SELECTIVE DISMANTLING OF *closo*-1,2-$C_2B_{10}H_{12}$ TO LOWER-CAGE DICARBABORANE SYSTEMS

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A modified, high-yield synthesis of the two isomeric *nido* twelve-vertex $[C_2B_{10}H_{13}]^-$ anions, "reactive" [*nido*-7,9-$C_2B_{10}H_{13}]^-$ and "unreactive" [*nido*-7,12-$C_2B_{10}H_{13}]^-$, has been developed. A solution structure for the "reactive" [*nido*-7,9-$C_2B_{10}H_{13}]^-$ isomer is proposed on the basis of the results of two-dimensional ^{11}B and ^1H correlation NMR spectroscopy. It is concluded that there is a marked similarity between this species and the eleven-vertex congener [*nido*-7,8-$C_2B_9H_{12}]^-$. In accord with this parallel, the "reactive" twelve-vertex species is found to undergo selective boron-vertex elimination reactions in the presence of oxidizing agents. These reactions give excellent yields of smaller-cage *nido* dicarbaborane compounds, namely [*nido*-7,8-$C_2B_9H_{12}]^-$, [9-(SMe_2)-*nido*-7,8-$C_2B_9H_{11}$], and *nido*-5,6-$C_2B_8H_{12}$. NMR spectroscopy assigns cluster ^{11}B and ^1H resonances for all the compounds isolated, and thence permits comparison with the equivalent shielding patterns of structurally related analogues such as [*nido*-7-$CB_{10}H_{13}]^-$ and [*nido*-7,9-$C_2B_9H_{12}]^-$.

The previously reported synthesis[1,2] of the "reactive" isomer of the [*nido*-$C_2B_{10}H_{13}]^-$ anion (compound *I*, of schematic cluster structure *A* in Scheme 1 below) is based upon the reduction of the twelve-vertex *closo* dicarbaborane 1,2-$C_2B_{10}H_{12}$ (compound *II*, of schematic cluster structure *B*) by sodium in tetrahydrofuran (THF) solution, followed by treatment of the resulting intermediate [*nido*-$C_2B_{10}H_{12}]^{2-}$ dianion[3-5] with $BF_3.OEt_2$. In the original work[2], the available ^{11}B and ^1H NMR data were interpreted in terms of a twelve-vertex *nido* cluster configuration *C*, viz. [*nido*-7,11-$C_2B_{10}H_{13}]^-$, which is based essentially on an eleven-vertex [*nido*-7,9-$C_2B_9H_{12}]^-$ type of structure (structure *F*) with an additional $\{BH_2\}$ unit capping the B(6)B(10)B(11) triangle.

This initial investigation[1,2] also reported a facile rearrangement of compound *I* into the so-called "unreactive" isomer [*nido*-7,12-$C_2B_{10}H_{13}]^-$ (compound *III*, of schematic cluster configuration *D*), for which the structural type was established

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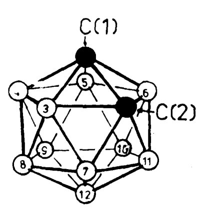
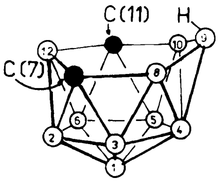
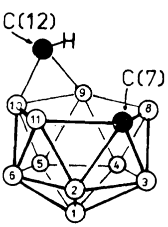
by single crystal X-ray diffraction work on its C,C′-dimethyl[6] and C,C′-diphenyl[7] derivatives. However, except for the thermal decomposition of the $[NMe_4]^+$ salt of the the "unreactive" anion *III*, to generate 1-(Me_3NBH_2)-*closo*-1,2-$C_2B_{10}H_{11}$ (refs[1,2]), and our recently reported preliminary results on the directed degradation of the "reactive" anion *I*, yielding various eight-to eleven-vertex monocarbaborane systems[8], the reactions of the two isomeric anions *I* and *III* have received little, if any, attention. Very recently[9], results of a single-crystal X-ray diffraction analysis on the C,C′-dimethyl derivative of the "reactive" isomer *I*, viz. [7,9-Me_2-*nido*-7,9-$C_2B_{10}H_{11}$]$^-$, have revealed a unique solid-state configuration for this structural type that involves two open faces, one hexagonal and one quadrilateral.



B, II



C



D, III

In addition to some further work and perceptions about synthetic aspects and detailed NMR behaviour of the unsubstituted anions *I* and *III*, we now report some further reactions of the unstable isomer *I*. In contrast to the degradations of anion *I* to give monocarbaboranes, reported elsewhere[8], the reactions described here result in the degradative elimination of boron vertices to give a number of smaller-cage dicarbaboranes in high yield. Although these particular smaller species have been previously reported, we here complement their previous characterisation by detailed ^{11}B and ^{1}H NMR assignments for the cluster atoms. The numbering schemes for ten-, eleven-, and twelve-vertex carbaborane skeletons encountered in this work are as in structures *A*, *J*. Since the numbering of particular atoms will change upon cluster degradation or rearrangement, in structures *H* and *J* we have used the enantiomers of the conventional "clockwise" numbering system to minimize confusion.

RESULTS AND DISCUSSION

Preparative Studies on the [nido-$C_2B_{10}H_{13}$]$^-$ Anions (Compounds I *and* III*)*

The principal modification in the preparation of the anion *I* that renders the procedure more convenient resides in the second stage of the procedure, in which the intermediate [*nido*-$C_2B_{10}H_{12}$]$^{2-}$ dianion is now treated with 20% aqueous sodium chloride solution at −40°C, rather than with $BF_3.OEt_2$. The function of the sodium chloride is both to salt out the product-containing THF layer and to decompose the [*nido*-$C_2B_{10}H_{12}$]$^{2-}$ intermediate. In the first stage, this latter intermediate is generated essentially according to the originally reported[4] method. Thus the *closo* dicarbaborane *II* is treated with two equivalents of sodium metal in THF in the presence of naphthalene: thence a slight variation of the original procedure generates a defined THF solution of $Na_2[C_2B_{10}H_{12}]$ (stock solution A, see Experimental), which is stable for at least one week at ambient temperature under nitrogen. The overall reaction [stoichiometry as in equation (*A*)] leads to an approximately 3 : 1 mixture of the "reactive" and "unreactive" anions *I* and *III* respectively, regardless of the acidity of the sodium chloride solution that is used in the second step.

