$, **1a**, in benzene. Using conc. H_2SO_4 at ambient temperature results in the evolution of gas and formation of *closo*-$C_2B_9H_{11}$, **2a** (see Scheme 2). Careful monitoring of the reaction by ^{11}B NMR spectroscopy provides no evidence for the formation of a '$C_2B_9H_{13}$' carborane intermediate. We suggest that in the reported reaction of '7,9-$C_2B_9H_{13}$' with 6-SB_9H_{11}, the starting carborane must be *closo* 2,3-$C_2B_9H_{11}$ **2a** as it is found as the main 'product'.[35] The high yields of *closo*-2,3-$C_2B_9H_{11}$ **2a** obtained from the reactions between salts of *nido*-7,9-$C_2B_9H_{12}^-$ **1a** and sulfuric acid suggest this to be superior to the reported polyphosphoric acid reaction (36% yield) and thermolysis of 7,8-$C_2B_9H_{13}$ (22% yield).[4]

At ambient temperatures, acidification of the corresponding C,C′-substituted derivatives *nido*-7,9-R,R′-7,9-$C_2B_9H_{10}^-$ (R,R′ = Me **1b**, Ph **1c**; R = Ph, R′ = Me **1d**) gives the neutral carboranes, *closo*-2,3-R,R′-2,3-$C_2B_9H_9$ **2b**–**d** in good yields. The reaction of **1c** is sluggish and requires heating for 1 hour at 40 °C for complete *nido*–*closo* conversion, presumably due to the electron-withdrawing and bulky phenyl groups. Similar yields of *closo*-2,3-R,R′-2,3-$C_2B_9H_9$ have been reported by acidification of the 7,8 isomers *nido*-7,8-R,R′-7,8-$C_2B_9H_{10}^-$ to give *nido*-7,8-R,R′-7,8-$C_2B_9H_{11}$ and subsequent thermolysis.[4–7] Our ^{11}B NMR data, listed in Table 1, agree with reported values for C,C′-substituted derivatives,[36] except for *closo*-2-Ph-3-Me-2,3-$C_2B_9H_9$ **1d** which was previously characterised in THF.[7] The ^{1}H NMR data for *closo*-2,3-$C_2B_9H_{11}$ **2a** are in agreement with reported values.[37]

Boron-substituted *nido*-clusters are of particular interest in exploring the mechanism of cage rearrangement involved in the *nido*–*closo* conversion. Reactions of isomeric mixtures of *nido*-1-X- and *nido*-6-X-7,9-$C_2B_9H_{11}^-$ anions (X = Cl **1e**/**1g**, I **1f**/**1h**) with H_2SO_4 gave air-sensitive *closo*-10-X-2,3-$C_2B_9H_{10}$ **2e** and **2f**. A simple cage closure of the *nido*-7,9-$C_2B_9H_{12}^-$ anion, by formation of two new bonds B8–B10 and B8–B11, would result in the B6 and B1 atoms being identical in the *closo*-cage, (*i.e.*, B10 and B11 in the *closo*-skeleton numbering, Scheme 1). Likewise the 3-substituted anion *nido*-3-F-7,9-(p-$FC_6H_4)_2$-7,9-$C_2B_9H_9^-$
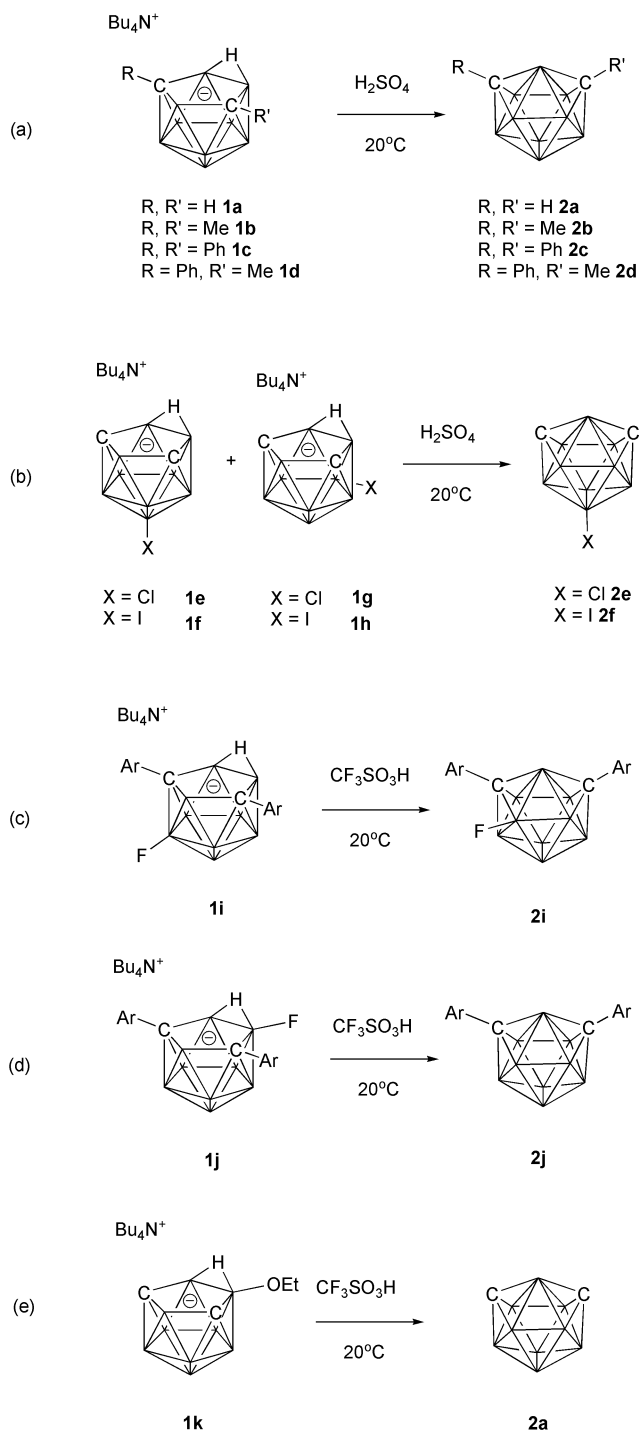
Scheme 2 The *nido*-to-*closo* conversions by acidification of 7,9-$C_2B_9H_{12}^-$ and derivatives carried out in this study (Ar = p-C_6H_4F).

1i gave the expected isomer *closo*-4-F-2,3-(p-$FC_6H_4)_2$-2,3-$C_2B_9H_8$ **2i** (Scheme 2c) with neat F_3CSO_3H. In addition to the phenyl groups, the electron-withdrawing fluorine substituent makes the bridging hydrogen on the open face less basic, thus a superacid is required in place of conc. H_2SO_4 for the *nido*–*closo* reaction to proceed.

Acidification of *nido*-10-F-7,9-(p-$FC_6H_4)_2$-7,9-$C_2B_9H_9^-$ **1j** and *nido*-10-EtO-7,9-$C_2B_9H_{11}^-$ **1k** with neat CF_3SO_3H resulted in *closo*-2,3-(p-$FC_6H_4)_2$-2,3-$C_2B_9H_9$ **2j** and *closo*-2,3-$C_2B_9H_{11}$ **2a**, as the major carborane products respectively (Scheme 2d and Scheme 2e). Adding conc. H_2SO_4 to *nido*-10-F-7,9-(p-$FC_6H_4)_2$-7,9-$C_2B_9H_9^-$ **1j** did not result in the formation of any *closo*-carborane, even at elevated temperatures. Again it appears that the proximity of the bulky electron-withdrawing phenyl groups and the fluorine substituent increases the basicity of the bridging hydrogen. The loss of the ethoxy and fluoro

Table 1 Observed and calculated ^{11}B, ^{13}C and ^{1}H NMR data for *closo*-carboranes discussed in this study. All experimental data recorded in C_6D_6

