Crystal and molecular structures of the *nido*-carborane anions, 7,9- and 2,9-C$_2$B$_9$H$_{12}$$^-$ †

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Deboronation of *meta*-carborane, *closo*-1,7-C$_2$B$_{10}$H$_{12}$, with refluxing piperidine results in the quantitative formation of [(C$_5$H$_{10}$NH)$_2$H$^+$](*nido*-7,9-C$_2$B$_9$H$_{12}$$^-$) whose structure was determined by X-ray diffraction. Heating under vacuum liberates piperidine to give (C$_5$H$_{10}$NH$_2$$^+$)(*nido*-7,9-C$_2B_9H_{12}$$^-$). The reaction of *meta*-carborane with KOH in refluxing ethanol yields K$^+$ *nido*-7,9-C$_2$B$_9$H$_{12}$$^-$ and the cage substituted anion 10-EtO-7,9-C$_2$B$_9$H$_{11}$$^-$. The protonated Proton Sponge salt (PSH$^+$)(*nido*-7,9-C$_2$B$_9$H$_{12}$$^-$) (PS = 1,8-*N*,*N*,*N'*,*N'*-tetramethylnaphthalenediamine) was obtained by metathesis from the potassium salt, an X-ray crystallographic study located the bridging hydrogen in the anion on the open face between the two adjacent boron atoms. Anaerobic deboronation of *para*-carborane, *closo*-1,12-C$_2$B$_{10}$H$_{12}$, with KOH in refluxing tetraglyme–toluene gives the potassium salt of *nido*-2,9-C$_2$B$_9$H$_{12}$$^-$ from which 2,9-C$_2$B$_9$H$_{13}$ was isolated in 45% yield by protonation. The salt (PSH$^+$)(*nido*-2,9-C$_2$B$_9$H$_{12}$$^-$), obtained from *nido*-2,9-C$_2$B$_9$H$_{13}$ and PS, was shown by single crystal X-ray crystallography to contain a hydrogen bridging two boron atoms opposite the carbon atom on the open face. Aerobic deboronation of *para*-carborane with KOH forms *closo*-1,10-C$_2$B$_8$H$_{10}$ and 2-HO-*closo*-1,10-C$_2$B$_8$H$_9$ in low yields. Fully assigned multinuclear NMR (^{11}B, ^{13}C and ^{1}H) data are reported for the isomeric 7,8-, 7,9- and 2,9-*nido*-C$_2$B$_9$H$_{12}$$^-$ anions and neutral 7,8- and 2,9-C$_2$B$_9$H$_{13}$, and compared with computed shifts (at the GIAO B3LYP/6-311G* level) from optimized (at MP2/6-31G*) geometries.

Introduction

Nido-carboranes found in the literature are usually of the 12-vertex (icosahedral) cage geometry with one vertex removed,[1] and containing one to four carbons,[2–4] though cages containing two carbons are the most common. The latter carboranes are isolated as either the neutral species *nido*-C$_2$B$_9$H$_{13}$ or the mono-anion *nido*-C$_2$B$_9$H$_{12}$$^-$,[5–9] which can be deprotonated to the di-anions *nido*-C$_2$B$_9$H$_{11}$$^{2-}$, precursors to many *closo* icosahedral metallacarboranes with the twelfth vertex occupied by a metal atom.[10] These *nido*-dicarbanes are also precursors to many carboranes,[1,11] *e.g.*, oxidation of C$_2$B$_9$H$_{12}$$^-$ (or C$_2$B$_9$H$_{13}$) results in removal of one and two cage atom(s) to produce the 10-vertex and 9-vertex carboranes.[12] Of the nine possible cage conformations for the carborane mono-anions, *nido*-C$_2$B$_9$H$_{12}$$^-$, three are known, the 7,8-, 7,9- and 2,9-isomers generated by removal of the most positive boron vertex in the three icosahedral *closo*-carboranes 1,2-, 1,7- and 1,12-C$_2$B$_{10}$H$_{12}$ respectively (Fig. 1).[5–9]

Only the most widely used mono-anion, *nido*-7,8-C$_2$B$_9$H$_{12}$$^-$, has been structurally determined experimentally, and of the ten salts studied,[13–17] the (Me$_2$SO)$_2$H$^+$, (Me$_2$N)$_3$PNH$_2$$^+$ and PSH$^+$ salts[13–15] contain well defined *nido*-7,8-C$_2$B$_9$H$_{12}$$^-$ clusters (**I** or **II** in Fig. 2) where all hydrogen atoms could be located. We have recently reported a neutron diffraction study of the PSH$^+$ salt, demonstrating that in this salt there is a B–H–B bridging hydrogen.[15] No structural studies have been reported for the other 11-vertex *nido*-dicarbanes containing *endo* hydrogens, namely the mono-anions *nido*-7,9-C$_2$B$_9$H$_{12}$$^-$ (**III** in Fig. 2) and *nido*-2,9-C$_2$B$_9$H$_{12}$$^-$, (**IV** or **V**) and the neutral species *nido*-7,8-C$_2$B$_9$H$_{13}$ (**VI**) and *nido*-2,9-C$_2$B$_9$H$_{13}$ (**VII**).
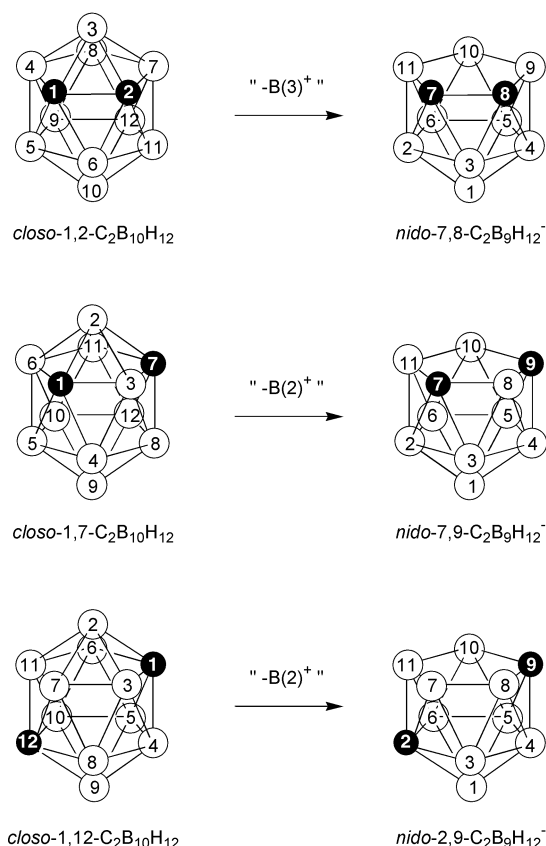

Fig. 1 Changes in numbering of cage atoms of the three *closo*-carboranes into their respective *nido*-carboranes on removal of the most positive boron atom. Hydrogen atoms are omitted for clarity.

The *nido*-7,9-C$_2$B$_9$H$_{12}$$^-$ anion has long been expected to contain a hydrogen bridging between B10 and B11 (**III**) a structure supported in solution by a recent *ab initio*/GIAO/NMR
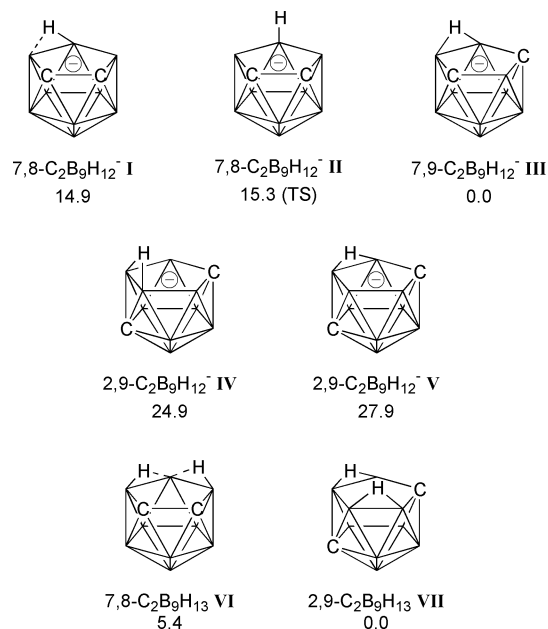
DOI: 10.1039/b108937d