$$1,2\text{-}C_2B_{10}H_{12} + 2\,e \rightarrow [C_2B_{10}H_{12}]^{2-} + H_2O \rightarrow$$
$$\rightarrow [C_2B_{10}H_{13}]^- + OH^- \qquad (A)$$

I and *III*

The same 3 : 1 ratio (as assessed by integrated ^{11}B NMR spectroscopy) was also found upon repetition of the original[1,2] $BF_3.OEt_2$ procedure (in the original work any presence of the 25 mole % of "unreactive" *III* was not noted). Both methods lead to a well-defined solution of the "reactive" anion *I* in THF–H_2O (stock solution B, containing also c. 25 mole % of anion *III*), which can be stored for about a week without any noticeable change. It should be noted (a) that the stock solution thus obtained is stable *only if the THF is not removed*, and (b) that the contamination by the "unreactive" anion *III* does not adversely affect the further syntheses (described below) because of an apparent unreactivity of *III* under the reaction conditions used.

Solid salts of the "reactive" anion *I* (containing c. 25 mole % of the corresponding salts of *III*) can be isolated if an aqueous solution of an appropriate counter-ion, e.g. $[NHR_3]^+$, $[NR_4]^+$, $[PR_4]^+$, or Cs^+, is added at pH 2–3 before the THF is removed. The pure Cs^+ salt of "reactive" *I* can be obtained by repeated crystallizations from aqueous THF using a procedure involving the simultaneous removal of THF. The $[NBu_4]^+$ salt of *I*, used for NMR studies (see following section below), can be obtained by preparative thin-layer chromatography.

NMR Studies and the Solution Structure of the "Reactive" Anion I

The NMR data for anion *I* in solution (Table I) are not inconsistent with a structure of mirror-plane symmetry as in *A* (Scheme 1), which approximates to that of a *nido*-type twelve-vertex cluster configuration of type *5* in the classification of Grimes[10]. However, it should be noted that the recently reported solid-state structure[9] of the C,C′-dimethyl derivative of *I* contains a pair of enantiomers of a closely related configuration (structures A_1 and A_2 in Scheme 1) of which each has an alternative *nido*-type twelve-vertex configuration (not included in the Grimes' classification)

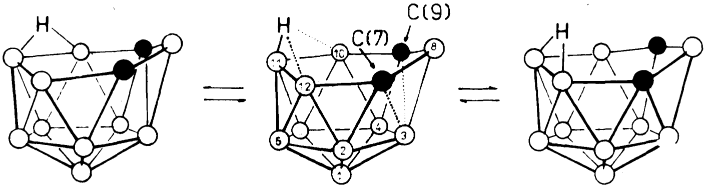
TABLE I

^{11}B and ^{1}H NMR parameters for $[NBu_4]^+[\textit{nido}\text{-}7,9\text{-}C_2B_{10}H_{13}]^-$ (compound *I*) in CD_2Cl_2 solution at 294 K

Assignment[a]	$\delta(^{11}B)$	$^1J(^{11}B\text{-}^1H)$	[^{11}B-^{11}B]-COSY correlations[b]	$\delta(^1H)$[c]	[^{1}H-^{1}H]-COSY correlations[b,d]
8	+12·7	130	—	+4·01	(3)s(7,9)s
10, 12	+2·5	137	(2,4)w(5,6)s(11)s	+2·80	(2,4)w(5,6)s(7,9)s(11)s(μ)s
3	−4·65	151	(1)s(2,4)s	+2·34	(1)m(2,4)w(8)s
5, 6	−7·9	136	(1)s(2,4)s(10,12)s(11)s	+2·47	(1)m(2,4)w(10,12)s(11)m(μ)s^4
1	−17·7	136	(2,4)s(3)s(5,6)s	+1·21	(2,4)m(3)m(5,6)m
11	−20·1	145, 40	(5,6)s(10,12)s	+0·98	(5,6)m(10,12)s(μ)s^2
2, 4	−21·4	150	(1)s(3)s(5,6)s(10,12)w	+0·59	(1)m(3)w(5,6)w(10,12)w
7, 9	—	—	—	+4·49[e,f]	(2,4)s(8)s(10,12)s
μH	—	40	—	−4·57[g]	(5,6)s^4(10,12)s(11)s^2

[a] Assignment by relative intensities and COSY correlations; [b] s = strong, w = weak; m = intermediate; [c] $\delta(^1H)$ related to directly bound *B* positions by $^1H\{^{11}B(\text{selective})\}$ experiments; additional signals from $[N^nBu_4]^+$ at +3·11 (triplet, *J* = c. 8 Hz), +1·62, +1·46 (multiplets), and +1·02 (triplet, *J* = c. 7 Hz); [d] measured under conditions of $\{^{11}B(\text{broad band})\}$ decoupling[29]; correlations arise from $^3J(^1H\text{-}^1H)$ couplings except where superscript n indicates ^nJ path; [e] signal from cluster {CH} unit; [f] additional doublet splitting (*J* = c. 6 Hz); [g] doublet of doublets (*J* = 87/37 Hz) on selective $\{^{11}B(10,12)\}$ irradiation.

that has a quadrilateral open face. The NMR behaviour can therefore equally be interpreted in terms of a "floating" quadrilateral open face (defined by B(2)B(3). .C(7)B(8) in A_1 and B(3)B(4)C(9)B(8) in A_2), i.e. in terms of a rapid equilibration between A_1 and A_2 in solution via A as a transition state or intermediate (Scheme 1). It is in any way apparent that A and A_1/A_2 must be very similar chemically and energetically, and that substituents (compare *IV* versus *VII*) or solid-state packing forces (ref.[11] for comparison) could cause one form to be favoured over the other.



