REVISION OF *nido*-2,6-$C_2B_7H_{11}$ TO THE *arachno*-4,5-$C_2B_7H_{13}$ STRUCTURE. DETERMINATION OF THE STRUCTURE FROM NMR SPECTRA AND CHEMICAL ORIGIN

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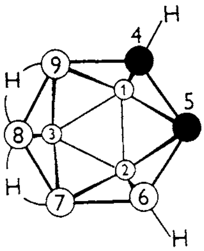
Dedicated to the memory of Dr Karel Bláha.

The asymmetric C_2B_7 carborane held untill the present for 2,6-$C_2B_7H_{11}$, is in reality the *arachno*-4,5-$C_2B_7H_{13}$ carborane (*I*) with two adjacent B—H—B bridges, one BH_2, one CH_2 and one CH group in the hexagonal open-face. The arrangement of the boron network was determined on the basis of the ^{11}B, ^{11}B-^{11}B COSY, ^1H and ^{13}C NMR spectra, and on the T_1(B) study. The connection of B- with C-skeletal atoms was deduced from the positions of deuterium in the deutero analogs prepared by the CH_2O/D_3O^+ degradation of three selectively deuterated *nido*-[7,8-$C_2B_9H_{12}$]$^-$ anions. A selective transmission of D from CD_2O to the B(9) vertex in the course of the CD_2O/D_3O^+ degradation was observed. The structure of arachno-4,5-$C_2B_7H_{13}$ is consistent with the different pathways of its preparation.

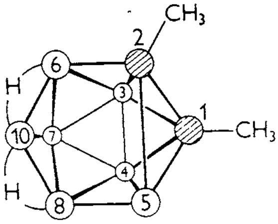
In 1971, Rietz and Schaeffer[1–3] described the incorporation of acetylene and dimethylacetylene into B_8H_{12}. In these reactions, besides the *nido*-C_2B_8 carboranes, degradation C_2B_7 products were also isolated. The structure of the dimethyl derivative was proved[4] by the single crystal X-ray diffraction study to be 1,2-$(CH_3)_2$-1,2-$C_2B_7H_9$ (*II*).

On the other hand, the structure of the glassy; non-methylated C_2B_7 species had to be solved by spectral methods only. Mass spectroscopy was found to be useless, showing fragmentation to several compounds[1,3]. The first proposal of its structure was therefore based on the NMR characteristics only: the published ^1H NMR spectrum (220 MHz) in CS_2 was interpreted[1,3] as composed of a total of eleven hydrogens, namely of two relatively narrow CH signals of intensity one at 2·81 and 1·95 ppm, and of one B—H—B bridge at −0·87 ppm, superimposed by eight broad and low HB quartets. The number of boron atoms was deduced[1,3] from the ^{11}B NMR spectrum at 70·6 MHz which showed six BH doublets and one BH_2 triplet (Table I). On the basis of these data, the $C_2B_7H_{11}$ formula was estimated and the *nido* structure *III* with a hexagonal face was proposed[1,3].

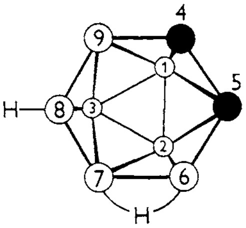
Shortly after this, we reinterpreted the ^{11}B NMR spectrum as favoring the *nido*-structure *IV* with two C-atoms in the pentagonal face[5]. The structure *IV* was consistent with the absence of an H-tautomerism between BH_2 and B—H—B, as well as with the geometrical arrangement of the skeletons, belonging to nine-vertex *nido* compounds according to the Williams' systematization[6]. Moreover, the *nido*-character and the $C_2B_7H_{11}$ formula seemed to be confirmed by the detailed mass spectral study in which $(C_2B_7H_{11})^+$ was the highest ion observed[7]. The *nido* character of the C_2B_7 species was also inferred by the structure of the analogously obtained dimethyl isomer *II* (ref.[4]).