Fig. 2 Optimized geometries and relative energies (kcal mol^{-1}) of the *nido*-carboranes discussed in this paper.
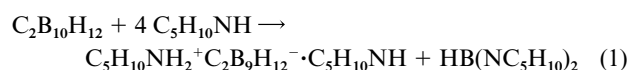
study.[18] In the *nido*-anion 2,9-C$_2$B$_9$H$_{12}$$^-$, the position of the *endo* hydrogen has not been discussed. The reported boron NMR revealed a 2 : 2 : 2 : 2 : 1 pattern pointing to either a geometry with mirror plane symmetry containing a bridging hydrogen at B7/B11 (**IV**) or solution fluxionality of the *endo* hydrogen between two mirror geometries with a bridging hydrogen at B7/B8 or B10/B11 (**V**). However diagrams of the non-symmetrical geometry (**V**) have appeared in the literature.[19] In *nido*-7,8-C$_2$B$_9$H$_{13}$, the two *endo* hydrogens were proposed[20] to occupy asymmetrical bridging positions at B9/B10 and B10/B11 with long B10–H distances (**VI**) whereas in *nido*-2,9-C$_2$B$_9$H$_{13}$ bridging positions at B7/B8 and B10/B11 (**VII**) have been proposed.[8]

This study reports the geometries of *nido*-7,9- and 2,9-C$_2$B$_9$H$_{12}$$^-$ anions determined experimentally for the first time by X-ray crystallography. The cage compounds, 10-OEt-7,9-C$_2$B$_9$H$_{11}$$^-$ and 2-HO-1,10-C$_2$B$_8$H$_9$, formed unexpectedly during the syntheses of these anions are also discussed. In addition the experimental ^{11}B, ^{13}C and ^{1}H NMR data for the isomeric 7,8-, 7,9- and 2,9-*nido*-C$_2$B$_9$H$_{12}$$^-$ anions and for the two neutral carboranes *nido*-7,8- and 2,9-C$_2$B$_9$H$_{13}$ (whose molecular geometries have not been determined experimentally) are fully assigned and compared with computed NMR data generated from optimized geometries.
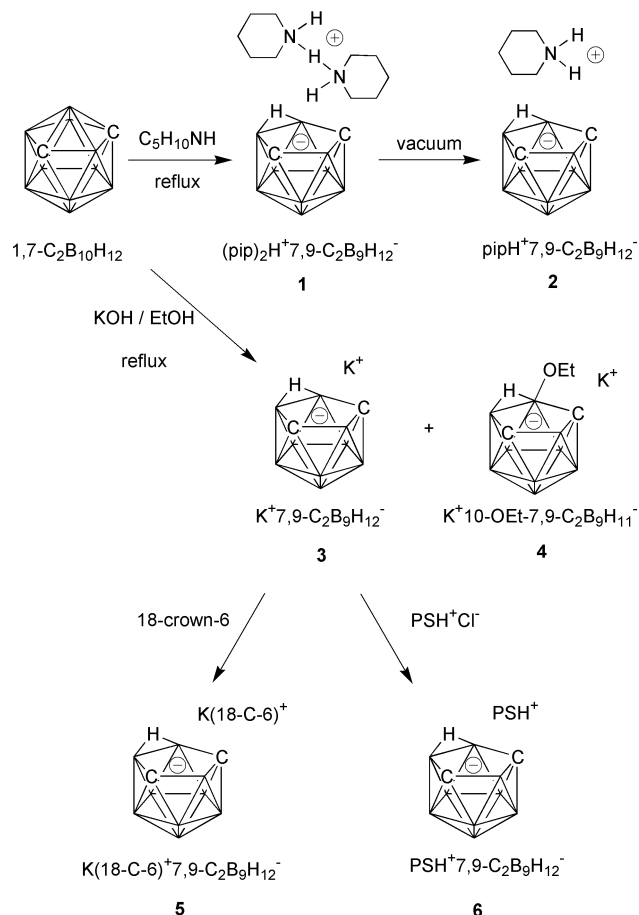
Results and discussion

Syntheses

Piperidine is reported to be a very effective deboronating agent for *ortho*-carborane, 1,2-C$_2$B$_{10}$H$_{12}$, converting it to *nido*-7,8-C$_2$B$_9$H$_{12}$$^-$ at ambient temperature in minutes.[21] The product is known to contain two piperidine groups for each carborane moiety, and it was initially suggested that one piperidine molecule was loosely bound to the cage, although this was later disputed.[22] The overall equation was quoted as

C$_2$B$_{10}$H$_{12}$ + 4 C$_5$H$_{10}$NH →
  C$_5$H$_{10}$NH$_2$$^+C_2B_9H_{12}$$^-$·C$_5H_{10}$NH + HB(NC$_5H_{10}$)$_2$ (1)

In contrast, no reports are found in the open literature for the reaction of piperidine with *meta*-carborane, although C-phenyl-*meta*-carborane, 1-Ph-1,7-C$_2$B$_{10}$H$_{11}$ is deboronated to
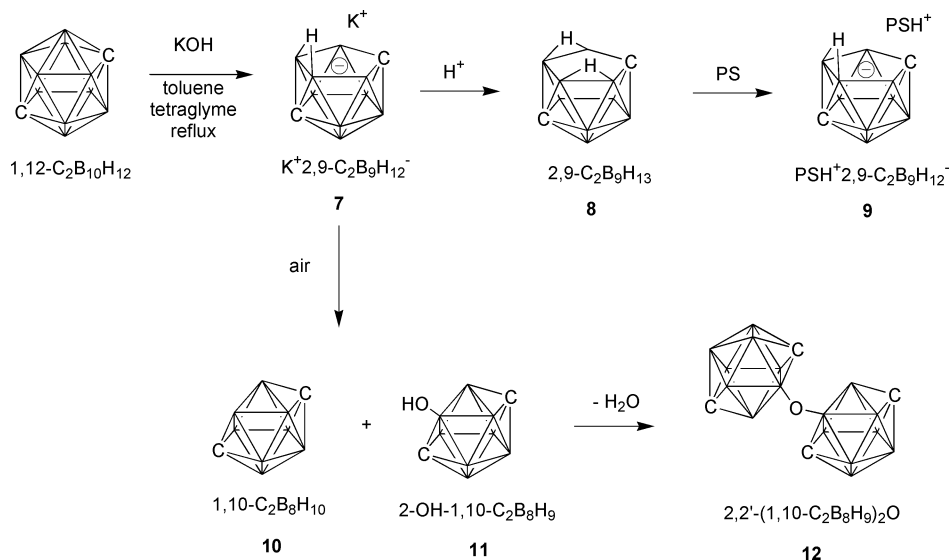

Scheme 1 Deboronation of *meta*-carborane.

7-Ph-7,9-C$_2$B$_9$H$_{11}$$^-$.[22] Whilst C-phenyl-*meta*-carborane is easily deboronated by comparison with *meta*-carborane,[22,23] here we report that the latter is quantitatively converted into *nido*-7,9-C$_2$B$_9$H$_{12}$$^-$ in refluxing piperidine (Scheme 1). An X-ray structural determination on crystals formed from the reaction revealed the formula of the salt to be [(C$_5$H$_{10}$NH)$_2$H$^+$](*nido*-7,9-C$_2$B$_9$H$_{12}$$^-$) **1** with a piperidine molecule linked to the piper-idinium cation by a N–H · · · N hydrogen bond. Prolonged application of vacuum to the solid adduct leads to removal of one equivalent of piperidine leaving (C$_5$H$_{10}$NH$_2$$^+$)(*nido*-7,9-C$_2B_9H_{12}$$^-$) **2**. We propose that the (C$_5$H$_{10}$NH)$_2$H$^+$ cation exists in the *nido*-7,8-C$_2$B$_9$H$_{12}$$^-$ salt reported from piperidine and *ortho*-carborane.

As the anions in the crystals of [(C$_5$H$_{10}$NH)$_2$H$^+$](*nido*-7,9-C$_2$B$_9$H$_{12}$$^-$) are disordered and the crystals of the recently reported salt (Bu$_4$N$^+$)(*nido*-7,9-C$_2$B$_9$H$_{12}$$^-$) crack below −50 °C,[24] different salts of *nido*-7,9-C$_2$B$_9$H$_{12}$$^-$ were targeted for crystal structure determination, and a solution of the potassium salt K$^+$ *nido*-7,9-C$_2$B$_9$H$_{12}$$^-$ was required in order to synthesise salts by cation metathesis. However the reaction of *meta*-carborane with KOH in refluxing ethanol overnight only resulted in the conversion of half the starting carborane. After removal of the excess starting material, the product was identified by ^{11}B NMR as a 4 : 1 ratio mixture of potassium salts of *nido*-7,9-C$_2$B$_9$H$_{12}$$^-$ **3** and a cage-substituted carborane anion, 10-EtO-*nido*-7,9-C$_2$B$_9$H$_{11}$$^-$ **4**. (Scheme 1) Anion **4** has been isolated previously from the reaction of *closo*-2,3-C$_2$B$_9$H$_{11}$ with ethoxide ion.[25]

Isolation of a 10-substituted anion from *closo*-1,7-C$_2$B$_{10}$H$_{12}$ and ethanolic potassium hydroxide is unexpected as previous reports describe isolation of only the *nido*-7,9-C$_2$B$_9$H$_{12}$$^-$ anion from the same reactants.[7,26] The degradative-substitution process is general for reactions of C-disubstituted-*meta*-carboranes 1,7-R$_2$-*closo*-1,7-C$_2$B$_{10}$H$_{10}$ (R = Me or Ph) with alcoholic KOH or wet fluoride to give 3- or 10-X-7,9-R$_2$-*nido*-7,9-C$_2$B$_9$H$_9$$^-$ (X =
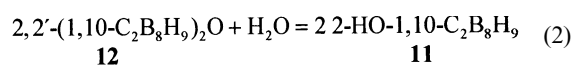
Scheme 2 Deboronation of *para*-carborane.