A_1 A, I A_2

SCHEME 1

Within the structure of *I*, the results of [^{11}B-^{11}B]-COSY, [^{1}H-^{1}H]-COSY, and ^{1}H-{^{11}B(selective)} NMR experiments permitted the assignments of all the ^{11}B and ^{1}H resonances, and also yielded some information on possible bonding interactions. All interboron COSY correlations were observed for all mutually adjacent positions, except for the one between ^{11}B(3) and ^{11}B(8) which is adjacent to two carbon atoms. However, interboron couplings for linkages adjacent to carbon are generally found to be weak (see for example ref.[12]) and the $^3J(^1H\text{-}^1H)$ correlation between H(3) and H(8) was found to be strong in the [^{1}H-^{1}H]-COSY experiments. These latter experiments also revealed all the other expected interproton correlations, including those involving the CH(7) and CH(9) cluster units, although it is interesting in the context of the cluster bonding that the [H(7)/H(9)-H(3)] correlation (via the dotted pathway in structure A) was absent. An additional point of interest is that the high-field proton resonance associated with the non-*exo* open-face hydrogen atom was found to exhibit strong coupling to the protons at the (5,6), (10,12), and (11) positions, which could also be consistent either (a) with a unique *endo*-bridging configuration involving interaction with B(10) and B(12) as well as B(11) (Structure A) (compare the similarly bound hydrogen atom[13-16] in the closely related [*nido*-7,8-$C_2B_9H_{12}$]$^-$ {anion *IV*, see below}), or (b) with a rapid equilibration between the extreme enantiomeric forms A_1 and A_2.

An inspection of structure A readily suggests that this is geometrically very closely related to that of the [*nido*-7,8-$C_2B_9H_{12}$]$^-$ anion (species *IV*, structure E, Scheme 3 below)[13-16] from which it may be notionally derived by capping the B(3)—C(7)—C(8) triangular face (numbering as in E) with a {BH} unit. This striking structural similarity between *I* and *IV* is parallelled by chemical similarities, and that there may be also a close similarity of electronic structure is strongly suggested by a consideration of the diagrams in Figure 1 (bottom part) that show the relationship between the ^{11}B NMR chemical shifts for equivalent cluster positions in the anions *I* and *IV*. Thus it can be seen that, although the ^{11}B NMR shielding patters of anion *I* exhibit a systematic downfield shift of c. 10–20 ppm in most positions as compared to anion *IV*, the overall pattern nevertheless remains very similar indeed. These supposed electronic similarities also seem to be supported strongly by chemical similarities. On the other hand there appears to be no systematic parallel between the ^{11}B NMR shielding patterns of the twelve-vertex anion *I* and the 7,9 isomer of anion *IV*, viz. the [*nido*-7,9-$C_2B_9H_{12}$]$^-$ anion *V* (of schematic structure *F*). Indeed, because there is no real structural relationship, it is not really possible to decide which positions may correspond in the structures of both species in order to assess any shielding parallels.

Of additional interest in the NMR behaviour of the twelve-vertex anion *I* is the markedly lower ^{11}B shielding associated with the unique "capping" BH(8) vertex. Whether this lower shielding arises from lower electronic symmetry, lower excitation energies, or from a very marked decrease in electron density, is not clear on present evidence. However, any of these might be expected to lead to an enhanced reactivity at this site, consistent with the chemical evidence discussed below.

Another NMR consideration arising from this work is that the interrelated ^{1}H and ^{11}B NMR chemical shift assignments of the *nido*-7,9 isomer *V* are in fact previously unreported. It is convenient briefly to deal with these here. The data are summarized in Table II, and a plot of $\delta(^{11}B)$ versus $\delta(^1H)$ for directly bound BH(*exo*) units, together with those of anions *I* and *IV* for comparison, are given in Figure 1 (uppermost diagram).

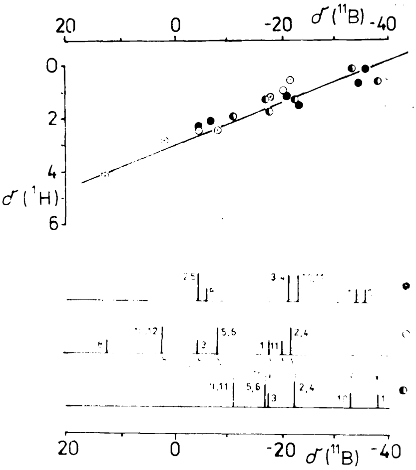
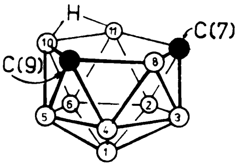


FIG. 1

The upper diagram is a plot of $\delta(^1H)$(*exo*) versus $\delta(^{11}B)$ for directly attached BH(*exo*) units in the anions [7,9-$C_2B_{10}H_{13}$]$^-$ (○) [7,8-$C_2B_9H_{12}$]$^-$ (◑), and in [7,9-$C_2B_9H_{12}$]$^-$ (●). The line drawn has a slope $\delta(^1H)$: : $\delta(^{11}B)$ of c. 1 : 13 with intercept +2·9 ppm in $\delta(^1H)$. The lower diagram (same scale in $\delta(^{11}B)$) gives stick representations of the chemical shifts and relative intensities in the ^{11}B NMR spectra of the anions mentioned above. Dotted lines join equivalent sites in the first two compounds

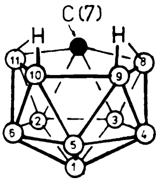


F, V

As with anions I and IV, the results of $[^{11}B-^{11}B]$- and $[^{1}H-^{1}H]$-COSY experiments assign unambiguously all ^{1}H and ^{11}B resonances to their individual cluster positions, with all the interproton and interboron cross-correlations expected for structure F being apparent. Of particular interest are the correlations to the "extra" non-*exo* proton, which displays strong coupling exclusively to the H(10,11) protons, consistent with a hydrogen bridge located on the open face between the B(10) and B(11) vertices. Additionally, it is apparent that the close parallel for $\delta(^{1}H)$ and $\delta(^{11}B)$, mentioned above for anions I and IV, also holds for anion V.