	Exp. (^{11}B, ^{13}C)^a	Calc.(^{11}B, ^{13}C)^a	Exp. (^{1}H)	Calc. (^{1}H)
2,3-C$_2$B$_9$H$_{11}$ **2a**	−4.2 (B4,5,6,7)	−5.8 (B4,5,6,7)	2.76 (B4,5,6,7H)	3.31 (B4,5,6,7H)
	−8.5 (B8,9)	−9.7 (B8,9)	2.76 (B10,11H)	2.98 (B10,11H)
	−10.2 (B10,11)	−10.2 (B10,11)	2.25 (B8,9H)	1.76 (B8,9H)
	−15.8 (B1)	−18.9 (B1)	0.62 (B1H)	1.40 (B1H)
	<u>87.3</u>	<u>93.9</u>	5.19 (CH)	5.74 (CH)
2,3-Me$_2$-2,3-C$_2$B$_9$H$_9$ **2b**	−3.2 (B4,5,6,7)	−4.6 (B4,5,6,7)	2.86 (B10,11H)	3.24 (B4,5,6,7)
	−7.0 (B8,9)	−6.3 (B8,9)	2.75 (B4,5,6,7H)	2.85 (B8,9H)
	−10.4 (B10,11)	−11.6 (B10,11)	2.43 (B8,9H)	2.80 (B10,11H)
	−11.7 (B1)	−15.7 (B1)	0.65 (B1H)	1.38 (B1H)
	<u>102.5</u>	<u>108.9 (C2,3)</u>	2.06 (CH$_3$)	2.57 (CH$_3$)
	<u>24.4</u>	<u>28.2 (CH$_3$)</u>		
2,3-Ph$_2$-2,3-C$_2$B$_9$H$_9$ **2c**	−4.0 (B4,5,6,7)	−4.5 (B4,5,6,7)	3.06 (B4,5,6,7H)	3.46 (B4,5,6,7)
	−5.8 (B8,9)	−6.9 (B8,9)	3.00 (B10,11H)	3.12 (B8,9H)
	−9.6 (B10,11)	−8.3 (B10,11)	2.73 (B8,9H)	2.93 (B10,11H)
	−11.5 (B1)	−11.8 (B1)	1.50 (B1H)	2.13 (B1H)
	<u>140.6</u>	<u>148.7 (*ipso* C)</u>	7.27 (2H, d, 7)	7.43 (*ortho* CH)
	<u>130.3</u>	<u>133.3 (*ortho* C)</u>	7.02 (3H, m)	7.25 (*meta* CH)
	<u>129.8</u>	<u>132.0 (*para* C)</u>		7.25 (*para* CH)
	<u>129.2</u>	<u>131.2 (*meta* C)</u>		
	<u>110.2</u>	<u>115.7 (C2,3)</u>		
2-Ph-3-Me-2,3-C$_2$B$_9$H$_9$ **2d**	−4.6 (B4,5,6,7)	−4.8 (B6,7)	3.07 (B4,5H)	3.45 (B4,5H)
	−5.5 (B9)	−5.4 (B4,5)	2.97 (B10,11H)	3.29 (B6,7H)
	−7.3 (B8)	−5.7 (B9)	2.81 (B6,7H)	3.03 (B8H)
	−9.0 (B10,11)	−7.5 (B8)	2.70 (B8H)	2.95 (B10,11H)
	−11.7 (B1)	−10.5 (B10,11)	2.52 (B9H)	2.91 (B9H)
		−14.7 (B1)	1.11 (B1H)	1.81 (B1H)
	<u>141.9</u>	<u>150.6 (*ipso* C)</u>		
	<u>130.3</u>	<u>136.8 (*para* C)</u>	7.27 (2H, d, 7)	7.72 (*ortho* CH)
	<u>129.8</u>	<u>136.6 (*ortho* C)</u>	7.03 (3H, m)	7.51 (*meta* CH)
	<u>129.2</u>	<u>134.0 (*meta* C)</u>	2.08 (CH$_3$)	7.51 (*para* CH)
	<u>108.5</u>	<u>115.4 (CPh)</u>		2.61 (CH$_3$)
	<u>104.9</u>	<u>110.9 (CMe)</u>		
	<u>25.3 (CH$_3$)</u>	<u>28.3 (CH$_3$)</u>		
10-Cl-2,3-C$_2$B$_9$H$_{10}$ **2e**	4.3 (B10)	6.1 (B10)	3.46 (B11H)	3.66 (B11H)
	1.2 (B5,6)	−3.1 (B5,6)	2.99 (B4,7H)	3.52 (B4,7H)
	−5.8 (B11)	−5.7 (B11)	2.64 (B5,6H)	3.34 (B5,6H)
	−5.8 (B4,7)	−7.4 (B4,7)	2.22 (B8,9H)	2.62 (B8,9H)
	−8.8 (B8,9)	−10.2 (B8,9)	0.67 (B1H)	1.84 (B1H)
	−10.8 (B1)	−13.6 (B1)		
	<u>81.2 (C2,3)</u>	<u>86.2 (C2,3)</u>	4.69 (C2,3H)	5.41 (C2,3H)
4-F-2,3-(*p*-FC$_6$H$_4$)$_2$-2,3-C$_2$B$_9$H$_8$ **2i**$^{b c}$	10.2 (B4)	7.4 (B4)	3.34 (B7H)	3.64 (B7H)
	2.2 (B7)	0.2 (B7)	3.19 (*B6H*)	3.49 (B8H)
	−4.2 (B8)	−6.6 (B8)	2.99 (B8H)	3.27 (B6H)
	−5.3 (*B11*)	−8.0 (B11)	2.89 (B10H)	3.09 (B10H)
	−8.2 (*B9*)	−9.5 (B9)	2.89 (*B11H*)	3.04 (B11H)
	−8.2 (*B6*)	−10.0 (B6)	2.79 (*B9H*)	2.92 (B9H)
	−9.4 (B1)	−10.4 (B1)	2.33 (B5H)	2.91 (B5H)
	−13.1 (B10)	−12.0 (B10)	1.68 (B1H)	2.72 (B1H)
	−19.7 (B5)	−18.8 (B5)		
	<u>164.3 (252)</u>	<u>174.8 (C3 *para*)</u>	7.15 (m)	7.78 (*ortho* C3)
	<u>164.0(252)</u>	<u>174.3 (C2 *para*)</u>	6.69 (m)	7.74 (*ortho* C2)
	<u>132.7</u>	<u>145.5 (C3 *ipso*)</u>		7.11 (*meta* C3)
	<u>132.1</u>	<u>142.5 (C2 *ipso*)</u>		7.07 (*meta* C2)
	<u>132.0</u>	<u>138.4 (C2 *ortho*)</u>		
	<u>132.0</u>	<u>138.2 (C3 *ortho*)</u>		
	<u>116.3 (21)</u>	<u>121.5 (C3 *meta*)</u>		
	<u>116.2 (21)</u>	<u>121.2 (C2 *meta*)</u>		
	<u>107.8</u>	<u>115.5 (C3)</u>		
	<u>105.5</u>	<u>100.5 (C2)</u>		
2,3-(*p*-FC$_6$H$_4$)$_2$-2,3-C$_2$B$_9$H$_9$ **2j**^{c}	−4.2 (B4,5,6,7)	−5.6 (B4,5,6,7)	3.02 (B4,5,6,7H)	3.49 (B4,5,6,7H)
	−5.6 (B8,9)	−6.3 (B8,9)	3.02 (B10,11H)	3.12 (B10,11H)
	−9.6 (B10,11)	−9.7 (B10,11)	2.70 (B8,9H)	3.11 (B8,9H)
	−11.4 (B1)	−13.3 (B1)	1.37 (B1H)	2.17 (B1H)
	<u>164.3 (250)</u>	<u>174.7 (*para* C)</u>		
	<u>132.0 (4)</u>	<u>146.1 (*ipso* C)</u>	7.17 (dd)	7.74 (dd)
	<u>131.8</u>	<u>138.3 (*ortho* C)</u>	6.67 (dd)	7.08 (dd)
	<u>116.1 (21)</u>	<u>121.2 (*meta* C)</u>		
	<u>109.1 (C2,3)</u>	<u>109.1 (C2,3)</u>		
4-Me-2,3-C$_2$B$_9$H$_{10}$ **2l**	9.5 (B4)	6.8 (B4)	2.88 (B7H)	3.38 (B7H)
	2.7 (B7)	−1.1 (B7)	2.77 (B11H)	3.14 (B6H)
	−7.4 (B8)	−8.6 (B11)	2.72 (B10H)	3.14 (B5H)
	−8.6 (B11)	−8.8 (B8)	2.62 (B6H)	2.97 (B10H)
	−8.6 (B6)	−8.9 (B6)	2.58 (B5H)	2.95 (B11H)
	−9.2 (B9)	−9.7 (B10)	2.35 (B8H)	2.83 (B8H)
	−10.0 (B10)	−10.3 (B9)	2.21 (B9H)	2.69 (B9H)
	−11.0 (B5)	−10.4 (B5)	0.80 (B1H)	1.49 (B1H)
	−13.9 (B1)	−17.0 (B1)		

Table 1 (Contd.)

	Exp. (^{11}B, ^{13}C)^a	Calc.(^{11}B, ^{13}C)^a	Exp. (^{1}H)	Calc. (^{1}H)
4-Me-2,3-C$_2$B$_9$H$_{10}$ **2l**	86.7 (C)	94.3(C3)	5.24 (CH)	5.80 (C3H)
	85.8 (C)	92.7(C2)	4.80 (CH)	5.40 (C2H)
	3.2 (CH$_3$)	5.5 (CH$_3$)	0.42 (CH$_3$)	0.58 (CH$_3$)
1-Me-2,3-C$_2$B$_9$H$_{10}$ **2m**	−1.9 (B4,5,6,7)	−3.5 (B4,5,6,7)	2.97 (B4,5,6,7H)	3.46 (B4,5,6,7H)
	−5.3 (B1)	−8.3 (B10,11)	2.87 (B10,11H)	3.05 (B10,11H)
	−8.6 (B10,11)	−8.5 (B1)	2.12 (B8,9H)	2.56 (B8,9H)
	−12.4 (B8,9)	−13.3 (B8,9)		
	90.6 (C2,3)	97.6 (C2,3)	4.92 (C2,3H)	5.48 (C2,3H)
	0.0 (CH$_3$)	2.9 (CH$_3$)	−0.50 (CH$_3$)	−0.04 (CH$_3$)
8-Me-2,3-C$_2$B$_9$H$_{10}$ **2n**^{d}	1.3 (B8)	0.6 (B8)		3.34 (B4,5H)
	−3.4 (2B)	−4.6 (B4,5)		3.25 (B6,7H)
	−4.7 (2B)	−6.4 (B6,7)		2.95 (B10,11H)
	−9.5 (2B)	−9.4 (B9)		2.78 (B9H)
	−9.5 (1B)	−9.7 (B10,11)		1.22 (B1H)
	−18.5 (1B)	−21.2 (B1)	5.24 (CH)	5.74 (C2H)
	90.7	96.3 (C2)	5.02 (CH)	5.60 (C3H)
	81.6	90.0 (C3)	0.32 (CH$_3$)	0.38 (CH$_3$)
		0.9 (CH$_3$)		

^{a} Underlined values are ^{13}C shifts. ^{b} 'C2' in computed shifts corresponds to the phenyl group at C2. Uncertain peak assignments are shown in italics. ^{c} Coupling constants (J_{CF}; Hz) in parentheses for observed ^{13}C data. ^{d} Proton peaks obscured by the major isomers 4-Me- and 1-Me-2,3-C$_2$B$_9$H$_{10}$.

substituents upon formation of the *closo*-carboranes suggests that EtOH and HF are formed as co-products respectively rather than H$_2$. Based on our findings, the reported acidification of the salt (Me$_4$N)[(7-Ph-7,9-C$_2$B$_9$H$_{10}$(OH)] to give *closo*-2-Ph-2,3-C$_2$B$_9$H$_{10}$ indicates the formula of the starting anion to be [10(or 11)-OH-7-Ph-7,9-C$_2$B$_9$H$_{10}$$^-$].[4]

Recently we obtained *nido*-11-Me-2,7-C$_2$B$_9$H$_{12}$ **4**, (Me$_3$NH)-(*nido*-8-Me-7,9-C$_2$B$_9$H$_{11}$) **1l** and (Me$_3$NH)(*nido*-9-Me-7,8-C$_2$B$_9$H$_{11}$) **6** (Scheme 3) as precursors to *B*-methylated tantalum

Scheme 3 Formation of *nido-B*-methyl-carboranes from *nido*-7,8-C$_2$B$_9$H$_{13}$.

carboranes.[38] As depicted in Scheme 3, the neutral carborane **4** was formed by reacting *nido*-7,8-C$_2$B$_9$H$_{13}$ with BuLi to give Li$_2$C$_2$B$_9$H$_{11}$ which then reacts with MeI to give Li(*nido*-11-Me-2,7-C$_2$B$_9$H$_{11}$) **5** followed by acetic acid to give *nido*-11-Me-2,7-C$_2$B$_9$H$_{12}$ **4**. Both the anions **1l** and **6** were generated from **4**. Detailed syntheses of these *B*-methyl *nido*-carboranes (which are modifications of literature methods[18]) are given in the Experimental section.