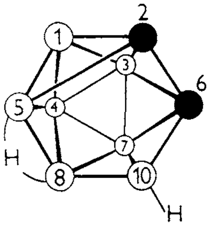
I



II



III



IV

○ BH ● CH ▨ C

Isolation of the C_2B_7 species from the mixture resulting from the oxidative degradation of the $[7,8\text{-}C_2B_9H_{12}]^-$ anion[7] and, especially its direct preparation in almost 60% yield with an acid degradation of this anion in the presence of formaldehyde[8,9], made the title compound one of the best accessible open-face dicarbaboranes. Its utility was illustrated by the preparation of a whole series of metallaboranes[8,10–12]. In all these papers, the *nido* character of the starting C_2B_7 carborane was considered.

The structure of the discussed C_2B_7 carborane, which incluted a BH_2 vertex, was exceptional among *nido* skeletons from the point of view of the Williams' systematization[6]. Attempts to solve it by the X-ray diffraction analysis failed[3] and asymmetry within skeleton precluded an unambiguous interpretation of the conventional ^{11}B NMR spectra. The ability of the ^{11}B–^{11}B two dimmensional NMR spectroscopy[13–16] to show mutual B–B connections within cluster framework, prompted us to study the C_2B_7 species by this method.

RESULTS AND DISCUSSION

A detailed ^{11}B NMR study of the C_2B_7 species, analysing selected spectra (Fig. 1), has indicated six doublets A – E, G and one BH_2 triplet F of equal intensities (see Table I). The boron atoms, associated with the ^{11}B signals A and B, must lie on the edge of the open framework, due to μH bridge splitting of their signals (cf. Figs 1*a*, 1*d* and their line-narrowed counterparts 1*b*, 1*e*). The μH splitting was confirmed by the μH selectively decoupled ^{11}B spectrum (Fig. 1*c*) which shows a narrowing of the A and B signals when compared with the undecoupled ^{11}B NMR spectrum (Fig. 1*a*). The BH_2 vertex must also be located in the open face, as its signal F is split to a triplet. The discussed ^{11}B NMR spectra (Fig. 1*a* – 1*e*) seemed to be consistent with the pentagonal *nido* skeleton *IV* in which an H-tautomerism was improbable and the existence of an unusual BH_2 group was compelled.

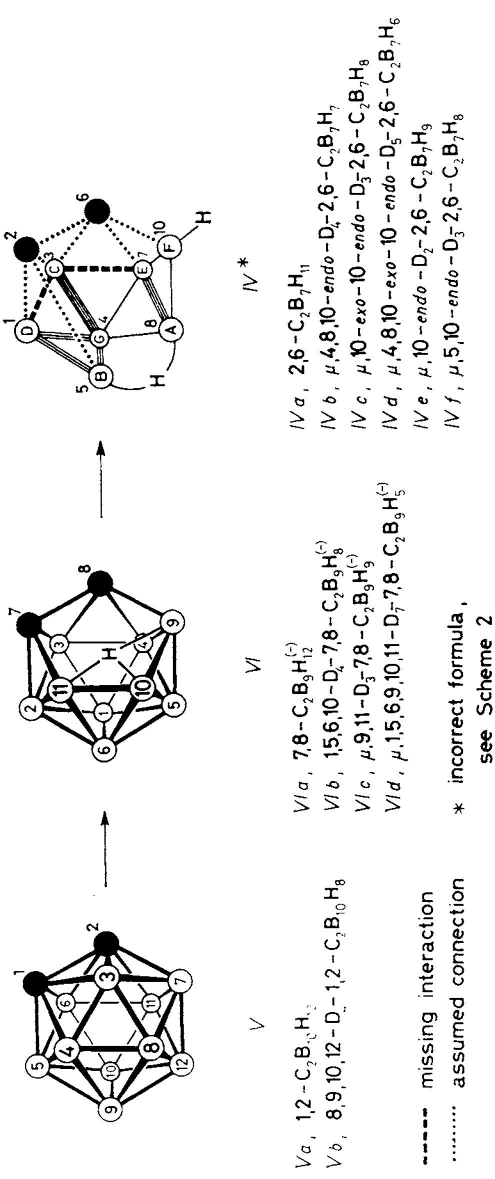
TABLE I

Assignments of the ^{11}B NMR signals for 4,5-$C_2B_7H_{13-x}D_x$ *Ia*–*If*: δ_B ±0·05 ppm, $J(^{11}B/\mu H)$ in Hz, [T_1] in ms