OH, OR or F)[27,28] but this appears to be the first case of degradative-substitution for an unsubstituted *meta*-carborane. As in the case of the degradation of 1,7-Me$_2$-*closo*-1,7-C$_2$B$_{10}$H$_{10}$ with alcoholic base, there appears to be a delicate balance of conditions dictating the results when *meta*-carborane is treated with potassium ethoxide.

Straightforward and complete conversion of *meta*-carborane, *closo*-1,7-C$_2$B$_{10}$H$_{12}$, into *nido*-7,9-C$_2$B$_9$H$_{12}^-$ is achieved by neat piperidine, or by wet fluoride in refluxing THF.[24] To examine whether piperidine gives degradative-substitution products with disubstituted-*meta*-carboranes, the reaction of 1,7-Ph$_2$-*closo*-1,7-C$_2$B$_{10}$H$_{10}$ with piperidine was carried out and the *nido*-anion 7,9-Ph$_2$-*closo*-7,9-C$_2$B$_9$H$_{10}^-$ was obtained as the only carborane product. We conclude that piperidine is an ideal deboronating agent for the complete conversion of the disubstituted-*meta*carboranes 1,7-R$_2$-*closo*-1,7-C$_2$B$_{10}$H$_{10}$ into their respective 7,9-R$_2$-*nido*-7,9-C$_2$B$_9$H$_{10}^-$ anions.

Adding 18-crown-6 to the solution containing a mixture of K$^+$ *nido*-7,9-C$_2$B$_9$H$_{12}^-$ and K$^+$10-EtO-*nido*-7,9-C$_2$B$_9$H$_{11}^-$, resulted in a precipitate and recrystallization of the solid gave crystalline [K(18-crown-6)$^+$](*nido*-7,9-C$_2$B$_9$H$_{12}^-$) 5. Unfortunately, cage disorder was evident from an X-ray study on one of these crystals. From metathesis with Proton Sponge hydrochloride, crystals of (PSH$^+$)(*nido*-7,9-C$_2$B$_9$H$_{12}^-$) 6 were obtained, allowing the geometry of the undisordered *nido*-7,9-C$_2$B$_9$H$_{12}^-$ anion to be determined by X-ray crystallography.

Deboronation of *para*-carborane has been reported using potassium hydroxide in refluxing isopropanol[8] or 18-crown-6 and refluxing benzene.[9] We find that one boron atom can be removed from *closo*-1,12-C$_2$B$_{10}$H$_{12}$ by reaction with potassium hydroxide in a mixture of tetraglyme and toluene at 120 °C on a multigram scale, allowing the isolation of *nido*-2,9-C$_2$B$_9$H$_{13}$ 8 from acidification of the intermediate potassium salt K$^+$ *nido*-2,9-C$_2$B$_9$H$_{12}^-$ 7 in 45% yield. (Scheme 2) Adding Proton Sponge to the neutral carborane resulted in the air-sensitive protonated Proton Sponge salt, (PSH$^+$)(*nido*-2,9-C$_2$B$_9$H$_{12}^-$) 9, in quantitative yield. A crystal of the salt was subjected to X-ray crystallography which revealed no cage disorder.

In the presence of air, deboronation of 1,12-C$_2$B$_{10}$H$_{12}$ gives boric acid residues and the *closo*-carboranes, 1,10-C$_2$B$_8$H$_{10}$ 10 and 2-HO-1,10-C$_2$B$_8$H$_9$ 11 as determined by ^{11}B NMR spectroscopy. Vacuum sublimation of the degraded products gives a 3 : 2 ratio mixture of the ether 2,2′-(1,10-C$_2$B$_8$H$_9$)$_2$O 12 and 1,10-C$_2$B$_8$H$_{10}$ 10. On subsequent exposure to moist air, the ether reverts to the hydroxy carborane 2-HO-1,10-C$_2$B$_8$H$_9$ 11, demonstrating that a relationship exists between the hydroxy compound 2-HO-1,10-C$_2$B$_8$H$_9$ and the ether 2,2′-(1,10-C$_2$B$_8$H$_9$)$_2$O.

$$2,2'\text{-}(1,10\text{-}C_2B_8H_9)_2O + H_2O = 2\ 2\text{-}HO\text{-}1,10\text{-}C_2B_8H_9 \quad (2)$$
$$\mathbf{12} \qquad\qquad\qquad\qquad\qquad \mathbf{11}$$

Formation of the very stable *closo*-1,10-C$_2$B$_8$ carboranes from *closo*-1,12-C$_2$B$_{10}$H$_{12}$ probably occurs *via* the *nido*-2,9-C$_2$B$_9$H$_{12}^-$ anion. The most likely pathway to these ten-vertex carboranes is the removal of the boron atom B7 or B11 from the *nido*-C$_2$B$_9$ cage followed by closure of the C$_2$B$_8$ framework with three new B–B links to the *closo*-C$_2$B$_8$ cage as shown in Fig. 3.
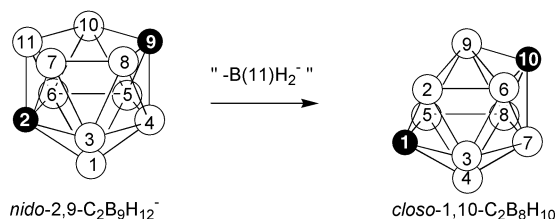

Fig. 3 Changes in numbering of cage atoms on converting from *nido*-2,9-C$_2$B$_9$H$_{12}^-$ into *closo*-1,10-C$_2$B$_8$H$_{10}$. All hydrogen atoms omitted for clarity.

Structural aspects

The crystals of the salts [(C$_5$H$_{10}$NH)$_2$H$^+$](*nido*-7,9-C$_2$B$_9$H$_{12}^-$) 1 and [K(18-crown-6)$^+$](*nido*-7,9-C$_2$B$_9$H$_{12}^-$) 5 were found by X-ray structural determination to contain disordered cages. In both cases the cage atoms randomly occupy eleven of the twelve positions to give an apparent icosahedron. The molecular structure of the [(C$_5$H$_{10}$NH)$_2$H$^+$] cation is shown in Fig. 4; the

Fig. 4 Molecular structure of the cation in [(C$_5$H$_{10}$NH)$_2$H$^+$](*nido*-7,9-C$_2$B$_9$H$_{12}^-$) 1 showing 50% probability ellipsoids for the non-hydrogen atoms, only one of the disordered sites for H2N is shown, hydrogen atoms are represented by arbitrary sized spheres.

N · · · N bond distance is 2.660(2) Å and an hydrogen atom is located in two positions at half occupancy between these nitrogen atoms with N–H distances of 0.88(2) and 0.93(2) Å, the

Table 1 Selected bond distances [Å] and angles [°] for (PSH⁺)-(*nido*-7,9-C₂B₉H₁₂⁻), **6**

C(7)–B(8)	1.624(4)
B(8)–C(9)	1.626(4)
C(9)–B(10)	1.641(4)
B(10)–B(11)	1.845(4)
C(7)–B(11)	1.646(4)
B(10)–H(12)	1.23(3)
B(11)–H(12)	1.23(3)
B(8)–C(7)–B(11)	107.6(2)
C(7)–B(8)–C(9)	112.4(2)
B(8)–C(9)–B(10)	107.5(2)
C(9)–B(10)–B(11)	105.30(19)
C(7)–B(11)–B(10)	104.9(2)

Table 2 Selected bond distances [Å] and angles [°] for (PSH⁺)-(*nido*-2,9-C₂B₉H₁₂⁻), **9**

C(2)–B(7)	1.707(2)
C(2)–B(11)	1.709(2)
B(7)–B(8)	1.772(2)
B(8)–C(9)	1.644(2)
C(9)–B(10)	1.642(2)
B(10)–B(11)	1.768(2)
B(7)–B(11)	1.891(2)
B(7)–H(12)	1.293(17)
B(11)–H(12)	1.261(16)
B(8)–B(7)–B(11)	104.63(11)
C(9)–B(8)–B(7)	106.72(11)
B(8)–C(9)–B(10)	107.5(2)
C(9)–B(10)–B(11)	106.62(12)
B(10)–B(11)–B(7)	105.08(11)

N1–H1 ··· N1′ angle is 1.6°. In [K(18-crown-6)⁺](*nido*-7,9-C₂B₉H₁₂⁻) there is a stacking of alternate cage and potassium crown moieties with distances of 3.498(8) and 3.436(7) Å between the potassium atom and the neighbouring triangular cage faces.