The anion *nido*-8-Me-7,9-C$_2$B$_9$H$_{11}$$^-$ **1l** is reported to form *nido*-11-Me-2,7-C$_2$B$_9$H$_{12}$ **4** on addition of acetic acid.[39] This reaction involves an interesting rearrangement of the carborane skeleton to accommodate both bridging hydrogens on the open face. We re-examined the acidification of Cs(*nido*-8-Me-7,9-C$_2$B$_9$H$_{11}$) **1l**. Spectroscopic characterisation of the caesium salt formed by deprotonation of *nido*-11-Me-2,7-C$_2$B$_9$H$_{12}$ **4** shows it
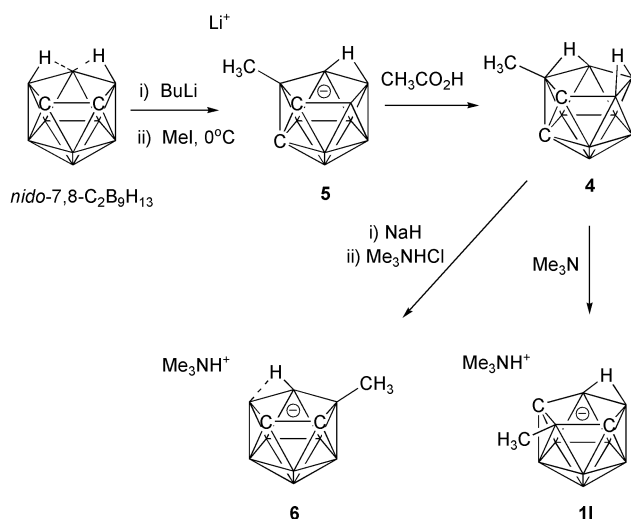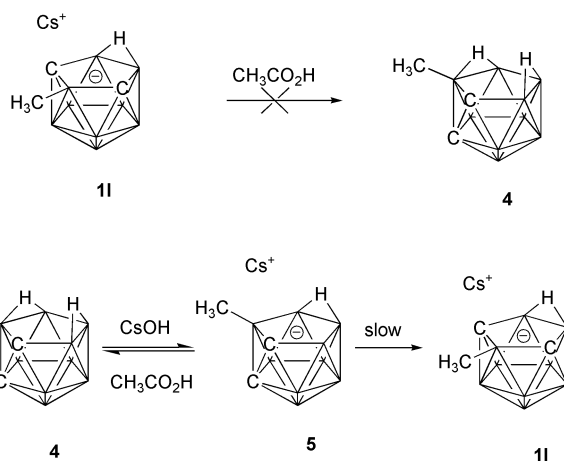
Scheme 4 Re-investigation of the reported acid-promoted cage rearrangement of the anion *nido*-8-Me-7,9-C$_2$B$_9$H$_{11}$$^-$ **1l**.

to be pure Cs(*nido*-11-Me-2,7-C$_2$B$_9$H$_{11}$) **5**. Reaction of Cs(*nido*-11-Me-2,7-C$_2$B$_9$H$_{11}$) **5** with acetic acid (Scheme 4) gave *nido*-11-Me-2,7-C$_2$B$_9$H$_{12}$ **4** as expected. The salt **5** rearranges slowly in the solid state under nitrogen at ambient temperature overnight to Cs(*nido*-8-Me-7,9-C$_2$B$_9$H$_{11}$) **1l**. No reaction occurred on addition of acetic acid to the 'carbons-apart' salt **1l**. This investigation rules out a reversible cage rearrangement between *nido*-11-Me-2,7-C$_2$B$_9$H$_{12}$ **4** and the anion *nido*-8-Me-7,9-C$_2$B$_9$H$_{11}$$^-$ **1l**.[40]

Addition of H$_2$SO$_4$ to (Me$_3$NH)(*nido*-8-Me-7,9-C$_2$B$_9$H$_{11}$) **1l** gave a 10 : 3 : 1 ratio mixture of *B*-monomethyl-*closo*-carboranes, 4-Me-2,3-C$_2$B$_9$H$_{10}$ **2l**, 1-Me-2,3-C$_2$B$_9$H$_{10}$ **2m** and 8-Me-2,3-C$_2$B$_9$H$_{10}$ **2n** (Scheme 5). A straightforward closure mechanism of the 8-substituted anion would generate *closo*-1-Me-2,3-C$_2$B$_9$H$_{10}$ only. Acidification of the related anion *nido*-10-Me-7,9-C$_2$B$_9$H$_{11}$$^-$ **1m** (see below) gave the same mixture of *B*-monomethyl *closo* carboranes. As the same isomeric mixture of *B*-monomethyl-*closo*-carboranes is obtained from acidification of salts of *nido*-8-Me- and *nido*-10-Me-7,9-C$_2$B$_9$H$_{11}$$^-$ anions, this suggests either a common carborane intermediate in both reactions or that the *B*-monomethyl carborane is fluxional in solution.

An equilibrium occurs between the three possible isomers of *B*-monomethyl 7-vertex *closo-B*-Me-2,4-C$_2$B$_5$H$_6$ at 300 °C.[41] On this basis 11-vertex *closo-B*-Me-2,3-C$_2$B$_9$H$_{10}$ isomers are likely to be in equilibrium at ambient temperature. Cage rearrangements in the 11-vertex compound are expected to be facile as an

Table 2 Observed and calculated ^{11}B, ^{13}C and ^{1}H NMR data for *nido*-carboranes discussed in this study, all data in CD$_3$CN unless otherwise stated