Compound	A: B(7)	B: B(9)	C: B(8)	D: B(1)	E: B(2)	F: B(6)	G: B(3)
Ia	9·91 (154/30) [19·7]	3·85 (159/46) [21·2]	−3·76 (142) [23·8]	−4·57 (161) [22·8]	−6·31 (155) [32·6]	−30·07[a] (124) [26·0]	−56·65 (158) [81·3]
Ib	9·85 (−)	3·77 (157/−)	−4·26 (−)	−4·80 (175)	−6·43 (157)	−30·18 (123)	−56·77 (−)
Ic	9·65 (150/−)	3·49 (160/−)	−4·12 (140/−)	−4·74 (168)	−6·56 (145)	−30·21 (−)	−56·85 (154)
Id	9·57 (−)	3·45 (159/−)	−4·12 (−)	−4·86 (170)	−6·37 (155)	−30·29 (−)	−56·96 (−)
Ie	9·72 (152/−[b])	3·70 (159/−)	−4·09 (147/−)	−4·79 (176)	−6·29 (155)	−30·13 (126[c])	−56·82 (154)
If	9·51 (−)	3·51 (−)	−3·71 (−)	−4·68 (167)	−6·33 (155)	−30·32 (−)	−56·90 (−)

[a] Triplet; [b] influenced by a μD coupling; [c] multiplet, a result of a partial *endo* deuteration.

The mutual connections of boron atoms in the C_2B_7 skeleton and the assignment of their ^{11}B signals followed from the ^{11}B COSY 2D spectrum (Fig. 2) in which nine cross-peaks were found. On the presumption of the presence of only one B—H—B bridge[1,3], i.e. of the bonding proximity of A and B atoms due to their μH splitting, the boron network as in *IV* (see Scheme 1) was deduced.



SCHEME 1

The uncertainity of the presence of two remaining cross-peaks between C–E and C–D signals was comprehensible due to a considerable proximity of the C, D, E signals (see Fig. 1).

The assignment of the signal G was in agreement with our NMR empirical Rule 1 which states that the boron atom opposite to the H-bridge resonates in the highest part of the given ^{11}B NMR spectrum[16–18]. Similarly, a distinct μH splitting of the signal B was in accord with our earlier empirical μH rule stating that boron atoms adjacent to a skeletal carbon atom or bearing a classical two electron bond are significantly μH split[19].

While the boron network, constructed on the basis of the ^{11}B–^{11}B interactions, corresponded to the appropriate part of the *IV* skeleton, evidence of the C–B connections was still missing.

The formation of the asymmetrical C_2B_7 carborane from the *o*-carborane (*Va*) through the $[7,8\text{-}C_2B_9H_{12}]^-$ intermediate (*VIa*), followed by its CH_2O/H_3O^+ degradation (refs[8,9]) indicated that the 3, 4 and 8 boron atoms were removed step-