For the protonated Proton Sponge salt, (PSH⁺)(*nido*-7,9-C₂B₉H₁₂⁻) **6**, the cage geometry in the crystal is well defined according to the X-ray structural determination. Two tri-substituted derivatives of *nido*-7,9-C₂B₉H₁₂⁻, in the form of 10-HO- and 3-OEt-7,9-Ph₂-*nido*-7,9-C₂B₉H₉⁻, have been previously structurally determined by X-ray crystallography and contain similar gross cage geometries but the locations of their *endo*/bridging hydrogens on the open face were not well resolved.[28] Also relevant to the geometry of the *nido*-7,9-cage, the crystal structure of the neutral adduct 8-Me₂S-*nido*-7,9-C₂B₉H₁₁ has been shown to contain a hydrogen bridging between B10 and B11.[29]

As predicted from spectroscopic and theoretical methods,[18] geometry **III** is that experimentally found for *nido*-7,9-C₂B₉H₁₂⁻ with the *endo* hydrogen symmetrically bridging between the adjacent boron atoms (B10 and B11) on the open face (Fig. 5).

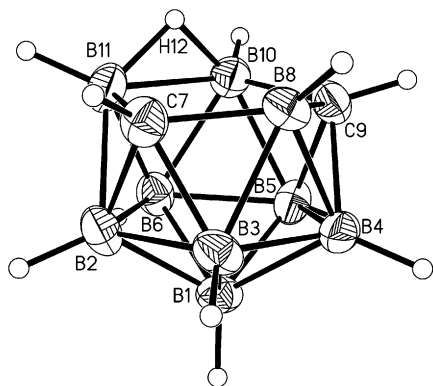**Fig. 5** Molecular structure of the anion in (PSH⁺)(*nido*-7,9-C₂B₉H₁₂⁻) **6** showing 50% probability ellipsoids for the non-hydrogen atoms, hydrogen atoms are represented by arbitrary sized spheres.
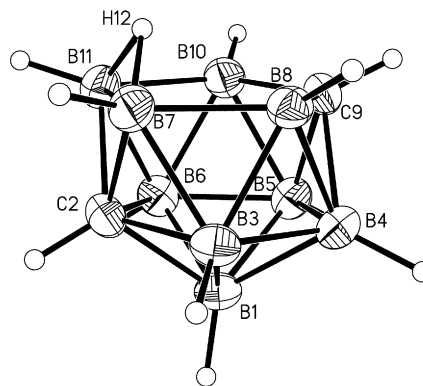
The boron atom (B8) between the two carbon atoms is significantly above the plane containing the other four atoms on the open face by 0.246(4) Å. Table 1 lists the cage bond lengths, which are typical of carborane cages with the B–C bonds (1.624–1.700 Å) shorter than the B–B bonds (1.747–1.845 Å). The longest B–B bond and the shortest B–C bonds are situated in the open face.

In contrast to many reports on the geometries of *nido*-7,8-, *nido*-7,9-C₂B₉H₁₂⁻ and their derivatives, the geometry of *nido*-2,9-C₂B₉H₁₂⁻ has not been determined by diffraction methods, although authors consistently draw geometry **V** with a bridging hydrogen between the adjacent boron atoms (B7 and B8 or B10 and B11) next to the carbon atom (C9).[19] In the solid-state structure of the salt (PSH⁺)(*nido*-2,9-C₂B₉H₁₂⁻) **9**, geometry **IV** is in fact observed with the symmetrically bridging hydrogen

located between the two boron atoms (B7 and B11) opposite the carbon atom (C9) on the open face (Fig. 6 and Table 2). The carbon atom (C9) is below the plane containing the four boron atoms on the open face by only 0.064(2) Å. The B7–B11 bond, which accommodates the bridging hydrogen, is long at 1.891(2) Å and, in the lower belt, the B–C bonds are longer than the neighbouring B–B bonds by 0.01 Å. The rest of the cage bond lengths are as expected with the B–C bonds (1.642–1.720 Å) shorter than B–B bonds (1.750–1.801 Å).

Fig. 6 Molecular structure of the anion in (PSH⁺)(*nido*-2,9-C₂B₉H₁₂⁻) **9** showing 50% probability ellipsoids for the non-hydrogen atoms, hydrogen atoms are represented by arbitrary sized spheres.

Theoretical studies

Fully optimized 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.[30] These geometry optimizations were therefore carried out on the *nido*-monoanions here to determine the discrete structures most likely to be found in solution experimentally.

The most stable geometry, **III**, of 7,9-C₂B₉H₁₂⁻ found by optimization at the MP2/6-31G* level of theory is in full agreement with the experimental geometry determined here for **6** and with that reported at the lower levels of theory.[18] Best fitting (r.m.s. method) between experimental and theoretical geometries for the heavy atoms is excellent, with a misfit value of only 0.0074 Å, which suggests that the experimental solid state structure of *nido*-7,9-C₂B₉H₁₂⁻ in **6** is largely unaffected by neighbouring forces such as crystal packing.

Geometry optimizations of the 2,9-C₂B₉H₁₂⁻ anion located two minima, geometry **IV** with bridging hydrogen between the boron atoms (B7 and B8 or B10 and B11) adjacent to the carbon atom (C9) on the open face, and geometry **V** as found in the experimental structure of **9**. Geometry **V** is 3.0 kcal mol⁻¹ lower in energy than **IV**. Best geometrical fitting between the experimental and the most stable optimized molecular structures

Table 3 Misfit values [Å] between geometries for the *nido*-7,8-C$_2$B$_9$H$_{12}^-$ anion

	Optimized (**I**)	Optimized (**II**)	(Me$_2$SO)$_2$H$^+$ salt	(Me$_2$N)$_3$PNH$_2^+$ salt
PSH$^+$ salt	0.0118	0.0151	0.0190	0.0145
(Me$_2$SO)$_2$H$^+$ salt	0.0162	0.0097		0.0104
(Me$_2$N)$_3$PNH$_2^+$ salt	0.0145	0.0096	0.0104	
Optimized (**I**)		0.0204	0.0162	0.0145
Optimized (**II**)	0.0204		0.0097	0.0096

Table 4 Energies of MP2/6-31G* optimized geometries^a

Optimized geometries		ZPE (NIMAG)/a.u.	MP2/a.u.	Relative energy/kcal mol^{-1}
7,8-C$_2$B$_9$H$_{12}^-$	**I**	111.90(0)	−306.06799	14.89
7,8-C$_2$B$_9$H$_{12}^-$ (TS)	**II**	110.67(1)	−306.06565	15.27
7,9-C$_2$B$_9$H$_{12}^-$	**III**	112.39(0)	−306.09242	0.00
2,9-C$_2$B$_9$H$_{12}^-$	**IV**	111.50(0)	−306.05149	24.89
2,9-C$_2$B$_9$H$_{12}^-$	**V**	111.44(0)	−306.04664	27.88
7,8-C$_2$B$_9$H$_{13}$	**VI**	120.16(0)	−306.55322	5.36
2,9-C$_2$B$_9$H$_{13}$	**VII**	120.03(0)	−306.56158	0.00
10-EtO-7,9-C$_2$B$_9$H$_{11}^-$	**VIII**	154.12(0)	−459.49100	
2-HO-1,10-C$_2$B$_8$H$_9$	**IX**	100.72(0)	−355.17419	
2,2′-(1,10-C$_2$B$_8$H$_9$)$_2$O	**X**	185.60(0)	−634.16055	

^{a} 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}.

of the anion is very good with a misfit value of 0.0085 Å for heavy atoms only. This points to the anion being largely discrete in the solid state in the salt (PSH$^+$)(*nido*-2,9-C$_2$B$_9$H$_{12}^-$).

As the misfit values between experimental and theoretical geometries are very good, the best fitting method was applied to the much discussed geometry of *nido*-7,8-C$_2$B$_9$H$_{12}^-$. The geometries of 7,8-C$_2$B$_9$H$_{12}^-$ found experimentally in the three high-quality X-ray determinations[13–15] were compared with two optimized geometries. One minimum, geometry **I**, has an asymmetric bridging hydrogen between two borons (B9 and B10 or B10 and B11) on the open face and one transition state minimum; geometry **II**, has an *endo* hydrogen at the boron atom (B10) opposite the two carbon atoms on the open face. Interestingly two of the three experimental geometries fit best with the more symmetrical geometry whereas the anion in the PSH$^+$ salt fits best with the minimum geometry as shown in Table 3. It seems the geometry of *nido*-7,8-C$_2$B$_9$H$_{12}^-$ in the solid state depends on the cation and forces involved in the crystal packing.