	Exp. (^{11}B, ^{13}C)[a]	Calc.(^{11}B, ^{13}C)[a]	Exp. (^{1}H)	Calc. (^{1}H)
nido-8-Me-7,9-C$_2$B$_9$H$_{11}$$^-$ **1l**[b]	2.4 (B8)	0.3 (B8)	2.04 (B2,5H)	2.80 (B2,5)
	−6.2 (B2,5)	−5.8 (B2,5)	1.37 (B10,11H)	1.81 (B10,11H)
	−20.1 (B3,4)	−20.4 (B3,4)	1.04 (B3,4H)	1.68 (B3,4H)
	−23.1 (B10,11)	−26.0 (B10,11)	0.62 (B1H)	1.29 (B1H)
	−33.1 (B1)	−34.0 (B1)	−0.11 (B6H)	0.62 (B6H)
	−37.8 (B6)	−38.2 (B6)	−2.20 (Hμ)	−2.33 (Hμ)
	<u>33.4 (C7,9)</u>	<u>39.1 (C7,9)</u>	0.94 (C7,9H)	0.97 (C7,9H)
	<u>3.5 (CH$_3$)</u>	<u>5.3 (CH$_3$)</u>	0.02 (CH$_3$)	0.00 (CH$_3$)
nido-10-Me-7,9-C$_2$B$_9$H$_{11}$$^-$ **1m**[b]	−2.6 (B5)	−1.8 (B5)	2.17 (B5H)	2.96 (B5H)
	−4.5 (B2)	−5.0 (B2)	2.08 (B2H)	2.84 (B2H)
	−6.4 (B8)	−7.1 (B8)	1.91 (B8H)	2.55 (B8H)
	−12.8 (B10)	−16.5 (B10)	1.38 (B11H)	1.86 (B11H)
	−21.3 (B4)	−22.4 (B4)	1.01 (B4H)	1.65 (B4H)
	−23.2 (B11)	−25.0 (B3)	0.92 (B3H)	1.51 (B3H)
	−24.7 (B3)	−25.7 (B11)	0.56 (B1H)	1.28 (B1H)
	−33.6 (B6)	−35.1 (B1)	−0.05 (B6H)	0.65 (B6H)
	−34.3 (B1)	−35.4 (B6)	−1.92 (Hμ)	−1.97 (Hμ)
	<u>36.2 (C)</u>	<u>42.3 (C9)</u>	1.17(CH)	1.12 (C9H)
	<u>30.0 (C)</u>	<u>36.7 (C7)</u>	1.10 (CH)	1.05 (C7H)
	<u>1.7 (CH$_3$)</u>	<u>4.5 (CH$_3$)</u>	0.02 (CH$_3$)	0.01 (CH$_3$)
nido-3-Me-7,9-C$_2$B$_9$H$_{11}$$^-$ **1o**[c]	−3.5 (1B)	−3.4 (B2)		2.87 (B5H)
	−3.5 (1B)	−3.8 (B5)		2.83 (B2H)
	−4.0 (1B)	−5.2 (B8)		2.50 (B8H)
	−13.4 (B3)	−14.9 (B3)		1.82 (B11H)
	−21.3 (1B)	−22.2 (B4)		1.68 (B4H)
	−23.1 (1B)	−25.8 (B11)		1.66 (B10H)
	−25.6 (1B)	−28.2 (B10)		1.28 (B1H)
	−33.4 (1B)	−34.3 (B1)		0.66 (B6H)
	−35.2 (1B)	−36.7 (B6)	−2.38 (Hμ)	−2.40 (Hμ)
		<u>43.3 (C7)</u>		1.10 (C9H)
		<u>38.0 (C9)</u>		1.07 (C7H)
		<u>5.3 (CH$_3$)</u>	−0.03 (CH$_3$)	−0.02 (CH$_3$)
nido-10-*endo*-Me-7,9-C$_2$B$_9$H$_{11}$$^-$ **1n**[d e f]	−2.0 (B2,5)	−2.7 (B2,5)	2.49 (B10,11H)	3.00 (B2,5H)
	−3.2 (B10,11)	−5.5 (B10,11)	2.32 (B2,5H)	2.95 (B10,11H)
	−5.7 (B8)	−6.9 (B8)	2.05 (B8H)	2.70 (B8H)
	−20.1 (B1)	−20.2 (B1)	1.43 (B1H)	2.12 (B1H)
	−20.1 (B3,4)	−20.4 (B3,4)	1.21 (B3,4H)	1.85 (B3,4H)
	−22.1 (B6)	−22.4 (B6)	0.76 (B6H)	1.48 (B6H)
	<u>46.0 (C7,9)</u>	<u>54.5 (C7,9)</u>	1.95 (C7,9H)	1.78 (C7,9H)
	<u>10.8 (CH$_3$)</u>	<u>17.0 (CH$_3$)</u>	0.66 (CH$_3$)	0.84 (CH$_3$)
nido-10-(CD$_3$CN)-7,9-C$_2$B$_9$H$_{11}$ **3**[g]	−2.5 (B2)	−0.9 (B5)	2.59 (B2H)	3.31 (B5H)
	−4.2 (B5)	−2.9 (B8)	2.33 (B5H)	3.19 (B2H)
	−4.8 (B8)	−3.3 (B2)	2.16 (B8H)	2.99 (B8H)
	−18.2 (B10)	−18.8 (B3)	1.95 (B11H)	2.56 (B11H)
	−20.2 (B3)	−19.3 (B4)	1.36 (B3H)	2.21 (B4H)
	−22.7 (B4)	−23.8 (B10)	1.14 (B4H)	2.03 (B3H)
	−22.7 (B11)	−24.0 (B11)	0.93 (B1H)	2.00 (B1H)
	−33.3 (B1)	−30.0 (B1)	0.52 (B6H)	1.29 (B6H)
	−33.3 (B6)	−30.0 (B6)	0.30 (Hμ)	−0.75 (Hμ)
	<u>35.0 (C7,9)</u>	<u>119.9 (CN)</u>	1.95 (CH)	2.28 (CH$_3$)
		<u>47.0 (C7)</u>	1.61 (CH)	2.01 (C9H)
		<u>43.3 (C9)</u>		1.99 (C7H)
		<u>3.9 (CH$_3$)</u>		
nido-11-Me-2,7-C$_2$B$_9$H$_{12}$ **4**[h]	1.6 (B5)	3.5 (B5)	3.19 (B5H)	3.60 (B5H)
	−0.1 (B11)	−4.1 (B11)	2.52 (B9H)	3.10 (B3H)
	−7.7 (B9)	−9.5 (B9)	2.48 (B8H)	3.04 (B8H)
	−9.0 (B3)	−10.4 (B3)	2.29 (B3H)	2.78 (B9H)
	−9.0 (B8)	−10.9 (B8)	2.12 (B1H)	2.53 (B1H)
	−22.5 (B10)	−22.7 (B10)	1.66 (B10H)	2.10 (B10H)
	−25.3 (B1)	−26.4 (B1)	1.34 (B6H)	1.76 (B6H)
	−29.0 (B6)	−31.8 (B6)	1.23 (B4H)	1.49 (B4H)
	−32.8 (B4)	−33.6 (B4)	−2.81(Hμ10,11)	−2.82 (Hμ 10,11)
	<u>58.6 (C2)</u>	<u>67.4 (C2)</u>	−3.27 (Hμ 8,9)	−3.31 (Hμ 8,9)
	<u>36.7 (C7)</u>	<u>41.0 (C7)</u>	2.29 (C2H)	3.30 (C2H)
	<u>1.0 (CH$_3$)</u>	<u>2.7 (CH$_3$)</u>	1.18 (C7H)	2.04 (C7H)
			0.14 (CH$_3$)	0.52 (CH$_3$)
nido-11-Me-2,7-C$_2$B$_9$H$_{11}$$^-$ **5**[b]	−7.1 (B11)	−11.8 (B11)	1.56 (B6H)	2.31 (B6H)
	−15.1 (B6)	−15.3 (B6)	1.25 (B4H)	2.07 (B4H)
	−17.0 (B4)	−16.2 (B4)	1.25 (B3H)	1.92 (B8H)
	−17.6 (B8)	−17.7 (B8)	1.18 (B8H)	1.75 (B3H)
	−20.3 (B9)	−23.4 (B9)	1.00 (B5H)	1.40 (B5H)
	−22.2 (B3)	−24.7 (B3)	0.95 (B10H)	1.20 (B10H)
	−24.8 (B10)	−26.5 (B10)	0.84 (B9H)	1.02 (B9H)
	−26.6 (B5)	−27.6 (B5)	0.84 (B1H)	0.96 (B1H)
	−44.1 (B1)	−46.1 (B1)	−3.29 (Hμ)	−3.13 (Hμ)
	<u>51.2 (C7)</u>	<u>47.4 (C7)</u>	1.85 (CH)	1.60 (C2H)
	<u>49.1 (C2)</u>	<u>40.6 (C2)</u>	1.25 (CH)	1.18 (C7H)

Table 2 (*Contd.*)

	Exp. (^{11}B, ^{13}C)[a]	Calc.(^{11}B, ^{13}C)[a]	Exp. (^{1}H)	Calc. (^{1}H)
nido-11-Me-2,7-C$_2$B$_9$H$_{11}^-$ **5**[b]	6.5 (CH$_3$)	2.7 (CH$_3$)	0.08 (CH$_3$)	0.07 (CH$_3$)
nido-9-Me-7,8-C$_2$B$_9$H$_{11}^-$ **6**[be]	−2.5 (B9)	−4.6 (B9)	1.90 (B11H)	2.28 (B11H)
	−10.0 (B11)	−14.4 (B11)	1.68 (B3H)	2.21 (B3H)
	−14.4 (B6)	−15.6 (B5)	1.27 (B6H)	1.92 (B5H)
	−17.7 (B3)	−17.4 (B6)	1.22 (B5H)	1.83 (B6H)
	−18.9 (B5)	−19.3 (B3)	1.00 (B4H)	1.65 (B4H)
	−18.9 (B4)	−20.6 (B4)	0.83 (B2H)	1.57 (B2H)
	−27.4 (B2)	−26.2 (B2)	0.40 (B1H)	1.01 (B1H)
	−33.2 (B10)	−34.5 (B10)	0.00 (B10H)	0.54 (B10H)
	−38.0 (B1)	−39.4 (B1)	−2.74 (Hμ)	−2.87 (Hμ)
	43.4 (C)	47.5 (C8)	1.72 (CH)	1.53 (C7H)
	42.0 (C)	46.0 (C7)	1.66 (CH)	1.49 (C8H)
	1.3	4.7 (CH$_3$)	0.25 (CH$_3$)	0.24 (CH$_3$)
nido-7-Me-2,8-C$_2$B$_9$H$_{12}$ **7**[hj]	−1.1 (B7)	−1.6 (B6)	2.93 (B6H)	3.53 (B6H)
	−1.9 (B6)	−3.1 (B7)	2.57 (B3H)	3.06 (B3H)
	−4.8 (B9)	−7.1 (B9)	2.54 (B9H)	3.00 (B9H)
	−9.7 (B4)	−9.6 (B4)	2.39 (B4H)	2.89 (B4H)
	−11.5 (B3)	−12.2 (B3)	2.27 (B1H)	2.65 (B1H)
	−19.5 (B10)	−20.8 (B10)	2.05 (B10H)	2.46 (B10H)
	−22.0 (B11)	−24.0 (B11)	1.64 (B11H)	2.01 (B11H)
	−24.9 (B1)	−26.4 (B1)	1.17 (B5H)	1.44 (B5H)
	−32.9 (B5)	−33.8 (B5)	−2.18 (Hμ 7,11)	−1.90 (Hμ 7,11)
		43.9 (C8)	−3.47 (Hμ 9,10)	−3.48 (Hμ 9,10)
		30.2 (C2)		2.09 (C8H)
		2.7 (CH$_3$)		1.56 (C2H)
			0.14 (CH$_3$)	0.49 (CH$_3$)