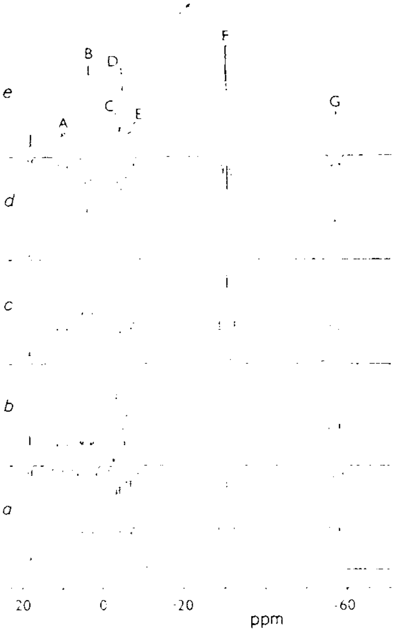


FIG. 1

^{11}B NMR spectra of 4,5-$C_2B_7H_{13}$ in $CDCl_3$ at 64·184 HMz. *a* Undecoupled; *b* undecoupled, line narrowed (very strong and sharp signal F omitted); *c* μH decoupled; *d* H decoupled; *e* H decoupled, line narrowed

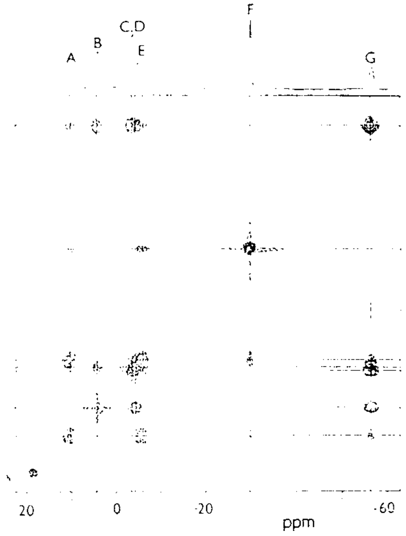


FIG. 2

^{11}B COSY spectrum of 4,5-$C_2B_7H_{13}$

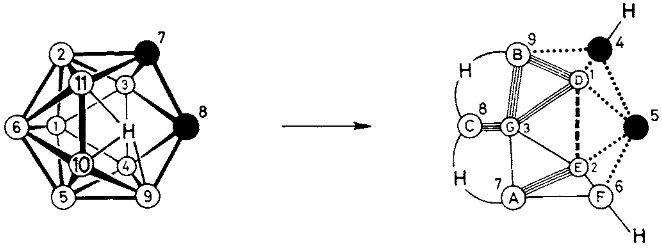
wise from the *o*-carborane. According to this presumption, the degradation of 8,9,10,12-D_4-1,2-$C_2B_{10}H_8$ (*Vb*) should afford the C_2B_7 skeleton deuterated at the boron vertices, corresponding to signals A, B and G. At variance with this presumption, only deuteration on boron vertices, corresponding to the signals A and G was observed (Table I). The surprising absence of deuterium in the position corresponding to the signal B was found not to be a result of an additional H/D exchange as the asymmetrical C_2B_7 carborane itself exchanged hydrogen atoms in D_3O^+ at the μ and *endo*-H positions only (see *IVe* (later reinterpreted as *Ie*)), leaving the signal B unchanged.

Similar unexpected results were obtained when starting from the $[\mu,9,11\text{-}D_3\text{-}7,8\text{-}C_2B_9H_9]^-$ (*VIc*) and $[\mu,1,5,6,9,10,11\text{-}D_7\text{-}7,8\text{-}C_2B_9H_5]^-$ (*VId*) anions which afforded under the above degradation conditions compounds held to be carboranes *IVc* and *IVd* with deuterium in the positions corresponding to the signals F, and A, F and G, respectively. The exchange of D_3O^+ for H_3O^+ medium in the CH_2O degradation resulted in the latter case only in an additional introduction of deuterium into the μ and *endo*-H positions, affording compound *IVe*. In no case, however, deuterium was observed in the position corresponding to the signal B.

From the above observations we judged that the absence of deuterium in the B position was caused by a selective re-exchange by means of CH_2O of hydrogen for the deuterium already present at the position corresponding to the signal B. The substitution of CD_2O for CH_2O supported this idea as the C_2B_7 carborane *IVf*, with the deuterium in the B position, was obtained. This result, together with the percepted presence of one B—H—B bridge and two individual CH signals, were fully compatible with the structure *IV*, which was held to be a proven one, and the communication was almost ready to be published.