Relative energies calculated from optimized geometries of the three known *nido*-C$_2$B$_9$H$_{12}^-$ anions show the 7,9-isomer to have most stable geometry followed by the 7,8-isomer then the 2,9-isomer (Table 4). This order is expected for two reasons: (i) the two cage carbon atoms prefer sites of low connectivity and non-adjacent to each other; and (ii) one B–B bond on the open face to accommodate the sole bridging hydrogen is favoured over two (or three) B–B bonds.

For the two known neutral *nido*-carboranes, C$_2$B$_9$H$_{13}$, the 2,9-isomer **VII** is more stable than the 7,8-isomer **VI**. The availability of non-adjacent B–B bonds on the open face to accommodate the two bridging hydrogens appears to lower the overall energy more significantly than the preference for low connectivity sites by the cage carbons. No structural characterizations have been carried out on *nido*-C$_2$B$_9$H$_{13}$ isomers and their derivatives.[31,32] The structure of the double 11-vertex : 11-vertex tetracarborane cluster C$_4$B$_{18}$H$_{22}$ recently determined by X-ray crystallography is perceived as two *nido*-C$_2$B$_9$ subclusters.[33] Here the subclusters in C$_4$B$_{18}$H$_{22}$ fit best with the optimized geometry of C$_2$B$_9$H$_{13}$ **VI** (misfit value 0.0272 Å) rather than the optimized geometries of C$_2$B$_9$H$_{12}^-$ **I** (0.0377 Å) and **II** (0.0439 Å). These heavy atom fittings exclude the boron atoms with no hydrogens attached as they are 'fused' atoms and therefore treated as 'anomalous'. C$_4$B$_{18}$H$_{22}$ is viewed here as a fusion of two C$_2$B$_9$H$_{13}$ clusters and is considered as the first structurally determined derivative of C$_2$B$_9$H$_{13}$.

Experimental and theoretical NMR data

Multinuclear (^{11}B, ^{13}C and ^{1}H NMR) data for the carboranes involved in this study are listed in Table 5. For the first time peaks are fully assigned for the two carborane compounds *nido*-2,9-C$_2$B$_9$H$_{12}^-$ and *nido*-2,9-C$_2$B$_9$H$_{13}$ with the aid of 2D ^{11}B–^{11}B COSY and ^{1}H{^{11}B selective} experiments. Based on the assumption that the short B–C bonds on the open face lead to significant J_{BC} couplings and thus peak broadening, the broader ^{13}C peaks in the 2,9-isomers are assigned to the open-face carbon, *i.e.*, C9. Using the line-narrowing technique, the ^{11}B{^{1}H} NMR spectrum of *nido*-2,9-C$_2$B$_9$H$_{12}^-$ reveals an unusually well resolved 1 : 1 : 1 : 1 quartet for B7,11 and a poorly resolved quartet for B8,10 arising from substantial J_{BB} couplings between B7/11 and B8/10. Our data are in agreement with experimental chemical shifts previously reported for *nido*-7,8-C$_2$B$_9$H$_{12}^-$ (reference 20) and *nido*-7,9-C$_2$B$_9$H$_{12}^-$.[34]

If ^{11}B NMR shifts computed at various levels (*e.g.* IGLO, GIAO) from an optimized geometry (MP2/6-31G*) of a carborane show a very good correlation with its experimental solution-state NMR data then the optimized geometry is considered the best representation of its molecular structure in solution.[30,35] Comparison of various levels of theory (*e.g.* IGLO–DZ, IGLO–II', GIAO–SCF, GIAO–B3LYP, GIAO–MP2) for calculated ^{11}B NMR shifts carried out on optimized (MP2/6-31G*) geometries of small boranes and carboranes with their experimental ^{11}B NMR shifts revealed the best correlation to be at the GIAO–B3LYP/6–311G* level ($r^2 = 0.9977$) closely followed by GIAO–MP2/TZP' ($r^2 = 0.9976$).[36] Thus the less computationally intensive level of theory GIAO–B3LYP/6–311G* was used to compute the NMR shifts of all the MP2-optimized geometries here. Table 5 reveals a very good agreement between experimental and calculated ^{11}B NMR shifts in all *nido*- and *closo*-carboranes discussed here. On this basis these *nido*-anions exist as discrete molecules in solution. For *nido*-7,8-C$_2$B$_9$H$_{12}^-$ (**I**), bridging hydrogen fluxionality between B9/10 and B10/11 occurs in solution.[15,18] Bridging hydrogen fluxionality between B7/11 and B7/B8 is unlikely in the *nido*-2,9-C$_2$B$_9$H$_{12}^-$ anion (*i.e.* between **IV** and **V**) as the averaged NMR chemical shifts calculated for a fluxional system do not agree with the observed values.

Correlation is also good for ^{13}C NMR shifts at the GIAO-B3LYP/6–311G* level in these compounds as the calculated shifts for the cage carbons are consistently 5–10 ppm to low frequency of shifts found experimentally. By contrast, calcu-

Table 5 Observed solution-state NMR data for carboranes and computed NMR data for optimized geometries of carboranes