[a] Underlined values are ^{13}C shifts. [b] Unassigned ^{11}B NMR data reported in ref. 18. [c] Proton and carbon peaks obscured by major isomers, 8-Me- and 10-Me-7,9-C$_2$B$_9$H$_{11}^-$. [d] Unassigned ^{11}B NMR data reported in ref. 19. [e] Averaging of calculated shifts. [f] Unassigned ^{11}B NMR data reported in refs. 18 and 39. [g] ^{1}H and ^{13}C NMR peaks corresponding to the CD$_3$CN ligand were not observed – they are probably hidden in peaks corresponding to free CD$_3$CN, calculated NMR shifts are for 10-(CH$_3$CN)-7,9-C$_2$B$_9$H$_{11}$ **XXXV**. [h] In C$_6$D$_6$. [i] Measured at 0 °C. [j] Proton peaks corresponding to carboranyl C–H obscured by organic impurities, ^{13}C NMR not recorded. Unassigned ^{11}B NMR reported in ref. 20.
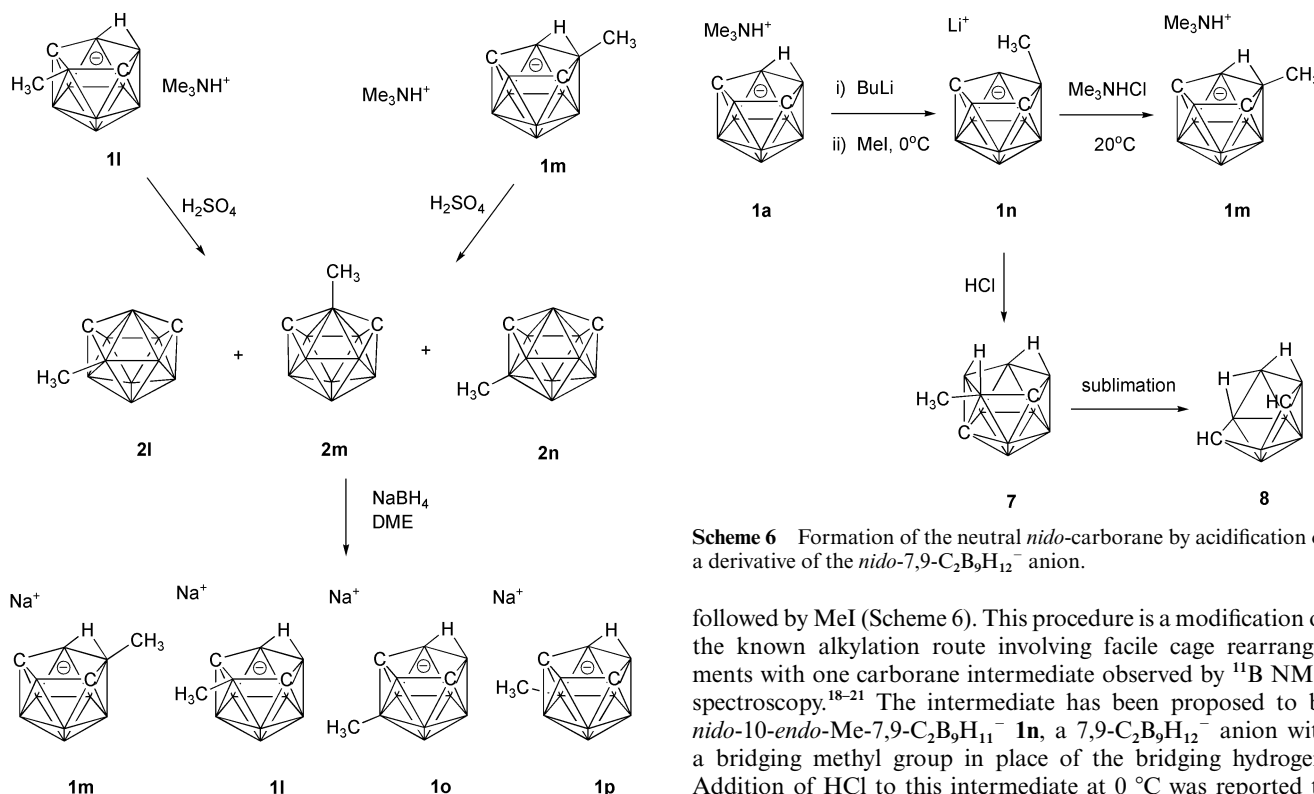
Scheme 5 The synthesis of isomeric 11-vertex *closo-B*-methyl carboranes, by acidification of *nido-B*-methyl carboranes, and their subsequent reduction by hydride ion.

Scheme 6 Formation of the neutral *nido*-carborane by acidification of a derivative of the *nido*-7,9-C$_2$B$_9$H$_{12}^-$ anion.

unfavourable seven-coordinate boron atom (B1) is present. Cage fluxionality occurs in solutions of related 11-vertex *closo*-compounds, B$_{11}$H$_{11}^{2-}$ and CB$_{10}$H$_{11}^-$.[42]

The salt (Me$_3$NH)(*nido*-10-Me-7,9-C$_2$B$_9$H$_{11}$) **1m** was prepared by the reaction of (Me$_3$NH)(*nido*-7,9-C$_2$B$_9$H$_{12}$) with BuLi

followed by MeI (Scheme 6). This procedure is a modification of the known alkylation route involving facile cage rearrangements with one carborane intermediate observed by ^{11}B NMR spectroscopy.[18–21] The intermediate has been proposed to be *nido*-10-*endo*-Me-7,9-C$_2$B$_9$H$_{11}^-$ **1n**, a 7,9-C$_2$B$_9$H$_{12}^-$ anion with a bridging methyl group in place of the bridging hydrogen. Addition of HCl to this intermediate at 0 °C was reported to give *nido*-7-Me-2,8-C$_2$B$_9$H$_{12}$ **7**, the only known example of a *nido*-2,8-C$_2$B$_9$ cage, and a potential precursor to metalla-carboranes with 2,1,8-MC$_2$B$_9$ cages, normally obtained by cage rearrangements of the more common metallacarboranes with 3,1,2-MC$_2$B$_9$ cages.[22] Since this protonation reaction appears to form a neutral *nido* carborane rather than a *closo* carborane, we repeated this reaction and find that **7** is indeed formed. However we have not yet succeeded in obtaining a pure sample of **7**, sublimation gave *arachno*-C$_2$B$_7$H$_{13}$ **8**.[4]

Table 3 Energies of MP2/6-31G* optimized geometries[k]

Optimised geometries	ZPE/a.u.	MP2/a.u.	Relative energy/kcal mol⁻¹
2,3-$C_2B_9H_{11}$ **I**	105.83(0)	−305.43626[l]	
2,3-Me_2-2,3-$C_2B_9H_9$ **II**	143.23(0)	−383.78069	
2,3-Ph_2-2,3-$C_2B_9H_9$ **III**	214.87(0)	−766.05928	
2,3-(p-FC_6H_4)$_2$-2,3-$C_2B_9H_9$ **IV**	204.04(0)	−964.09598	
2-Ph-3-Me-2,3-$C_2B_9H_9$ **V**	179.06(0)	−574.91985	
10-Br-4,7-$(OH)_2$-2,3-Me_2-2,3-$C_2B_9H_6$ **VI**	145.68(0)	−3103.41997	
1-F-2,3-$C_2B_9H_{10}$ **VII**	101.51(0)	−404.51661	0.0
4-F-2,3-$C_2B_9H_{10}$ **X**	101.74(0)	−404.51657	0.2
8-F-2,3-$C_2B_9H_{10}$ **XIII**	101.36(1)	−404.51320	3.5
10-F-2,3-$C_2B_9H_{10}$ **XVI**	101.61(0)	−404.50984	4.1
1-Cl-2,3-$C_2B_9H_{10}$ **VIII**	100.54(0)	−764.51188	1.5
4-Cl-2,3-$C_2B_9H_{10}$ **XI**	100.83(0)	−764.51428	0.0
8-Cl-2,3-$C_2B_9H_{10}$ **XIV**	100.53(0)	−764.51187	1.7
10-Cl-2,3-$C_2B_9H_{10}$ **XVII**	100.71(0)	−764.51162	1.2
1-Me-2,3-$C_2B_9H_{10}$ **IX**	124.60(0)	−344.61660	0.7
4-Me-2,3-$C_2B_9H_{10}$ **XII**	124.74(0)	−344.61735	0.0
8-Me-2,3-$C_2B_9H_{10}$ **XV**	124.50(0)	−344.61553	1.8
10-Me-2,3-$C_2B_9H_{10}$ **XVIII**	124.62(0)	−344.61368	2.8
4-F-2,3-(p-FC_6H_4)$_2$-2,3-$C_2B_9H_8$ **XIX**	199.87(0)	−1063.17600	
1,3-$C_2B_7H_{13}$ **XX**	113.91(0)	−256.96314	
7,8-$C_2B_9H_{13}$[m]	120.16(0)	−306.55322	17.8
7,9-$C_2B_9H_{13}$ **XXI**	120.32(0)	−306.55349	10.8
2,7-$C_2B_9H_{13}$ **XXII**	120.11(0)	−306.54590	19.1
2,8-$C_2B_9H_{13}$ **XXIII**	120.71(0)	−306.56935	0.0
2,9-$C_2B_9H_{13}$[m]	120.03(0)	−306.56158	12.3
11-Me-2,7-$C_2B_9H_{12}$ **XXIV**	138.85(0)	−345.72519	18.9
7-Me-2,8-$C_2B_9H_{12}$ **XXV**	139.50(0)	−345.74847	0.0
8-Me-7,9-$C_2B_9H_{11}^-$ **XXXII**	131.11(0)	−345.27001	0.0
10-Me-7,9-$C_2B_9H_{11}^-$ **XXXIII**	129.77(0)	−345.26794	2.4
10-$endo$-Me-7,9-$C_2B_9H_{11}^-$ **XXVIIa**	130.61(0)	−345.23381	23.1
10,11-μ-Me-7,9-$C_2B_9H_{11}^-$ **XXVIIb**	130.80(1)	−345.22479	33.3
1-Me-7,9-$C_2B_9H_{11}^-$ **XXVIII**	131.15(0)	−345.26788	1.9
2-Me-7,9-$C_2B_9H_{11}^-$ **XXXI**	131.15(0)	−345.27092	0.0
3-Me-7,9-$C_2B_9H_{11}^-$ **XXX**	131.14(0)	−345.26988	0.5
6-Me-7,9-$C_2B_9H_{11}^-$ **XXIX**	131.12(0)	−345.26800	2.1
9-Me-7,8-$C_2B_9H_{11}^-$ (Hμ at B9,10) **XXXIVa**	130.60(0)	−345.24407	21.0
9-Me-7,8-$C_2B_9H_{11}^-$ (Hμ at B10,11) **XXXIVb**	130.56(0)	−345.24404	20.9
9-Me-7,8-$C_2B_9H_{11}^-$ (H at B10) **XXXIVc**	129.41(1)	−345.24225	21.9
11-Me-2,7-$C_2B_9H_{11}^-$ (Hμ at B9,10) **XXVIa**	129.93(0)	−345.20939	45.9
11-Me-2,7-$C_2B_9H_{11}^-$ (Hμ at B8,9) **XXVIb**	130.08(0)	−345.20490	46.8
10-(MeCN)-7,9-$C_2B_9H_{11}$ **XXXV**	139.26(0)	−437.77583	
3,4-μ-(OCH_2CH_2O)-7,9-Me_2-7,9-$C_2B_9H_8^-$ **XXXVI**	182.31(0)	−611.72394	0.0
10,11-μ-(OCH_2CH_2O)-7,9-Me_2-7,9-$C_2B_9H_8^-$ **XXXVII**	182.85(0)	−611.70712	11.0

[k] ZPE = zero point energy at HF/6-31G* level, NIMAG = number of imaginary frequencies. Non-SI unit employed 1 kcal mol⁻¹ = 4.184 kJ mol⁻¹.
[l] See also ref. 49. [m] From ref. 3.