Comparative NMR Data for the "Stable" $[nido\text{-}7,12\text{-}C_2B_{10}H_{13}]^-$ Anion (Species III*) and the Monocarbaborane Anion* $[nido\text{-}7\text{-}CB_{10}H_{13}]^-$ *(Species* VI)

We also report here the previously unestablished assigned ^{11}B and ^{1}H NMR spectra of the "unreactive" $[nido\text{-}7,12\text{-}C_2B_{10}H_{13}]^-$ anion (species *III*). This can be prepared in pure form by heating, in boiling toluene for three hours, the 3 : 1 mixture of *I* and *III* ($[NMe_4]^+$ or $[NBu_4]^+$ salts) that arises from reaction (*A*) above, this being a convenient modification of the original[1,2] procedure for the preparation of *III*. The work completes the previously missing ^{1}H and ^{11}B assignments of this important anion. The measured data are summarised in Table III, assignments being based on the results of the COSY NMR spectroscopy also summarised therein. Table III also includes equivalent data, again previously unreported, for the monocarbaborane[17–19] $[nido\text{-}7\text{-}CB_{10}H_{13}]^-$ (species *VI*, of schematic structure *G*), which is notionally related to anion *III* (schematic structure *D*) by replacement of the two-electron H(8,9) and H(10,11) hydrogen bridges by the four-electron *endo*-type $\{CH_2(9,10)\}$ bridging unit.



G, VI

TABLE II

^{11}B and ^{1}H NMR parameters for $Cs^+[nido\text{-}7,9\text{-}C_2B_9H_{12}]^-$ (compound *V*) in CD_3CN solution at 294 K

Assignments	$\delta(^{11}B)$	$^1J(^{11}B\text{-}^1H)$	[^{11}B-^{11}B]-COSY correlations	$\delta(^1H)$	[^{1}H-^{1}H]-COSY correlations
2, 5	−4·6	145	(1)s(3,4)m(6)s(10,11)m	+2·23	(1)s(3,4)s(6)s(7,9)s(10,11)s
8	−5·9	135	(3,4)m	+2·07	(3,4)s(7,9)s
3, 4	−21·5	144	(1)s(2,5)m(8)m	+1·16	(1)m(2,5)s(7,9)s^a(8)s
10,11	−22·9	131, 56^b	(2,5)m(6)s	+1·47	(2,5)s(6)s(7,9)m(μ)s^2
1	−34·2	145	(2,5)s(3,4)s(6)s	+0·76	(2,5)s(3,4)m(6)s
6	−35·3	140	(1)s(2,5)s(10,11)s	+0·20	(1)s(2,5)s(10,11)s
7, 9	—	—	—	+1·12^c	(2,5)s(3,4)s^a(8)s(10,11)m
μH	—	56	—	−2·32	(10,11)s^2

[a] Correlation uncertain due to ^{1}H peak overlap; [b] additional $J(^{11}B\text{-}^{11}B)$ c. 15 Hz; [c] signal from cluster {CH} unit.

TABLE III

^{11}B and ^{1}H NMR parameters for $[NMe_4]^+$ [*nido*-7-$CB_{10}H_{13}]^-$ [anion *VI*, $(CD_3)_2CO$ solution] and $[N^nBu_4]^+$ [*nido*-7,12-$C_2B_{10}H_{13}]^-$ (anion *III*, CD_2Cl_2 solution) at 294 K

Assignment	Compound *VI*				Compound *III*			
	$\delta(^{11}B)$	$^{1}J(^{11}B\text{-}^{1}H)$	$[^{11}B\text{-}^{11}B]$-COSY correlations	$\delta(^{1}H)^a$	$\delta(^{11}B)$	$^{1}J(^{11}B\text{-}^{1}H)$	$[^{11}B\text{-}^{11}B]$-COSY correlations	$\delta(^{1}H)$
5	−0·5	132	(1)w(4,6)w(9,10)s	+2·36	+11·1	137	(1)s(4,6)s(9,10)s	+3·80
2, 3	−11·9[b]	c. 138	(1)s(4,6)m	+1·95	−6·3	148	(1)s(4,6)s(8,11)m	+1·63
8, 11	−11·9	c. 138, 60	(4,6)m	+1·83	+16·0	152	(2,3)m(4,6)s(9,10)s	+3·67
9, 10	−23·0	143, 65	(4,6)m(5)s	+1·20	−16·2	133	(4,6)s(5)s(8,11)s	+1·34
1	−26·3	137	(2,3)s(4,6)w(5)w	+1·24	+0·2	136	(2,3)s(4,6)s(5)s	+2·73
4, 6	−31·2	137	(1)w(2,3)m(5)w(9,10)m	+0·47	−22·8	138	(1)s(2,3)s(5)s(8,11)s(9,10)s	+0·87
7	—	—	—	+1·48	—	—	—	+2·86
12	—	—	—	—	—	—	—	+1·44[c] +1·01[d]
μH	—	60, 65	—	−3·97	—	—	—	—

[a] Additional $[NMe_4]^+$ signal at +3·43 ppm (for compound *VI*), for the $[N^n\ Bu_4]^+$ signals (for compound *III*) see similar values in Table I; [b] signal overlap with the B(8,11) resonance; [c] *exo* H(12); [d] *endo* H(12).

Figure 2 presents some of these data in diagrammatic form. It can be seen from an inspection of Figure 2 (bottom part) that there is a systematic downfield shift of all the ^{11}B resonances associated with the dicarbaborane *III* compared to those of the corresponding skeletal positions in the monocarbaborane *VI*, although it is noteworthy that the shielding parallels do seem to be less apparent than those between anions *I* and *IV* as discussed above (see also Figure 1). The comparison reveals that the downfield shifts are particularly pronounced for the B(1), B(5), and B(8,11) positions (structure *D*). The reasons for the marked shifts at these last three positions may respectively reside in the quasi-antipodal position of the *endo*-bridging $\{CH_2\}$ unit with respect to the B(1) vertex, the special placement of the four-electron B(9)—C(12)—B(10) bridge with respect to the B(5) position (compare effect[20] of B—H—B bridges) and the electron-density changes brought about by the α-positioning of the four-electron bridge. However, there is also the removal of the two B—H—B bridging hydrogen atoms from the monocarbaborane *VI* to take into consideration, it being known that the positioning of the open-face bridging hydrogens can substantially affect cluster ^{11}B shielding patterns[20].

Reactivity Considerations and the Oxidative Degradation of the "Reactive" Anion I *to Give* 9-(SMe_2)-*nido*-7,8-$C_2B_9H_{11}$ (*Compound* VII), *and nido*-5,6-$C_2B_8H_{12}$ (*Compound* VIII)

As shown in Scheme 2, the thermal *I* → *III* isomerisation seems to be associated with the cleavage of the B(2)—B(3)—C(7) linkages in structure type *A*, perhaps via an A_1 type of intermediate, followed by the extrusion of C(7) and formation of the new C(7)—B(11) and B(2)—B(4)—B(8)—B(12) linkages (which become the C(12)—B(9) and B(2)—B(10)—B(11) linkages in the numbering scheme *D* for the product).