	Exp. (^{11}B, ^{13}C)[a]	Calc. (^{11}B, ^{13}C)[a]	Exp. (^{1}H)	Calc. (^{1}H)
7,8-C$_2$B$_9$H$_{12}$$^{-}$ [bcd]	−10.4 (B9,11)	−14.4 (B9,11)	1.91 (B9,11H)	2.27 (B9,11H)
	−15.9 (B5,6)	−17.2 (B5,6)	1.71 (B3H)	2.15 (B3H)
	−16.4 (B3)	−19.6 (B3)	1.24 (B5,6H)	1.83 (B5,6H)
	−21.4 (B2,4)	−23.2 (B2,4)	1.24 (B2,4H)	1.72 (B2,4H)
	−32.5 (B10)	−34.1 (B10)	0.56 (B1H)	1.05 (B1H)
	−37.2 (B1)	−39.2 (B1)	0.10 (B10H)	0.56 (B10H)
			−2.92 (Hμ)	−3.10 (Hμ)
	_42.2_	_46.8_	1.71 (CH)	1.56 (CH)
7,9-C$_2$B$_9$H$_{12}$$^{-}$ [ce]	−4.1 (B2,5)	−5.1 (B2,5)	2.82 (B2,5H)	2.82 (B2,5H)
	−5.5 (B8)	−7.5 (B8)	2.01 (B8H)	2.51 (B8H)
	−21.1 (B3,4)	−22.4 (B3,4)	1.42 (B10,11H)	1.79 (B10,11H)
	−22.3 (B10,11)	−26.2 (B10,11)	1.08 (B3,4H)	1.63 (B3,4H)
	−33.9 (B1)	−35.5 (B1)	0.66 (B1H)	1.27 (B1H)
	−35.0 (B6)	−36.8 (B6)	0.09 (B6H)	0.68 (B6H)
			−2.34 (Hμ)	−2.49 (Hμ)
	_31.8_	_38.2_	1.17 (CH)	1.14 (CH)
2,9-C$_2$B$_9$H$_{12}$$^{-}$ [c]	−13.7 (B8,10)	−15.4 (B8,10)	1.79 (B8,10H)	2.02 (B8,10H)
	−19.6 (B3,6)	−21.1 (B3,6)	1.60 (B3,6H)	1.98 (B3,6H)
	−22.0 (B4,5)	−23.2 (B4,5)	1.36 (B4,5H)	1.67 (B4,5H)
	−28.9 (B7,11)	−32.6 (B7,11)	0.88 (B1H)	1.07 (B1H)
	−43.3 (B1)	−45.7 (B1)	0.42 (B7,11H)	0.62 (B7,11H)
			−1.01 (Hμ)	−1.12 (Hμ)
	_50.6 (C9)_	_57.6 (C9)_	1.53 (_C2H_)	1.32 (C2H)
	_27.7 (C2)_	_32.8 (C2)_	1.14 (_C9H_)	1.14 (C9H)
7,8-C$_2$B$_9$H$_{13}$ [df]	4.6 (B2,4)	4.7 (B2,4)	2.90 (B2,4H)	3.59 (B2,4H)
	−3.9 (B5,6)	−3.9 (B5,6)	2.53 (B5,6H)	3.04 (B5,6H)
	−15.8 (B3)	−17.4 (B3)	1.93 (B1H)	2.49 (B10H)
	−16.4 (B8)	−19.4 (B8)	1.76 (B10H)	2.47 (B3H)
	−26.8 (B1)	−27.5 (B1)	1.76 (B3H)	2.32 (B1H)
	−26.8 (B9,11)	−30.4 (B9,11)	1.43 (B9,11H)	2.15 (B9,11H)
			−2.29 (Hμ)	−2.12 (Hμ)
	_65.3_	_71.7_	2.62 (CH)	3.51 (CH)
2,9-C$_2$B$_9$H$_{13}$ [f]	−8.0 (B8,10)	−11.0 (B4,5)	2.40 (B4,5H)	3.04 (B4,5H)
	−10.7 (B4,5)	−11.4 (B8,10)	2.16 (B8,10H)	2.82 (B8,10H)
	−25.5 (B7,11)	−28.1 (B1)	1.82 (B1H)	2.46 (B7,11H)
	−26.0 (B1)	−28.4 (B7,11)	1.67 (B7,11H)	2.40 (B1H)
	−35.3 (B3,6)	−36.0 (B3,6)	0.97 (B3,6H)	1.64 (B3,6H)
			−3.96 (Hμ)	−3.90 (Hμ)
	_71.1 (C2)_	_79.1 (C2)_	2.52 (_C2H_)	3.29 (C2H)
	_45.7 (C9)_	_53.7 (C9)_	1.74 (_C9H_)	2.23 (C9H)
10-OEt-7,9-C$_2$B$_9$H$_{11}$$^{-}$ [c]	0.4 (B10)	−2.9 (B10)	2.33 (_B5H_)	2.93 (B5H)
	−4.6 (B5)	−5.2 (B5)	2.18 (_B2H_)	2.72 (B2H)
	−4.6 (B2)	−5.6 (B2)	1.82 (B8H)	2.33 (B8H)
	−8.3 (B8)	−10.1 (B8)	1.35 (B11H)	1.85 (B11H)
	−21.7 (B4)	−22.4 (B4)	1.12 (B4H)	1.73 (B4H)
	−26.1 (B11)	−29.3 (B3)	0.74 (B3H)	1.27 (B3H)
	−29.1 (B3)	−31.1 (B11)	0.48 (B1H)	1.10 (B1H)
	−36.8 (B1)	−37.0 (B1)	0.16 (B6H)	0.80 (B6H)
	−36.8 (B6)	−38.8 (B6)	−0.42 (Hμ)	−0.10 (Hμ)
	_64.7 (CH$_2$)_	_69.2 (CH$_2$)_	3.46 (CH$_2$)	3.47 (CH$_2$)[b]
	_32.0 (C9)_	_41.4 (C9)_	1.35 (C9H)	1.38 (C9H)
	_26.3 (C7)_	_33.9 (C7)_	1.12 (_C7H_)	0.98 (CH$_3$)[b]
	_17.0 (CH$_3$)_	_20.6 (CH$_3$)_	1.05 (CH$_3$)	0.94 (C7H)
2-OH-1,10-C$_2$B$_8$H$_9$ [f]	2.3 (B2)	1.8 (B2)	2.59 (B3,5H)	3.16 (B3,5H)
	−8.8 (B7,8)	−9.0 (B3,5)	2.14 (B7,8H)	2.78 (B7,8H)
	−8.8 (B3,5)	−9.8 (B7,8)	1.89 (B6,9H)	2.55 (B6,9H)
	−15.2 (B6,9)	−15.9 (B6,9)	1.21 (B4H)	1.76 (B4H)
	−25.4 (B4)	−25.7 (B4)		
	_92.3_	_95.6 (C10)_	6.48	6.32 (C10H)
	_90.9_	_94.1 (C1)_	6.16	5.47 (C1H)
			0.81	3.34 (OH)
2,2′-(1,10-C$_2$B$_8$H$_9$)$_2$O [f]	0.5 (B2)	0.2 (B2)	2.50 (B3,5H)	3.12 (B3,5H)
	−8.7 (B3,5)	−9.7 (B3,5)	2.14 (B7,8H)	2.82 (B7,8H)
	−9.4 (B7,8)	−10.0 (B7,8)	1.89 (B6,9H)	2.82 (B6,9H)
	−14.9 (B6,9)	−16.5 (B6,9)	1.28 (B4H)	1.83 (B4H)
	−23.2 (B4)	−25.0 (B4)		
	_93.6_	_99.8 (C1)_	6.52	6.53 (C10H)
	_92.3_	_95.3 (C10)_	6.23	6.00 (C1H)

[a] Underlined values are ^{13}C shifts. [b] Computed NMR values averaged. [c] In CD$_3$CN at 298 K. [d] Assignments in agreement with ref. 20. [e] Assignments in agreement with ref. 34. [f] In CDCl$_3$ at 298 K.

lated ^{13}C NMR shifts at the GIAO-HF/6-31G* level (generated from optimized geometries at the HF/6-31G* level of over 40 known carboranes) of the cage carbons were consistently 5–15 ppm *to high frequency* of shifts found experimentally.[37]

While there is very good correlation between experimental and theoretical ^{11}B and ^{13}C chemical shifts, the correlation in the case of ^{1}H chemical shifts is generally poor. However the order of the assigned peaks for hydrogens attached to boron

atoms are correct in the *nido*-anions. In the case of the neutral carboranes the order of peaks differ only in peaks with the shifts close together experimentally and theoretically. Therefore calculated proton shifts at the GIAO-B3LYP/6–311G*//MP2/6-31G* level of theory could be useful in peak assignments of the hydrogens attached to boron in cases where these peak shifts cover a large ppm range (over 1 ppm).

Conclusions

Reactions of the *meta*-carboranes, 1,7-R$_2$-*closo*-1,7-C$_2$B$_{10}$H$_{10}$ (R = H or Ph) with piperidine give the corresponding mono-anions 7,9-R$_2$-*nido*-7,9-C$_2$B$_9$H$_{10}^-$ in quantitative yields. However in the reaction of *meta*-carborane with KOH in refluxing ethanol a mixture of the expected anion *nido*-7,9-C$_2$B$_9$H$_{12}^-$ and the cage substituted anion 10-OEt-*nido*-7,9-C$_2$B$_9$H$_{11}^-$ is formed. Under nitrogen, the conversion of *para*-carborane into *nido*-2,9-C$_2$B$_9$H$_{13}$ can be achieved with KOH in refluxing tetraglyme and toluene; in the presence of air, the *closo*-dicarbaboranes, 1,10-C$_2$B$_8$H$_{10}$ and 2-HO-1,10-C$_2$B$_8$H$_9$ are obtained in low yields.

Structures for the *nido*-carborane mono-anions 7,9- and 2,9-C$_2$B$_9$H$_{12}^-$, are determined here for the first time by X-ray crystallography. The experimental geometry of the *nido*-7,9-C$_2$B$_9$H$_{12}^-$ anion reveals the expected bridging position of the *endo*-hydrogen between the two adjacent boron atoms on the open face. In *nido*-2,9-C$_2$B$_9$H$_{12}^-$, for which the geometry has not been proposed before, the *endo* hydrogen is located in a bridging position at B7/B11 directly opposite the open-face carbon atom. Solution-state molecular structures for the five parent *nido*-dicarbaundecaboranes, 7,8-, 7,9- and 2,9-C$_2$B$_9$H$_{12}^-$, and 7,8- and 2,9-C$_2$B$_9$H$_{13}$, were also determined by comparison of detailed multinuclear ^{11}B, ^{13}C and ^{1}H NMR spectroscopy with computed ^{11}B, ^{13}C and ^{1}H NMR data from *ab initio* optimized geometries.

Experimental

NMR spectra including 2D ^{11}B–^{11}B{^{1}H} COSY and ^{1}H{^{11}B selective} were recorded on a Varian Unity 300 (299.9 MHz ^{1}H, 96.2 MHz ^{11}B and 75.4 MHz ^{13}C) instrument. ^{11}B, ^{1}H and ^{13}C NMR chemical shifts for compounds synthesized here are shown in Table 5. Mass spectra were recorded on a Fisons VG Trio 1000 mass spectrometer coupled directly to a Hewlett Packard 5890 Series II gas chromatograph (Column: HP-1; 25 m; 0.25 mm I.D.; 0.32 μm film thickness). Calculated values of M_r show the full isotope range ^{10}B$_n$ to ^{11}B$_n$. Infrared spectra were recorded as potassium bromide discs using a Perkin Elmer 1720X FTIR spectrometer. Elemental analysis was performed by the micro-analytical service within this department.