To complete the NMR characteristics, the ^{13}C NMR spectrum of the asymmetrical C_2B_7 carborane was measured in $CDCl_3$. Surprisingly, instead of two expected CH doublets, one broad CH doublet at 29·2 ppm and one sharp CH_2 triplet at 11·02 ppm were found[20]. The simultaneous presence of the BH_2 and CH_2 vertices indicates clearly that the C_2B_7 compound does not belong to the *nido* but to the *arachno* series and thus it must have the $C_2B_7H_{13}$ formula. The new formula was fully confirmed by remeasuring the ^1H NMR spectra in several solvents. These spectra, in contrast to that in CS_2 (see p. 2742) revealed two CH signals of intensity 1 and 2, respectively ($CDCl_3$: 2·15, 1·60 ppm; C_6D_6: 1·96, 0·44 ppm), and one broad B—H—B signal ($CDCl_3$: −1·32 ppm; C_6D_6: −2·15 ppm) which in C_6D_6 was fully separated from the BH quartets and showed the presence of two overlapped B—H—B bridges. The mass spectra of the carborane *I* were also remeasured using three techniques. The results (EI (70 eV): *m/z* 113, M-1; CI: *m/z* 115, M + 1; NICI: *m/z* 114) were consistent with the $^{12}C_2{}^{11}B_7{}^1H_{13}$ formula.

On the basis of these results, the *arachno* structure *I* with BH_2, CH_2 and CH vertices and two hydrogen bridges was proposed. The re-assignment of signals as



VI

I

VIa, $7,8-C_2B_9H_{12}^{(-)}$
VIb, $1,5,6,10-D_4-7,8-C_2B_9H_8^{(-)}$
VIc, $\mu,9,11-D_3-7,8-C_2B_9H_9^{(-)}$
VId, $\mu,1,5,6,9,10,11-D_7-7,8-C_2B_9H_5^{(-)}$

Ia, $4,5-C_2B_7H_{13}$
Ib, $\mu,\mu',3,6$-*endo*-$D_4-4,5-C_2B_7H_9$
Ic, $\mu,\mu',6$-*endo*,6-*exo*-$D_4-4,5-C_2B_7H_9$
Id, $\mu,\mu',3,6$-*endo*,6-*exo*,7,8-$D_7-4,5-C_2B_7H_6$
Ie, $\mu,\mu',6$-*endo*-$D_3-4,5-C_2B_7H_{10}$
If, $\mu,\mu',3,6$-*endo*,6-*exo*,7,8,9-$D_8-4,5-C_2B_7H_5$

------ missing interaction
········· assumed connection

SCHEME 2

shown in the Scheme 2, formula *I*, gave far better agreement with the $^{11}B-^{11}B$ 2 D NMR spectrum (Fig. 2) in which only the presence of the crosspeak D–E from ten expected ones was now uncertain. The assignment of the signal G to B(3) and of signal B to B(9) is in agreement with our NMR rules, i.e. the former resonating in the highest field, is opposite to the B—H—B bridge[16-18] and the latter is significantly μH-splitted due to the adjacent carbon vertex[19]. The T_1 relaxation time measurements bring further confirmation of the correctness of the signal assignments. Past experience indicated that in a given molecule, the boron nucleus with the most symmetrical electric field has the longest T_1 time[21,22] and, vice versa, the boron vertex with the greatest electric field gradient, due to the presence of heteroatom(s), should have the shortest T_1 time[23]. Of the three boron atoms of connectivity five (B(1), B(2), B(3)), the greatest T_1 value is expected for B(3), surrounded by five boron atoms, and the shortest one for B(1) which has two positively charged carbon atoms in its vicinity. These expectations are in agreement with the found T_1 values (Table I).