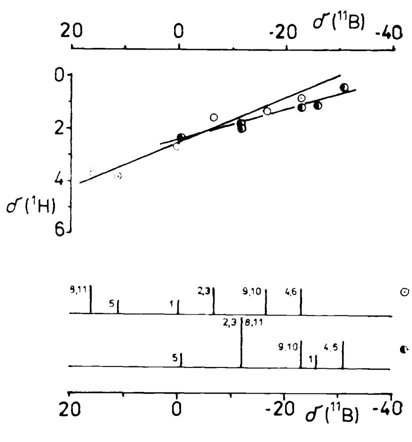
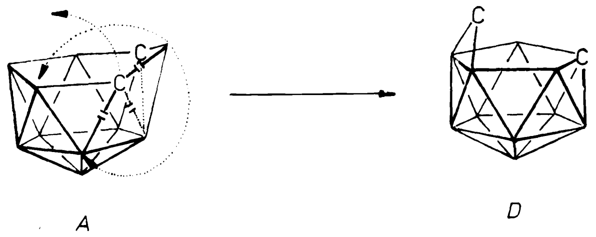


FIG. 2

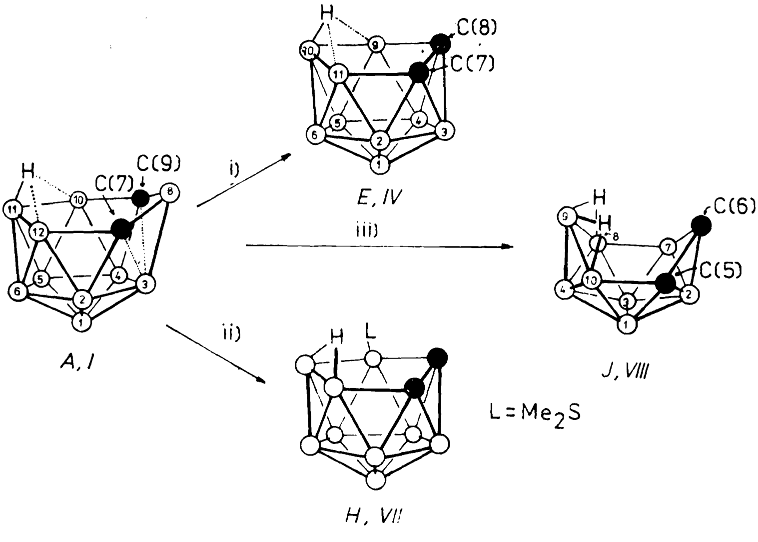
The upper diagram is a plot of $\delta(^1H)$(*exo*) versus $\delta(^{11}B)$ for directly bound BH(*exo*) units in the $[7,12\text{-}C_2B_{10}H_{13}]^-$ anion (⊙) and in the structurally related $[7\text{-}CB_{10}H_{13}]^-$ (◑) monocarbaborane analogue. The line drawn for compound *III* has slope $\delta(^1H)$: : $\delta(^{11}B)$ of c. 1 : 12 with intercept +2·5 ppm in $\delta(^1H)$, while that for compound *VI* has a slope of c. 1 : 18 with intercept +2·4 ppm in $\delta(^1H)$. The lower diagram (same scale in $\delta(^{11}B)$) shows stick representations of the chemical shifts and relative intensities in the ^{11}B NMR spectra of these anions. Equivalent sites have the same numbering

The removal of the structural constraints imposed by the twelve-vertex *nido* configuration *A* might well be a driving force for the isomerisation.



SCHEME 2

The unique floating capping position of the BH(8) vertex in structure *A*, of which the low ^{11}B nuclear magnetic shielding could suggest a potentially reactive site seems also to be associated with an extreme sensitivity of this site to attacks by nucleophilic centres to result in the facile removal of this vertex from the cage of anion *I*. This behaviour, along with the similarity between the twelve-vertex $[7,9\text{-}C_2B_{10}H_{13}]^-$ and eleven-vertex $[7,8\text{-}C_2B_9H_{12}]^-$ anions (*I* and *IV* respectively), is demonstrated by the essentially quantitative formation of anion *IV* from anion *I* (Na^+ salt, stock solution B) on treatment with hydrogen peroxide in the presence of potassium carbonate. The reaction [Scheme 3 (i)] is consistent with a clean removal of the B(8) vertex from anion *I* (structure *A*), accompanied by the ostensibly straightforward



SCHEME 3

formation of a new intercarbon linkage in the product (structure *E*), with the stoichiometry as in equation (*B*):

$$[C_2B_{10}H_{13}]^- + H_2O_2 + OH^- + 2\,H_2O \rightarrow$$
$$\rightarrow [C_2B_9H_{12}]^- + [B(OH)_4]^- + 2\,H_2 \qquad (B)$$

The similarity in chemical behaviour of the twelve-vertex anion *I* with the eleven-vertex anion *IV* is also apparent when $FeCl_3$ is used as oxidizing agent under a variety of conditions [Scheme 3, paths (ii) and (iii)]. Thus anion *I* gives 9-(SMe_2)-*nido*-7,8-$C_2B_9H_{11}$ (compound *VII*, of structure *H* in Scheme 3) in high yield when treated with aqueous $FeCl_3$ and dimethylsulphide, just like anion *IV* does[21]. Similarly, reaction between anion *I* and $FeCl_3$ in acidic medium affords the unsubstituted ten-vertex dicarbaborane *nido*-5,6-$C_2B_8H_{12}$ (compound *VIII*, of schematic structure *J* in Scheme 3] in nearly 60% yield, again in parallel[22] with the behaviour of anion *IV*. The syntheses of compounds *VII* and *VIII* via anion *I* thus represent very good alternatives to earlier reported[21-24] methods starting from anion *IV*.