Potassium hydroxide, Proton Sponge (PS) and piperidine were obtained commercially (Aldrich) and used as received. Toluene and tetraglyme were dried over sodium wire whereas benzene was dried with potassium metal. *Meta* and *para*-carborane (from Katchem, Czech Republic) were purified by sublimation under high vacuum. 1,7-Diphenyl-*meta*-carborane was made by the copper coupling method with iodobenzene and *meta*-carborane.[38]

Preparations

Deboronation of *closo*-1,7-C$_2$B$_{10}$H$_{12}$ with neat piperidine. *Meta*-carborane (2.88 g, 20 mmol) was refluxed in piperidine (100 ml) for 14 h when ^{11}B NMR spectrum of an aliquot revealed no peaks corresponding to the starting carborane. The excess piperidine was removed under reduced pressure at 40 °C. Under nitrogen, the residue was poured into a mixture of distilled water (100 ml) and dichloromethane (100 ml). The organic layer was separated and treated with hexanes (50 ml). The resulting precipitate was filtered off and recrystallized from hexanes : dichloromethane (1 : 10) at 0 °C. The crystals

were identified as [(C$_5$H$_{10}$NH)$_2$H$^+$](*nido*-7,9-C$_2$B$_9$H$_{12}^-$) **1** by X-ray crystallography. Prolonged heating of the crystals under vacuum (100 °C, 0.05 mmHg) gave an air-sensitive white solid identified as (C$_5$H$_{10}$NH$_2^+$)(7,9-C$_2$B$_9$H$_{12}^-$) **2** (2.95 g, 67%). Found C, 38.9; H, 10.2; N, 6.4; C$_7$H$_{24}$B$_9$N requires C, 38.3; H, 11.0; N, 6.4. δ_H (CD$_3$CN) for cation 4.26 (2H, NH), 2.94 (4H, NCH$_2$), 1.62 (6H, CH$_2$). IR (ν/cm^{-1}) 3197 (m, NH), 2927 (m, CH), 2528 (s, BH), 1576 (m), 1449 (m), 1113 (m), 1036 (m), 939 (m).

Deboronation of 1,7-C$_2$B$_{10}$H$_{12}$ with ethanolic potassium hydroxide. A solution of *meta*-carborane (2.88 g, 20 mmol) and KOH (6 g, 106 mmol) in absolute ethanol (100 ml) was refluxed for 14 h. After cooling, the volume of the reaction mixture was halved by rotary evaporation and 300 ml of distilled water was poured into the mixture. The resulting precipitate was isolated by filtration and identified as unreacted *meta*-carborane (1.30 g, 45%). Boron NMR spectroscopy on an aliquot of the filtrate revealed a 4 : 1 mixture of K$^+$ *nido*-7,9-C$_2$B$_9$H$_{12}^-$ **3** and K$^+$ 10-OEt-*nido*-7,9-C$_2$B$_9$H$_{11}^-$ **4**. A stream of CO$_2$ was bubbled through the filtrate (300 ml), giving a solution which was used in the following sections to form desired salts of *nido*-7,9-C$_2$B$_9$H$_{12}^-$.

Synthesis of (Me$_3$NH$^+$)(*nido*-7,9-C$_2$B$_9$H$_{12}^-$). 100 ml of the filtrate was treated with an aqueous solution of Me$_3$NHCl to form a white precipitate, which was isolated by filtration and recrystallized from ethanol. The resulting off-white solid was identified as pure (Me$_3$NH$^+$)(*nido*-7,9-C$_2$B$_9$H$_{12}^-$) (0.34 g, 53% based on *meta*-carborane used). Evaporation under reduced pressure of the solvent from the mother liquor afforded a white solid identified by NMR spectroscopy as (Me$_3$NH$^+$)(10-OEt-*nido*-7,9-C$_2$B$_9$H$_{11}^-$) (0.12 g, 15%). Additional NMR data for the anion 10-OEt-*nido*-7,9-C$_2$B$_9$H$_{11}^-$ δ_B (CD$_3$CN) 0.4 (1B, s; B10), −4.6 (2B, d; B2,5), −8.3 (1B, d, J_{BHt} = 135; B8), −21.7 (1B, d, 141; B4), −26.1 (1B, d, 130, J_{BHu} = 56; B11), −29.1 (1B, d, 144; B3), −6.8 (2B, d; B1,6); δ_C 64.7 (OCH$_2$), 32.0 (br, cage C), 26.3 (br, cage C), 17.0 (OCH$_2$CH$_3$); δ_H (CD$_3$CN) 3.46 (1H, q, 7; OCH$_2$), 3.45 (1H, q, 7; OCH$_2$), 2.33 (1H, s, B2H or B5H), 2.18 (1H, s, B5H or B2H), 1.82 (1H, s, B8H), 1.35 (2H, s; B11H and C7H or C9H), 1.12 (s, 2H, B4H and C9H or C7H), 1.05 (3H, t, 7; OCH$_2$CH$_3$), 0.74 (1H, s; B3H), 0.48 (1H, s; B1H), 0.16 (1H, s; B6H), −0.42 (1H, d, 13; Hμ). IR (ν/cm^{-1}) 3153 (s, NH), 3026 (m, CH), 2973 (m, CH), 2749 (m), 2533 (s, BH), 1477 (s).

Synthesis of [K(18-crown-6)$^+$](*nido*-7,9-C$_2$B$_9$H$_{12}^-$). Addition of 18-crown-6 to 50 ml of the filtrate gave a white precipitate, which was isolated by filtration and recrystallized from acetone–water at ambient temperature under nitrogen to yield white crystals of [K(18-crown-6)$^+$](*nido*-7,9-C$_2$B$_9$H$_{12}^-$) **5**. Found C, 38.6; H, 8.2; C$_{14}$H$_{36}$B$_9$O$_6$K requires C, 38.5; H, 8.3. IR (ν/cm^{-1}) 2902 (s, CH), 2530 (s, BH), 1472 (m), 1353 (m), 1103 (s), 960 (s).

Synthesis of (PSH$^+$)(*nido*-7,9-C$_2$B$_9$H$_{12}^-$). A solution of Proton Sponge in dilute hydrochloric acid was added to a 50 ml aliquot of the filtrate. Under nitrogen, the resulting precipitate was isolated by filtration and recrystallized from a layered hexane–dichloromethane mixture to yield crystals of (PSH$^+$)-(*nido*-7,9-C$_2$B$_9$H$_{12}^-$) **6** suitable for X-ray diffraction. Found C, 55.3; H, 9.1; N, 7.7; C$_{16}$H$_{31}$B$_9$N$_2$ requires C, 55.1; H, 9.0; N, 8.0. IR (ν/cm^{-1}) 3021 (w), 2962 (w), 2533, 2514 (s, BH), 1461 (m), 1112 (m), 1033 (m), 829 (m), 764 (m).

Deboronation of 1,7-Ph$_2$-1,7-C$_2$B$_{10}$H$_{10}$ with neat piperidine. A solution of diphenyl-*meta*-carborane (1.76 g, 10 mmol) in piperidine (100 ml) was refluxed for 24 h, when a ^{11}B NMR spectrum of an aliquot revealed no peaks corresponding to the starting carborane. The excess piperidine was removed under

reduced pressure at 40 °C and the residue was treated with deionised water (100 ml) and dichloromethane (100 ml). The organic layer was separated, dried over $MgSO_4$, filtered and the solvent was removed from the filtrate under reduced pressure. The resulting air-sensitive orange oil was dissolved in methanol and added with a saturated aqueous solution of Bu_4-NBr. The resulting off-white precipitate was identified by NMR spectroscopy as the previously reported salt $(Bu_4N^+)(7,9-Ph_2-nido-7,9-C_2B_9H_{10}^-)$.[27]

Synthesis of $nido$-2,9-$C_2B_9H_{13}$. A mixture of $para$-carborane (5.76 g, 0.04 mol) and powdered KOH (20 g, 0.36 mol) in dry toluene (100 ml) and dry tetraglyme (100 ml) was refluxed under nitrogen for 18 h. The solution was cooled and a stream of CO_2 was bubbled through to neutralise the solution. The solvent was removed under reduced pressure, and to the residue was added benzene (100 ml). With vigorous stirring the slurry was slowly treated with 85% orthophosphoric acid (100 ml). The benzene layer was isolated, washed with deionised water, dried ($MgSO_4$), and the solvent carefully removed under reduced pressure. Sublimation of the residue at 80 °C/0.1 mmHg gave a white glassy solid identified by NMR spectroscopy as a 9 : 1 mixture of $nido$-2,9-$C_2B_9H_{13}$ **8** and $closo$-1,12-$C_2B_{10}H_{12}$. Careful resublimation at 30 °C/0.1 mmHg gave a white crystalline solid identified as pure 2,9-$C_2B_9H_{13}$ (2.42g, 45%). Found C, 17.3; H, 9.7. $C_2H_{13}B_9$ requires C, 17.9; H, 9.8. Additional NMR data for $nido$-2,9-$C_2B_9H_{13}$ δ_B ($CDCl_3$) -8.0 (2B, 141; B8,10), -10.7 (2B, 164; B4,5), -25.5 (2B, dd, $J_{BHt} = 166$, $J_{BH\mu} = 68$; B7,11), -26.0 (1B, d, 158; B1), -35.3 (2B, d, 164; B3,6); δ_C 71.1 (sh), 45.7 (br).