The structure of **7** is consistent with 1D ¹¹B and ¹H NMR spectra – however eight other isomers of $MeC_2B_9H_{12}$ also fit the data. The molecular geometry of *nido*-7-Me-2,8-$C_2B_9H_{12}$ was previously proposed[19,21] on the basis of cage rearrangement mechanisms determined for the formation of the structurally-known neutral *nido*-11-Me-2,7-$C_2B_9H_{12}$.[24] Here we find that *nido*-7-Me-2,8-$C_2B_9H_{12}$ is the only isomer compatible with the cross peaks observed in the 2D ¹¹B–¹¹B{¹H} COSY spectrum of **7**.

Unlike the *nido*-7,9-C_2B_9 to *closo*-2,3-C_2B_9 conversion, the reverse process has been well documented prior to this study, and the existence of a facile synthesis of *closo*-2,3-$C_2B_9H_{11}$ **2a** makes these reactions a viable route to substituted *nido*-7,9-clusters. Thus, *closo*-2,3-$C_2B_9H_{11}$ **2a** reacts with hydride ion to give *nido*-7,9-$C_2B_9H_{12}^-$ **1a** and with Lewis bases (L) to afford *nido*-10-L-7,9-$C_2B_9H_{11}$,[4,11,43,44] – dissolving *closo*-2,3-$C_2B_9H_{11}$ in CD_3CN gives the adduct *nido*-10-CD_3CN-7,9-$C_2B_9H_{11}$ **3** (Scheme 7). The reported ¹¹B NMR chemical shifts for *closo*-2-Ph-3-Me-2,3-$C_2B_9H_9$ **2d** in THF are likely to correspond to the adduct $PhMeC_2B_9H_9$·THF. The reaction of the isomeric mixture of *B*-Me-2,3-$C_2B_9H_{10}$ with $NaBH_4$ gave four products 10-Me **1m**, 8-Me- **1l**, 3-Me- **1o** and 2-Me-7,9-$C_2B_9H_{11}^-$ **1p** in a 16 : 5 : 2 : 1 ratio (Scheme 5). A strong preference for the methyl group to be at the open face is noted.
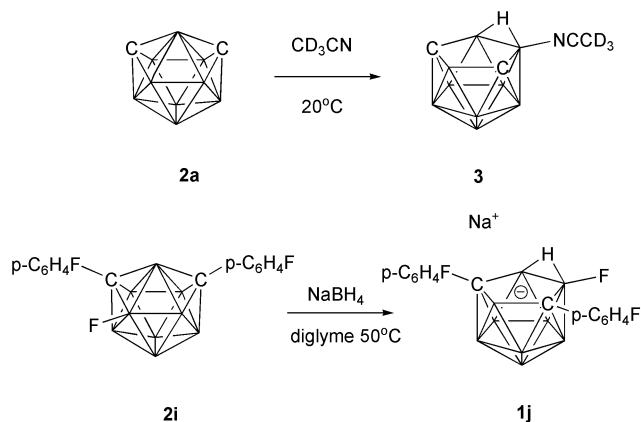
Scheme 7 Typical *closo*-11 vertex to *nido*-11 vertex conversions performed by the addition of Lewis bases or nucleophiles.

Addition of $NaBH_4$ to the fluoro-carborane *closo*-4-F-2,3-(p-FC_6H_4)$_2$-2,3-$C_2B_9H_8$ **2i** gave the monoanion 10-F-7,9-(p-FC_6H_4)$_2$-7,9-$C_2B_9H_9^-$ **1j** with the fluorine located at the open face as shown in Scheme 7. Salts of *nido*-3-F-7,9-R,R′-7,9-$C_2B_9H_9^-$ anions, obtained from the deboronation of *meta*-carboranes *closo*-1,7-R,R′-1,7-$C_2B_{10}H_{10}$ by Bu_4NF, may therefore be defluorinated by acidification and reduction twice

to yield *nido*-7,9-R,R′-7,9-$C_2B_9H_{10}^-$ anions. Likewise *nido*-3-OR″-7,9-R,R′-7,9-$C_2B_9H_9^-$ anions, formed from *meta*-carboranes with KOH in alcohol,[45,46] would generate *nido*-7,9-R,R′-7,9-$C_2B_9H_{10}^-$ anions by this four-step route.

Computational studies

Fully optimised geometries at the electron correlated and computationally intensive MP2/6-31G* level of theory can be regarded as excellent representations of molecular structures found experimentally in the gas phase and in solution for carboranes. If ^{11}B NMR shifts computed at various levels (*e.g.*, IGLO, GIAO) from an optimised geometry (MP2/6-31G*) of a carborane show a very good correlation with its experimental solution-state NMR data then the optimised geometry is considered to be a good representation of its molecular structure in solution.[23]

The molecular geometries of two 11-vertex *closo*-carboranes, 2,3-Me_2-2,3-$C_2B_9H_9$ **2b** and 10-Br-4,7-$(HO)_2$-2,3-Me_2-2,3-$C_2B_9H_6$, were determined by X-ray crystallography over 20 years ago.[47,48] The difference in the cage skeleton between these two compounds is marked, the cage in *closo*-$Me_2C_2B_9H_9$ **2b** is highly symmetrical whereas the brominated compound has the unique seven-coordinate boron atom (B1) shifted away from the hydroxy-substituted boron atoms (B4,7) to such an extent that the framework appears to have an open face geometry like that found in the *nido*-7,9-$C_2B_9H_{12}^-$ anion.[3] Nevertheless, geometric data are in broad agreement with the optimised geometries **II** and **VI** computed at the MP2/6-31G* level (see Fig. 1) of theory and their bond lengths are listed in
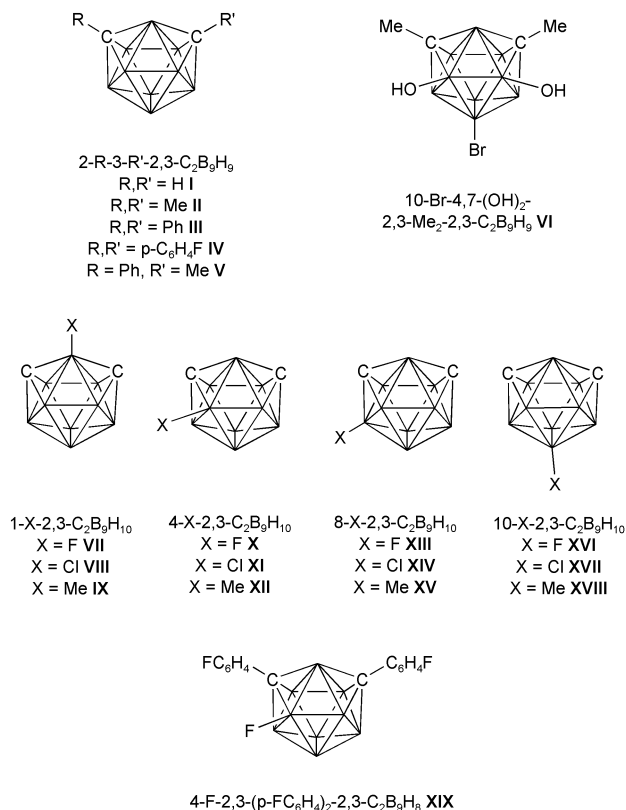
Fig. 1 11-Vertex *closo*-carboranes whose optimised geometries have been computed at the MP2/6-31G* level.

the ESI.† Best fitting between the experimental and MP2-optimized, **VI**, geometries of the bromo carborane showed a misfit value of 0.0351 Å for heavy cage atoms only. This demonstrates that optimised geometries of *closo*-$C_2B_9H_{11}$ derivatives at the correlated MP2 level are reasonable representations of their experimental geometries.

Geometry optimisations of other C-substituted derivatives 2,3-R,R′-2,3-$C_2B_9H_9$ (R,R′ = Ph **III**, p-FC_6H_4 **IV**, R = Ph R′ = Me **V**) and comparison with the unsubstituted carborane 2,3-$C_2B_9H_{11}$ **I**[49] revealed the influence of alkyl and aryl groups on the *closo*-cage framework to be small (misfit values in the region of 0.0163 to 0.0207 Å). By contrast the optimised geometries of the halogenated carboranes *closo*-4-X-2,3-$C_2B_9H_{10}$ (X = F **X**, Cl **XI**, Me **XII**) show substantial distortion of the cage geometry. The substituent causes a shift in the position of the unique six-coordinate boron B1 away from the substituted boron (B4) further lengthening the already long B–B bonds between B1 and B4/B7 like that found in the X-ray structure of the bromo carborane.[48] The misfit values by comparing these substituted compounds with the parent carborane **I** are 0.0389, 0.0254 and 0.0182 Å for X = F, Cl and Me respectively. Optimised geometries of 11-vertex *closo*-carboranes *B*-X-$C_2B_9H_{10}$ (X = F, Cl, Me) with the substituents at B1 (**VII**–**IX**), B8 (**XIII**–**XV**) or B10 (**XVI**–**XVIII**) have cage skeletons with little distortion compared to *closo*-2,3-$C_2B_9H_{11}$ **I** (misfit values of 0.0046–0.0163 Å).