NMR Studies of 9-(SMe_2)-*nido*-7,8-$C_2B_9H_{11}$ (*Compound* VII) *and nido*-5,6-$C_2B_8H_{12}$ (*Compound* VIII)

As part of our overall examination of the degradative reactions of the dicarbaboranes, and the characterisation of the products formed, it is convenient to present and discuss here aspects of the detailed NMR characteristics of the two compounds *VII* and *VIII* synthesized as described above. The ^{11}B and ^1H NMR properties of compounds *VII* and *VIII* are presented in Tables IV and V respectively. The given assignments arise from two-dimensional homonuclear correlation spectra together with ^1H-{^{11}B} selective heteronuclear double resonance experiments.

Of particular interest in the context of this present work is the comparison between the shielding pattern of compound *VII* with those of the closely related quasi-isoelectronic [*nido*-7,8-$C_2B_9H_{12}$]$^-$ anion *IV*. The close relationships are apparent from the NMR properties. The most obvious difference is the splitting in *VII* of the resonances of relative intensity 2 that arises from the loss of the mirror-plane symmetry of *IV*, although it can be seen from Figure 3 (bottom part) that the mean shielding of each split pair does not change substantially. The possible exception to this is the B(2) position antipodal to the substituted B(9) position, which exhibits a downfield shift of some 10 ppm. Although, as just stated, the mean values do not change very much, the differences in shielding within each of the other two split pairs, B(5)B(6) and B(9)B(11), is quite marked, particularly for the B(5)B(6) pair. This we ascribe not only to the α-substituent effect of the SMe_2 group on B(9), but also to the change in electronic structure arising from the conversion of the *endo*-type B(10) hydride in anion *IV* to a B—H—B bridging position at B(10)—B(11) in compound *VII*. As mentioned above in connection with anions *III* and *VI* a B—H—B bridging grouping has marked and quite site-specific cluster shielding effects[20]. In this regard it may be noted that the COSY NMR data for compound *VII* are entirely consistent with a B—H—B bridge localized between the B(10) and B(11) atoms[25], in contrast to the *endo*-type hydrogen on B(10) in compound *IV* which exhibits three-site bridging character among B(9), B(10) and B(11)[15,16]. The uppermost diagram in Figure 3 shows the general parallel between the ^{11}B and ^{1}H nuclear shielding for the BH(*exo*) groups in compound *VII*, with the gradient $\delta(^1H) : \delta(^{11}B)$ of c. 1 : 18 being somewhat similar to that found for compound *IV* (Figure 1 above; see also ref.[16]), again confirming the overall similarities between the two.

The complete assignments of all the ^{11}B and ^{1}H NMR resonance positions for *nido*-5,6-$C_2B_8H_{12}$ (compound *VIII*) were similarly made on the basis of [^{11}B-^{11}B]-COSY, [^{1}H-^{1}H]-COSY, and ^{1}H-{^{11}B(selective)} measurements (Table V). The ^{11}B assignments are in agreement with those previously made[26] on the basis of the

TABLE IV

^{11}B and ^{1}H NMR[a] parameters for 9-(SMe$_2$)-*nido*-7,8-$C_2B_9H_{11}$ (compound *VII*) in $(CD_3)_2CO$ solution at 294 K

Assignment	$\delta(^{11}B)$	$^{1}J(^{11}B-^{1}H)$	[^{11}B-^{11}B]-COSY	$\delta(^{1}H)$
5	−4·5	146	(1)m(4)m(6)m(9)w	+2·29
9	−6·3[b]	—	(5)w(10)s	+2·75[c] +2·89[c]
2	−12·7	154	(1)w(3)s(6)m(11)w	+1·99
11	−16·9	142, 46	(2)w(6)s(10)w	+1·72
3	−18·6	c. 170	(1)s(2)s(4)m	+1·81
4	−23·5	149	(1)m(3)m(5)m	+1·17
6	−26·6	141	(1)m(2)m(5)m(10)m(11)s	+0·91
10	−30·3	138, 41	(6)m(9)s(11)w	+0·77
1	−37·1	145	(2)w(3)s(4)m(5)m(6)m	+0·79
7	—	—	—	+2·77[d]
8	—	—	—	+2·15[d]
μH	—	41, 46	—	−3·31

[a] $\delta(^{13}C)$ +52·0 [1C, C(7)], +38·6 [1C, C(8)], +27·8 [3C, SMe$_2$], and +25·6 [3C, SMe$_2$] ppm, relative to SiMe$_4$ internal standard (tentative assignments); [b] singlet; [c] signals from SMe$_2$ methyls; [d] signals from cage {CH} units.

substitution chemistry of compound *VIII*, but the proton data are previously unreported. The parallel between the ^{11}B and ^{1}H shieldings generally observed for polyhedral borane species holds well for this compound, with all ($\delta(^{11}B)$, $\delta(^{1}H)$) data

TABLE V

^{11}B and ^{1}H NMR parameters for *nido*-5,6-$C_2B_8H_{12}$ (compound *VIII*) in CD_2Cl_2 solution at 294 K

Assignment	$\delta(^{11}B)$	$^{1}J(^{11}B-^{1}H)$	[$^{11}B-^{11}B$]-COSY correlations	$\delta(^{1}H)$
7	+7·3	c. 156[a]	(2)w(3)s(8)s	+3·49
1	+5·9	c. 178[a]	(2)s(3)s(4)s(10)w	+3·51
8	+4·0	152	(3)s(4)s(7)s	+3·09
3	−1·9	c. 122[a]	(4)s?(1)s(2)s(7)s(8)s	+2·89
9	−2·7	c. 128[a,b]	(4)s(10)w	+3·12
10	−9·0	157, 50[c]	(1)w(4)s(9)w	+2·61
2	−26·1	173	(1)s(3)s(7)w	+1·01
4	−38·1	155	(1)s(3)s?(8)s(9)s(10)s	+0·73
5	—	—	—	+5·04[d]
6	—	—	—	+6·52[d]
μH(8, 9)	—	—	—	−2·43[d]
μH(9, 10)	—	50	—	−2·16[d]

[a] Peak overlap area; [b] additional $J(^{11}B-^{11}B)$ coupling of c. 21 Hz; [c] coupling to μH(9, 10) on $^{1}H-\{^{11}B(10)\}$; [d] assignments based on [$^{1}H-^{1}H$]-COSY measurements on the 6-Ph derivative[33].