Synthesis of $(PSH^+)(nido$-2,9-$C_2B_9H_{12}^-)$. A hexane solution (40 ml) of 2,9-$C_2B_9H_{13}$ (0.134 g, 1 mmol) was treated with a hexane solution (40 ml) of Proton Sponge (0.214 g, 1 mmol) to produce a white precipitate. The precipitate was filtered and sublimed under vacuum at 150 °C/0.1 mmHg to give a pure sample of $(PSH^+)(nido$-2,9-$C_2B_9H_{12}^-)$ **9** (0.3 g, 85%). Crystals suitable for X-ray structural determination were obtained by recrystallization from a hexane–dichloromethane mixture at -30 °C. Found C, 54.7; H, 8.9; N, 7.7. $C_{16}H_{31}B_9N_2$ requires C, 55.1; H, 9.0; N, 8.0. Additional NMR data δ_B ($CDCl_3$) -13.7 (2B, dq, $J_{BH} = 121$, $J_{BB} = 26$; B8,10), -19.6 (2B, d, 152; B3,6), -22.0 (2B, d, 145; B4,5), -28.9 (2B, ddq, 135, $J_{BH\mu} = 55$, $J_{BB} = 28$; B7,11), -43.3 (1B, d, 150; B1); δ_C 50.6 (br), 27.7 (sh). IR (v/cm^{-1}) 3059 (w), 2997 (w), 2534, 2521, 2484 (s, BH), 1458 (m), 1098 (m), 991 (m), 765 (s).

Aerobic deboronation of 1,12-$C_2B_{10}H_{12}$ with KOH in tetraglyme and toluene. A solution of $para$-carborane (1.44 g, 0.01 mol) in toluene (25 ml) was treated with powdered KOH (5 g, 0.09 mol) and tetraglyme (25 ml). The mixture was refluxed in the presence of air for 10 h and then left to evaporate to dryness at 50 °C. The residue was suspended in 100 ml of benzene and with vigorous stirring the slurry was slowly treated with 85% orthophosphoric acid (100 ml). The benzene layer was then washed, dried ($MgSO_4$) and filtered. The benzene was removed from the filtrate under reduced pressure and sublimation of the residue at 80 °C/0.1 mmHg gave a solid (0.08 g, $ca.$ 6%) identified by NMR spectroscopy as a 3 : 2 mixture of 2,2′-$(1,10$-$C_2B_8H_9)_2$O **12** and 1,10-$C_2B_8H_{10}$ **10**. On exposure to air the solid converts to a 3 : 1 mixture of 2-OH-1,10-$C_2B_8H_9$ and 1,10-$C_2B_8H_{10}$. IR (v/cm^{-1}) 3219 (s, OH), 2592 (s, BH), 1457 (s). GC-MS, 2 peaks at M_r, 110–122 and M_r, 129–139, calculated $C_2B_8H_{10}$ M_r, 115–124 and $C_2B_8H_{10}$O M_r, 131–140. The solid was left exposed for 2 weeks to allow the 1,10-$C_2B_8H_{10}$ to evaporate, leaving pure 2-OH-1,10-$C_2B_8H_9$. Additional NMR data δ_B ($CDCl_3$) 2.3 (s, 1B, B2), -8.8 (d, 4B, $J_{BHt} = 164$; B3,5,7,8), -15.2 (d, 2B, 164; B6,9), -25.4 (d, 1B, 166; B4), δ_H 0.81 (OH).

Table 6 Crystal data for salts of 7,9-$C_2B_9H_{12}^-$ and 2,9-$C_2B_9H_{12}^-$

Compound	1	6	9
Formula	$C_6H_{17.5}B_{4.5}N$	$C_{16}H_{31}B_9N_2$	$C_{16}H_{31}B_9N_2$
M	152.35	348.72	348.72
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	6.517(1)	8.578(2)	8.456(1)
b/Å	8.799(2)	10.464(2)	10.317(1)
c/Å	9.158(2)	12.493(3)	12.945(1)
a/°	65.513(3)	70.326(6)	68.443(3)
β/°	85.279(3)	82.553(6)	84.683(3)
γ/°	83.910(3)	77.184(7)	76.976(3)
U/Å³	474.8(2)	1027.8(4)	1023.3(2)
Z	2	2	2
μ (Mo-K_a)/mm^{-1}	0.054	0.059	0.059
Reflections measured	5747	12457	8405
Unique reflections	2601	5616	2946
R_{int}	0.016	0.033	0.032
$R[F^2 \geq 2\sigma(F^2)]$	0.050	0.076	0.034
$wR(F^2)$, all data	0.152	0.273	0.093

Crystallography

Single-crystal structure determinations were carried out from data collected using graphite monochromated Mo-K_a radiation ($\bar{\lambda} = 0.71073$ Å) on a Bruker SMART 1K CCD diffractometer equipped with a Cryostream N_2 flow-cooling device.[39] Series of narrow ω-scans (0.3°) were performed at several ϕ-settings in such a way as to cover in each case a sphere of data to a maximum resolution of 0.70 Å. A mistake during data processing left us with data up to a maximum resolution of 0.90 Å for **9**. Data collections were carried out at 120 K for **1** and 150 K for **6** and **9**. Cell parameters were determined and refined using the SMART software[40] from the centroid values of 938 reflections with θ values between 13.8 and 30.8° for **1** (382, 7.6–25.2° for **6** and 669, 13.6–25.4° for **9**, respectively). Raw frame data were integrated using the SAINT program.[41] No absorption correction was applied to any of the data sets. The structures were solved using Direct Methods and refined by full-matrix least squares on F^2 using SHELXTL.[42] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters (adps). Hydrogen atoms were located from difference Fourier maps and their coordinates and isotropic displacement parameters refined. Due to the disorder of the $C_2B_9H_{12}^-$ anion in **1**, the B–H–B hydrogen atom was not located. Crystal data and experimental details are given in Table 6.

CCDC reference numbers 171782–171784.

See http://www.rsc.org/suppdata/dt/b1/b108937d/ for crystallographic data in CIF or other electronic format.

Computational details

All ab $initio$ computations here were carried out with the Gaussian 94 package.[43] All geometries were optimized at the HF/6-31G* level with no symmetry constraints. Frequency calculations were computed on these optimized geometries at the HF/6-31G* level for imaginary frequencies—none were found for cage geometries in Fig. 2 except for the symmetrical 7,8-$C_2B_9H_{12}^-$ **II** (Table 5). Optimization of these geometries were then carried out at the computationally intensive MP2/6-31G* level and calculated NMR shifts 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 have been referenced to B_2H_6 (16.6 ppm[44]) 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 TMS; $\delta(^{13}C) = 184.11 - \sigma(^{13}C)$, $\delta(^1H) = 32.28 - \sigma(^1H)$. The root mean squared fitting method used for comparison of experimental and theoretical geometries (Table 6) was carried out using the $ofit$ command in the xp program as part of the SHELXTL package.[42] Relative energies were computed at the MP23sh6-

31G* level with ZPE (calculated at HF/6-31G*) corrections scaled by 0.89. The hydrogen fluxionality barrier of 5.7 kcal mol^{-1} between the two fully optimized geometries of 2,9-$C_2B_9H_{12}^-$ was estimated from calculated energies of the optimized geometries with the H12–B7–B1–B5 dihedral angle as a constant in steps of 5 degrees at the HF/6-31G* level.

Computed NMR shifts (at GIAO–B3LYP/6–311G*//MP2/6-31G*) of the optimized geometries which are ruled out by poor agreement with experimental data in Table 3 are as follows: symmetrical 7,8-$C_2B_9H_{12}^-$ (II) δ_B −7.5 (B9,11), −18.3 (B3,5,6), −26.2 (B2,4), −38.9 (B1), −42.2 (B10); asymmetrical 2,9-$C_2B_9H_{12}^-$ (IV) δ_B −4.3 (B10), −14.5 (B4), −16.7 (B11), −24.7 (B5), −27.1 (B6), −27.6 (B8), −39.0 (B3), −41.2 (B1,7),– averaged −16.0 (B8,10), −19.6 (B4,5), −29.0 (B7,11), −33.1 (B3,6), −41.2 (B1).

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