The *B*-fluoro carborane, 4-F-2,3-(p-FC_6H_4)$_2$-2,3-$C_2B_9H_8$ **2i** is synthesized here, and Fig. 2 shows the distorted *closo*-skeleton
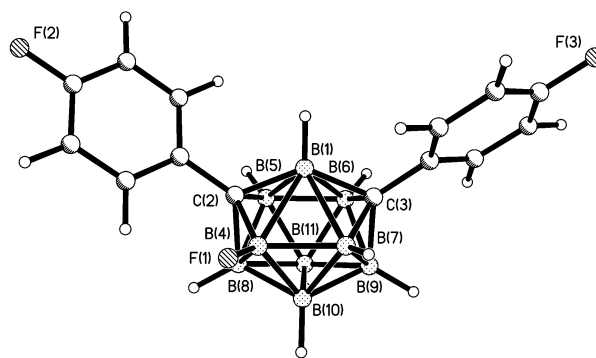
Fig. 2 MP2-optimized molecular geometry of *closo*-4-F-2,3-(p-FC_6H_4)$_2$-2,3-$C_2B_9H_8$ **XIX** for **2i**. Selected bond lengths (Å), B1–C2 1.655, B1–C3 1.650, B1–B4 2.114, B1–B7 2.069, B1–B5 1.966, B1–B6 1.983, B4–F1 1.357, B4–B8 1.808, B5–B8 1.780, B5–B6 1.830.

calculated in the MP2-optimized geometry **XIX** of this compound with selected bond lengths. The misfit values between the cage skeleton in **XIX** and the highly symmetrical *closo*-carboranes 2,3-(p-FC_6H_4)$_2$-2,3-$C_2B_9H_9$ **IV** and 2,3-$C_2B_9H_{11}$ **I** are respectively 0.0273 and 0.0326 Å.

Calculated relative energies of the isomeric *B*-Me-2,3-$C_2B_9H_{10}$ carboranes reveal the 4-isomer (**XII**) to be the most stable followed by 1- (**IX**), 8- (**XV**) and the least stable 10-isomer (**XVIII**). This energy order is also found for the *B*-methyl-*closo*-carboranes *B*-Me-2,3-$C_2B_9H_{10}$ where a 10 : 3 : 1 ratio mixture of 4- **2l**, 1- **2m** and 8- **2n** isomers was obtained experimentally here. The agreement between relative energies and the ratio of isomers observed here points to fluxional cage rearrangements taking place in *closo*-*B*-Me-2,3-$C_2B_9H_{10}$. Relative energies of *closo*-*B*-Cl-2,3-$C_2B_9H_{10}$ isomers indicate the 4-isomer (**XI**) to be the most stable followed by the 10-isomer (**XVII**). The chlorinated carborane isomer *closo*-10-Cl-2,3-$C_2B_9H_{10}$ **2e** obtained here on the other hand does not appear to rearrange into the more stable isomer. A different stability order is found for *closo*-*B*-F-2,3-$C_2B_9H_{10}$ isomers with the 1-isomer (**VII**) being more stable than the 4-isomer (**X**). It seems that the methyl group, but not halogens or carboranyl groups,[11] aids cage rearrangement of the *closo*-C_2B_9 skeleton.

Geometry optimisation, at the MP2/6-31G* level, of the neutral carborane *nido*-7,9-$C_2B_9H_{13}$ **XXI** (see Fig. 3) revealed a minimum containing an *endo* hydrogen at C9 and a hydrogen bridging between B10 and B11. This geometry is lower in energy than the known carborane 7,8-$C_2B_9H_{13}$.[3] An *endo*-hydrogen at a cage carbon in *nido*-carboranes is unusual but not without precedent, two are known experimentally, in the per-
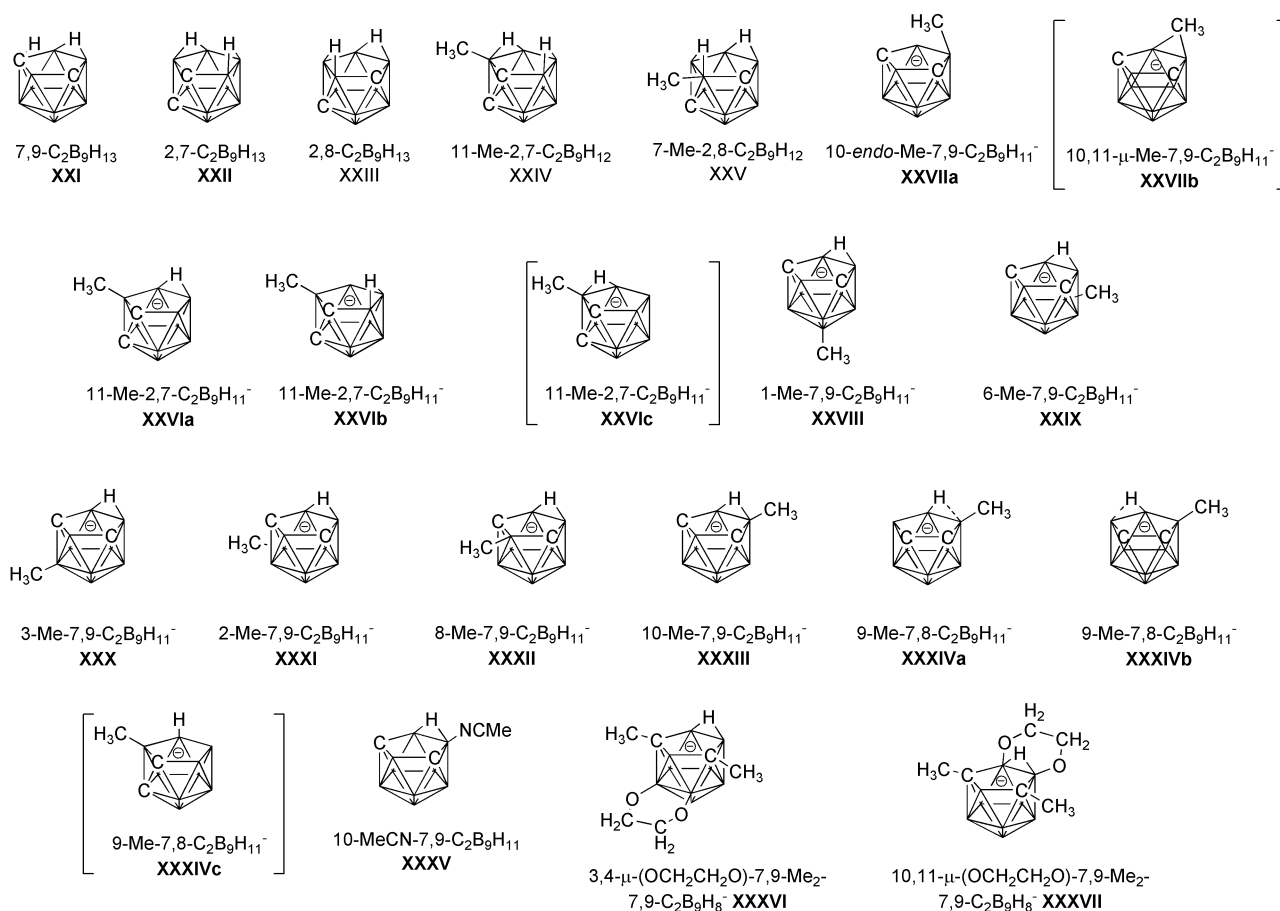
Fig. 3 11-Vertex *nido*-carboranes whose optimised geometries have been computed at the MP2/6-31G* level. Transition state minima are shown in square brackets.

alkylated derivatives of 2,4-$C_2B_4H_8$ and 2,3,5-$C_3B_3H_7$.[50–52] The geometries of the unknown compounds, 2,7- **XXII** and 2,8-$C_2B_9H_{13}$ **XXIII**, were also optimised. The 2,7-isomer is not as stable as the known 2,9-isomer[3] whereas the 2,8-isomer is the most stable – all geometries differ only in the position of the lower belt carbon. Although the existence of *nido*-7,9-$C_2B_9H_{13}$ is not ruled out theoretically it is so far not isolable experimentally as demonstrated in this study.

Best fitting between the experimental (X-ray)[24] and optimised (MP2 **XXIV**) geometries of *nido*-11-Me-2,7-$C_2B_9H_{12}$ showed a misfit value of only 0.0170 Å for the heavy cage atoms, indicating a very good agreement. This gives confidence in the accuracy of MP2-optimized geometries for 11-vertex *B*-monomethyl carboranes discussed in this study. The good agreement between X-ray and MP2-geometries for the parent anion *nido*-7,9-$C_2B_9H_{12}^-$ has been demonstrated recently.[3]

Deprotonation of the structurally known carborane *nido*-11-Me-2,7-$C_2B_9H_{12}$ removes one bridging hydrogen to give the monoanion *nido*-11-Me-2,7-$C_2B_9H_{12}^-$. Three minima (**XXVIa–c**) were located at the RHF/6-31G* level, each with the bridging hydrogen at a B–B bond on the open face. The most stable geometry (**XXVIa**) of *nido*-11-Me-2,7-$C_2B_9H_{11}^-$ contains the bridging hydrogen opposite the carbon atom on the open face. The structure of 11-Me-2,7-$C_2B_9H_{11}^-$ depicted in the literature with the bridging hydrogen next to the methyl substituted boron (**XXVIc**) is not a true minimum and is not located at the MP2/6-31G* level.

While *nido*-11-Me-2,7-$C_2B_9H_{12}$ was structurally determined over 20 years ago, the geometry of the isomer *nido*-7-Me-2,8-$C_2B_9H_{12}$ has not been described. It was predicted to be like *nido*-11-Me-2,7-$C_2B_9H_{12}$ differing only in the position of the cage carbon in the lower belt.[20,21] This proposed geometry, supported here by detailed NMR spectroscopy, is confirmed by geometry optimisations and NMR shift calculations. Fig. 4
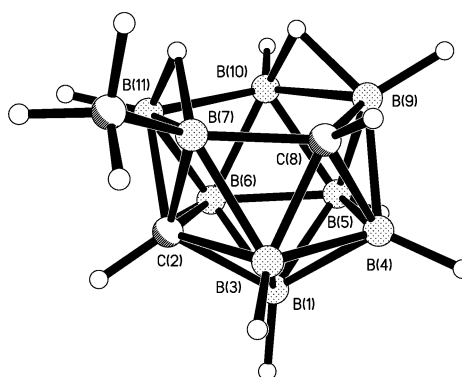

Fig. 4 MP2-optimized molecular geometry of *nido*-7-Me-2,8-$C_2B_9H_{12}$ **XXV** for **7**. Selected bond lengths (Å), B7–C8 1.635, C8–B9 1.664, B9–B10 1.893, B10–B11 1.867, C2–B11 1.697, C2–B7 1.716, B7–C(Me) 1.587.

shows the MP2-optimized geometry of *nido*-7-Me-2,8-$C_2B_9H_{12}$ **XXV**. Although the compound could not be isolated pure here it is computed to be more thermodynamically stable than 11-Me-2,7-$C_2B_9H_{12}$ **XXIV**.