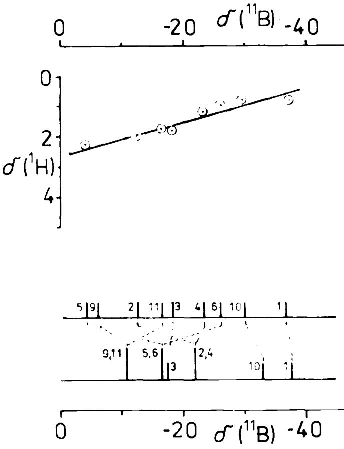


FIG. 3

The upper diagram is a plot of $\delta(^{1}H)(exo)$ versus $\delta(^{11}B)$ for directly attached BH(*exo*) units in 9-(SMe_2)-*nido*-7,8-$C_2B_9H_{11}$ (⊙). The line has a slope $\delta(^{1}H) : \delta(^{11}B)$ of c. 1 : 18, with intercept +2·7 ppm in $\delta(^{1}H)$. The lower diagram (same scale in $\delta(^{11}B)$) gives stick representations of the chemical shifts and relative intensities in the ^{11}B NMR spectra of the above compound and in the structurally related [7,8-$C_2B_9H_{12}$]$^-$ anion[16]. Dotted lines join equivalent sites in both species points lying within 0·5 ppm in $\delta(^{1}H)$ from a correlation line of slope $\delta(^{11}B) : \delta(^{1}H)$ 13 : 1, intercept +3·1 ppm in $\delta(^{1}H)$.

EXPERIMENTAL

Reactions were carried out under anaerobic conditions, and dried and degassed solvents were used throughout. $Cs^{+}[7,9\text{-}C_2B_9H_{12}]^{-}$ and $[NMe_4]^{+}[7\text{-}C_2B_{10}H_{13}]^{-}$ were prepared using previously reported methods[14,27]. All other substances were of reagent grade, and were used as purchased from commercial sources. Systematic monitoring of all reaction mixtures was effected by analytical TLC on Silufol sheets (silica on aluminium foil; detection by exposure to diiodine vapour followed by spraying with 2% aqueous $AgNO_3$).

Nuclear Magnetic Resonance Spectroscopy

NMR spectroscopy was carried out at 4·7 and 9·4 Tesla using commercially available instrumentation. The general techniques, and the techniques of $[^{11}B\text{-}^{11}B]$-COSY (ref.[28]), $[^{1}H\text{-}^{1}H]$-COSY (ref.[29]), and $^{1}H\text{-}(^{11}B)$ spectroscopy[30] used are essentially as described and illustrated in other recent papers describing NMR work in our laboratories[16,31]. Chemical shifts δ are given in ppm positive to high frequency (low field) of Ξ = 100 MHz ($SiMe_4$) for ^{1}H (quoted ±0·05 ppm) and Ξ = 32·083971 MHz (nominally $BF_3.OEt_2$ in $CDCl_3$) for ^{11}B (quoted ±0·5 ppm), Ξ being defined as in ref.[32]. Coupling constants $^{1}J(^{11}B\text{-}^{1}H)$ are given in Hz and are taken from resolution-enhanced ^{11}B spectra of digital resolution 8 Hz.

Preparation of a Stock Solution of $Na_2[C_2B_{10}H_{12}]$ in THF (Stock Solution A)

Using a variation of the basic route pioneered by Zakharkin et al.[4], a mixture of $1,2\text{-}C_2B_{10}H_{12}$ (14·5 g; 100 mmol), finely sliced sodium metal (5·5 g; 220 mg atom), naphtalene (1·0 g; 8 mmol), and THF (180 cm^3) was stirred, with cooling to maintain a temperature of 20°C, until the mixture turned green (c. 4 h). The THF solution thus prepared (c. 0·5 mol dm^{-3} in $Na_2C_2B_{10}H_{12}$; stock solution A) can be stored under nitrogen without apparent decomposition for about one week at ambient temperature. Aliquots can be used for subsequent reactions using conventional anaerobic syringe transfer techniques.

Preparation of a Stock Solution of $Na[7,9\text{-}C_2B_{10}H_{13}]$ (Species *I*) in Aqueous THF (Stock Solution B)

A sample of stock solution A (100 cm^3; prepared as described above) was cooled to c. −40°C, and 20% aqueous NaCl solution (100 cm^3) was then added dropwise under continuous cooling (ethanol–dry ice bath) and occasional shaking. The cooling bath was then removed and the reaction mixture allowed to warm to ambient temperature. The upper layer, which separated after the solid phase had disappeared on warming, was then separated at ambient temperature and diluted with water to a volume of 100 cm^3 to obtain stock solution B, which is c. 0·0375 mol . . dm^{-3} in $Na[7,9\text{-}C_2B_{10}H_{13}]$. This solution also contains c. 0·0167 mol dm^{-3} of the isomeric anion $[7,12\text{-}C_2B_{10}H_{13}]^{-}$ (species *III*), which does not affect the further syntheses described in this paper. This stock solution B of the anion *I* thus obtained is stable for at least a one-week period at ambient temperature under anaerobic conditions, *providing that the THF is not removed.*

The Preparation of Solid Salts of the $[7,9\text{-}C_2B_{10}H_{13}]^{-}$ Anion *I*

An equivalent volume of the stock solution B was treated with the same volume of an aqueous solution containing a c. 10% excess molar equivalent of the chloride of the appropriate counterion (e.g. $[NMe_4]^+$, $[N^nBu_4]^+$, $[NHMe_3]^+$, $[PPh_4]^+$, or Cs^+) at pH c. 2—3, and the THF was then removed in vacuo at ambient temperature (rotary evaporator, c. 20°C, water pump vacuum). The resulting slurry was filtered with suction, washed with water, and the crude product dried in vacuo at ambient temperature. With $[NMe_4]^+$, $[N^nBu_4]^+$, $[NHMe_3]^+$, and $[PPh_4]^+$ as counterions, the resulting products were mixtures that contained the anions *I* and *III* in the original ratio of c. 3 : 1 (as assessed by integrated ^{11}B NMR spectroscopy), whereas with Cs^+ the resulting salt was enriched in anion *I*, with the anion *III* being correspondingly accumulated preferentially in the mother liquor.

Properties of Some Salts of the $[7,9\text{-}C_2B_{10}H_{13}]^-$ Anion *I*

$[NMe_4]^+$ *salt*: insoluble in water, chloroform, and diethylether, sparingly soluble in ethanol and very soluble in acetone and acetonitrile; it can be recrystallized from acetonitrile–benzene (c. 1 : 1 v/v) by layering with an equal volume of diethylether.

$[N^nBu_4]^+$ *salt*: insoluble in water and diethylether, easily soluble in ethanol, chloroform, dichloromethane, acetone, and acetonitrile; chromatographic separation of the salt from the contaminant salt of anion *III* can be effected on silica gel (either column or TLC) using chloroform as liquid phase, the TLC fractions having R_F c. 0·35 and c. 0·13 corresponding to the salts of *I* and *III* respectively. These separated salts can be crystallized by the diffusion of hexane or diethylether vapour into concentrated solutions in dichloromethane.

$[PPh_4]^+$ *salt*: insoluble in water, ethanol, and diethylether, moderately soluble in chloroform, and readily soluble in dichloromethane, acetone, and acetonitrile; may be crystallized as leaflets from dichloromethane by the slow diffusion of diethylether.

Cs^+ *salt*: insoluble in chloroform and diethylether, moderately soluble in water, readily soluble in ethanol, and very soluble in THF; it can be purified by dissolution in 33% aqueous THF at pH 2—3, followed by the evaporation of the THF in vacuo at 20°C, and filtration to yield the solid product; a threefold iteration of this procedure gave a product of c. 97 mole % purity, as assessed by integrated ^{11}B NMR spectroscopy.

The Thermal Isomerisation of $[NR_4]^+[7,9\text{-}C_2B_{10}H_{13}]^-$ (Salts of Anion *I*, R = Me and ^{n}Bu) to Give the Corresponding Salts of $[7,12\text{-}C_2B_{10}H_{13}]^-$ (Anion *III*)

The $[NR_4]^+[7,9\text{-}C_2B_{10}H_{13}]^-$ salt (100 mmol) was refluxed in toluene (50 cm^3) for c. 3 h. The toluene was filtered off after cooling to ambient temperature, the solid was washed with two portions (each c. 20 cm^3) of hexane, and then dried in vacuo to obtain an essentially quantitative yield of $[NR_4]^+[7,12\text{-}C_2B_{10}H_{13}]^-$ (species *III*), of which the identity with the previously reported compound[1,2] was confirmed by ^{11}B NMR spectroscopy.

The Preparation of $[NMe_4]^+[7,8\text{-}C_2B_9H_{12}]^-$ (Compound *IV*) from $Na^+[7,9\text{-}C_2B_{10}H_{13}]^-$ (Compound *I*)

To a mixture made from stock solution B (10 cm^3; 3·75 mmol in *I*) and an aqueous solution of potassium carbonate (0·5 mol dm^{-3}; 10 cm^3; corresponding to 5 mmol K_2CO_3) was added 30% aqueous hydrogen peroxide (1·0 cm^3) dropwise with stirring. Stirring was continued for another 20 min, and then aqueous tetramethylammonium chloride (1·0 mol dm^{-3}; 10 cm^3; corresponding to 10 mmol $[NMe_4]Cl$) was added. The THF was then removed under reduced pressure at room tempeature, the resulting solid residue isolated by filtration, washed with water (c. 20 cm^3) and 50% aqueous ethanol (c. 20 cm^3), and then dried in vacuo to yield 1·1 g of a white solid consisting of 23% of the $[NMe_4]^+$ salt of anion *III*, and 77% of $[NMe_4]^+[7,8\text{-}C_2B_9H_{12}]^-$, corresponding to an essentially quantitative conversion of *I*→*IV* as assessed by integrated ^{11}B NMR spectroscopy.

The Preparation of 9-(SMe_2)-*nido*-7,8-$C_2B_9H_{11}$ (Compound *VII*) from $Na^+[7,9\text{-}C_2B_{10}H_{13}]^-$

A solution of $[FeCl_3(OH_2)_6]$ (5·4 g; 20 mmol) in water (30 cm^3) was added over a period of c. 10 min to a stirred mixture of dimethylsulphide (10 cm^3) and stock solution B (40 cm^3; corresponding to 15 mmol of anion *I*) maintained at 20°C. Stirring was continued for c. 1 h, and then the more volatile components were removed under reduced pressure (rotary evaporator at 20°C). The solid was filtered with suction, and washed with aqueous HCl solution (0·5 mol . . dm^{-3}; c. 30 cm^3). The resulting off-white residue was recrystallized from hot 50% aqueous ethanol to give white leaflets (2·16 g; 11·1 mmol; 71% based on anion *I* consumed), identified as 9-SMe_2-*nido*-7,8-$C_2B_9H_{11}$ (compound *VII*) (m.p. 147—148°C; R_F (silica, benzene) 0·20) by comparison with previously reported (refs[21,30]) ^{11}B NMR spectroscopic data.

Preparation of *nido*-5,6-$C_2B_8H_{12}$ (Compound *VIII*) from $Cs^+[7,9\text{-}C_2B_{10}H_{13}]^-$

A mixture consisting of a solution of $[FeCl_3(OH_2)_6]$ (5·4 g; 20 mmol) in water (c. 30 cm^3), aqueous HCl (0·1 mol dm^{-3}; 10 cm^3), diethylether (5 cm^3), and hexane (30 cm^3) was prepared and cooled to 0°C. $Cs^+[7,9\text{-}C_2B_{10}H_{13}]^-$ (96% purity; 1·4 g; 5 mmol) was then added in several portions to the stirred mixture at 0°C, and stirring was then continued for c. 6 h at ambient temperature. The upper layer was then separated, washed with water (c. 10 cm^3) and 10% aqueous K_2CO_3 solution (c. 30 cm^3), and then filtered with anhydrous $MgSO_4$ (c. 1 g). The filtrate was evaporated in vacuo at 20°C, and the resulting semi-solid residue sublimed at c. 60°C (rotary oil pump vacuum) onto a finger cooled to c. −10°C, to obtain 0·36 g (58%) of *nido*-5,6-$C_2B_8H_{12}$ (m.p. 98—99°C; R_F (silica; hexane) 0·25), identified by comparison with previously[22,26] reported NMR spectroscopic data.

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