In the formation of *nido*-7-Me-2,8-$C_2B_9H_{12}$ **7**, an intermediate was observed by ^{11}B NMR spectroscopy and proposed to be 10,11-μ-Me-7,9-$C_2B_9H_{11}^-$ **1n**.[19–21] A bridging methyl group is unusual in carborane chemistry. Geometry optimisation of 10,11-μ-Me-7,9-$C_2B_9H_{11}^-$ gave a transition state minimum **XXVIIb**. A true minimum **XXVIIa** was located with an *endo*-substituted methyl group at B10 (or 11) and is shown in Fig. 5. The difference in energy between these minima is only *ca.* 6 kcal mol^{-1}, thus methyl group fluxionality is expected. This fluxionality explains the apparent mirror symmetry in the observed NMR data for the anion. The molecular geometry
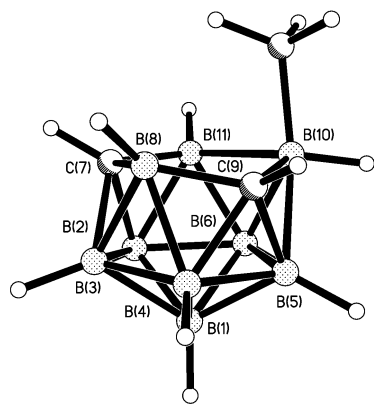
Fig. 5 MP2-optimized molecular geometry of *nido*-10-*endo*-Me-7,9-$C_2B_9H_{11}^-$ **XXVIIa** for **1n**. Selected bond lengths (Å), C7–B8 1.666, B8–C9 1.584, C9–B10 1.738, B10–B11 1.905, C7–B11 1.587, B10–C(Me) 1.665.

of the *nido*-11-vertex trimethyl carborane anion 10-*endo*-9,11-Me_3-7,8-$C_2B_9H_9^-$ containing an *endo*-methyl group like in **XXVIIa** (Fig. 5) has been determined by X-ray crystallography.[53]

Since in this study we have prepared several *B*-methyl-*nido*-7,9-$C_2B_9H_{11}^-$ anions, it was of interest to compare the relative energies of these anions. As expected from its facile cage rearrangement described above, the least stable anion is that with the methyl group on the open face, 10-*endo*-Me-7,9-$C_2B_9H_{11}^-$ **XXVIIa**. The most stable anion is the 2-methyl isomer **XXXI** followed by, in decreasing order of energy, 8- **XXXII**, 3- **XXX**, 6-**XXIX**, 10- **XXXIII** and 1- **XXVIII** isomer. The preferred formation of the 10-methyl anion **1m** over the 3-methyl isomer **1o** on hydride addition to *B*-Me-2,3-$C_2B_9H_{10}$ **2l**–**n** is therefore due to kinetic, not thermodynamic, factors. The reported sequence of relative energies for *B*-F-*nido*-7,9-$C_2B_9H_{11}^-$ isomers is similar to the methyl analogues, differing only in the reversed order of the 6-and 10-isomers.[16]

Consideration of the best fit between the optimised geometries of 10-MeCN-7,9-$C_2B_9H_{11}$ **XXXV** and 7,9-$C_2B_9H_{12}^-$,[3] reveals that the effect of the acetonitrile ligand on the cage skeleton is limited to the substituted boron atom (B10), which is shifted away from the centre of the cage resulting in longer bonds to neighbouring atoms. The misfit value between these geometries is 0.0300 Å for heavy cage atoms only.

In solution, the monoanion 7,8-$C_2B_9H_{12}^-$ is known to be fluxional with an unsymmetrical bridging hydrogen flipping between the two B–B bonds on the open face.[54] Two minima, with the bridging hydrogen at B9–B10 **XXXIVa** and at B10–B11 **XXXIVb**, of similar energy were located for the methyl-substituted anion 9-Me-7,8-$C_2B_9H_{11}^-$. The energy barrier to bridging hydrogen fluxionality between the two geometries (*i.e.*, *via* the 10-*endo*-H geometry **XXXIVc**) is estimated to be only 1.0 kcal mol^{-1} and the cluster is therefore expected to be fluxional in solution.

Table 1 and Table 2 reveal very good agreement between experimental and calculated ^{11}B, ^{13}C and ^{1}H NMR shifts in the majority of *nido*- and *closo*-carboranes discussed here. At the GIAO-B3LYP/6-311G* level of theory, the calculated shifts were generated from MP2-optimized geometries. The two carborane monoanions, 10-*endo*-Me-7,9-$C_2B_9H_{11}^-$ **1n** and 9-Me-7,8-$C_2B_9H_{11}^-$ **6**, are fluxional in solution based on comparison of their observed and calculated NMR data.

Recently the accuracy of the GIAO/NMR method has been demonstrated to be poor for carboranes containing bromine or iodine using optimized geometries at the B3LYP level of theory.[55] Comparison between the observed and computed shifts for 10-(MeCN)-7,9-$C_2B_9H_{11}$ **3/XXXV** and 10-Br-4,7-(HO)$_2$-2,3-Me_2-2,3-$C_2B_9H_6$ (Tables 4 and 5) here shows the substituted boron shifts to be in error by *ca.* 6 ppm.

Table 4 Comparison of literature ^{11}B NMR values with computed ^{11}B NMR shifts for *closo*-10-Br-4,7-(OH)$_2$-2,3-Me_2-2,3-$C_2B_9H_6$

Observed[6]	Calculated **VI**
16.1 (B4,7)	14.9 (B4,7)
1.5 (B1)	−1.4 (B1)
−3.4 (B8,9)	−2.8 (B8,9)
−7.5 (B11)	−7.8 (B11)
−14.8 (B10)	−8.6 (B10)
−21.4 (B5,6)	−22.3 (B5,6)

Table 5 Comparison of literature ^{11}B NMR data for 3,4-μ-(OC$_6$H$_4$O)-7,9-Me_2-7,9-$C_2B_9H_8^-$ together with calculated data for 3,4- **XXXVI** and 10,11-μ-(OC$_2$H$_4$O)-7,9-Me_2-7,9-$C_2B_9H_8^-$ **XXXVII**

Observed[27]	3,4-Isomer **XXXVI** calculated	10,11–Isomer **XXXVII** calculated
0.5 (B8)	−4.3 (B8)	−4.6 (B8)
−3.3 (B3,4)	−4.4 (B3,4)	−5.3 (B2,5)
−5.5 (B2,5)	−5.2 (B2,5)	−7.6 (B10,11)
−25.6 (B10,11)	−30.5 (B10,11)	−27.3 (B3,4)
−31.6 (B1)	−36.1 (B1)	−37.5 (B6)
−41.4 (B6)	−43.6 (B6)	−39.2 (B1)

This suggests that calculated NMR chemical shifts generated from MP2-optimized geometries are not accurate enough for brominated (and presumably iodinated) carboranes and acetonitrile–carborane adducts at the GIAO-B3LYP levels of theory. Poor agreement between observed and calculated NMR shifts has been reported previously for borane–acetonitrile adducts.[56]

Hydride addition to *closo*-4,7-(OC$_6$H$_4$O)-2,3-Me_2-2,3-$C_2B_9H_7$ has been reported to give *nido*-3,4-(OC$_6$H$_4$O)-7,9-Me_2-7,9-$C_2B_9H_8^-$ rather than the 10,11-analogue on the basis of a ^{11}B NMR study.[27] Comparison between computed ^{11}B NMR data for the model geometries *nido*-3,4-(OC$_2$H$_4$O)-7,9-Me_2-7,9-$C_2B_9H_8^-$ **XXXVI** and *nido*-10,11-(OC$_2$H$_4$O)-7,9-Me_2-7,9-$C_2B_9H_8^-$ **XXXVII** and observed values supports the proposed isomer (Tables 4 and 5). That hydride addition to *closo*-4,7-(OC$_6$H$_4$O)-2,3-Me_2-2,3-$C_2B_9H_7$ gives the *nido*-3,4- rather than the *nido*-10,11-isomer is believed to be due to the presence of both substituents preventing an hydride attack at the boron in the 4- or 7-position.

Conclusions

This study demonstrates that, in general, addition of acid to salts containing derivatives of the *nido*-7,9-$C_2B_9H_{12}^-$ anion results in the elimination of hydrogen and formation of *closo*-$C_2B_9H_{11}$ derivatives at ambient temperature. The only exception to the *nido–closo* conversion on acidification is the 10-*endo*-Me-7,9-$C_2B_9H_{11}^-$ anion which gives *nido*-7-Me-2,8-$C_2B_9H_{12}$. The molecular geometries of these unusual compounds are confirmed by detailed NMR spectroscopy and computations. The reported *nido–nido* conversion on acidification of 8-Me-7,9-$C_2B_9H_{11}^-$ is found to be incorrect.

nido-7,9-$C_2B_9H_{12}^-$ anions with substituents at boron atoms not at the open face gave the expected substituted carboranes on acidification based on simple cage closure. By contrast, anions with electron withdrawing fluorine, hydroxy and ethoxy substituents on the open face lead to removal of the substituent, as HF or EtOH, and formation of *closo*-carboranes. Salts containing anions with methyl groups substituted at boron produced a mixture of *B*-Me-2,3-$C_2B_9H_{10}$ isomers on acidification. A facile cage rearrangement equilibrium possibly exists for *B*-Me-2,3-$C_2B_9H_{10}$ at ambient temperature.

Conversion of Bu_4N^+ salts containing derivatives of the *nido*-7,9-$C_2B_9H_{12}^-$ anion into their Na^+ salts can be achieved by acidification then reduction as shown here. Unlike their alkali metal salts, Bu_4N^+ salts of derivatives of the *nido*-7,9-$C_2B_9H_{12}^-$

anion are easily obtained by deboronation of their respective *meta*-carboranes. The sodium salts are expected to be suitable precursors to metallacarboranes with non-adjacent cage carbon atoms.

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