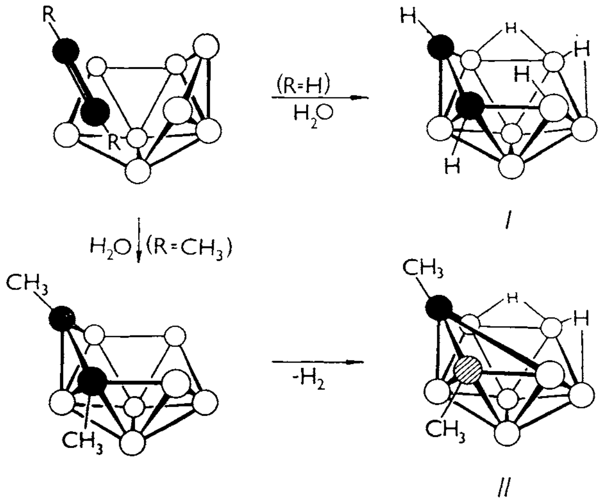
A new ^{11}B NMR measurement at 128·4 MHz of the carborane *Ib* prepared from $8,9,10,12-D_4-1,2-C_2B_{10}H_8$ (*VIb*) has shown that besides deuteration in the positions corresponding to signals A and G a partial deuteration of the boron belonging to the signal C can also be recognized in the CDE overlapped area.

These results have not only confirmed the real structure of the asymmetrical C_2B_7 carborane but they also have substantiated the absence of deuterium in the B position of the $4,5-C_2B_7H_{13}$ carborane.

The carborane *I* now has a conventional nine vertex *arachno* framework with $2n + 6 = 24$ skeletal electrons (see Refs[24,25]) and with two vicinal hydrogen bridges, one BH_2 group and adjacent CH—CH_2 vertices within the open hexagonal face of 4,5-$C_2B_7H_{13}$, thus being an isoskeletal and isotopological counterpart of the long known 4,6-$C_2B_7H_{13}$ carborane[26].

Taking into account the *arachno* structure of 4,5-$C_2B_7H_{13}$, some properties which appeared curious for *nido*-$C_2B_7H_{11}$ carborane are now understandable, namely: *a*) a resistance to the addition of sodium[23] or of Lewis bases as diethyl ether or tetrahydrofuran[1,3]; *b*) halogenation to *arachno*-4,5-$C_2B_7H_{12}X$ derivatives[27]; *c*) simultaneous incorporation of two C_5H_5Co vertices into the molecule[8], and *d*) the presence of the BH_2 vertex in the molecule.

The *arachno* character of the carborane *I*, appearing as a minor component in the reaction of B_8H_{12} with acetylene, suggests its origin via the hydrolytic elimination of one vertex from the primary adduct by traces of water (see Scheme 3) according to the general mechanism[28] rather than via the elimination of the BH_3 fragment[1,3]. The same pathway, followed by a dehydrogenation, can be considered in the formation of 1,2-$(CH_3)_2$-1,2-$C_2B_7H_9$ (*II*) from B_8H_{12} and dimethylacetylene. The reason for the subsequent contraction to the *nido* skeleton *II* is seen in the tendency towards cyclization evoked by two methyl groups. A similar tendency is observed in organic chemistry[29].



SCHEME 3

It is clear that the ^{11}B NMR analysis alone, inclusive of a ^{11}B–^{11}B two-dimmensional NMR study, though combined with a deuterium labelling, afforded results which supported the earlier incorrect structures. Only ^{1}H NMR measurements in different solvents and especially, the often neglected ^{13}C NMR spectra brought unambiguous evidence that the C_2B_7 species, for a long time considered to be *nido*-$C_2B_7H_{11}$, is in reality the *arachno*-4,5-$C_2B_7H_{13}$ carborane. This paper should therefore serve also as a warning to boron chemists, solving the structures of asymmetrical carboranes and heteroboranes by means of NMR methods (see e.g. an incorrect assignment[12] of signals with 4-CoC_5H_5-2,3-$C_2B_7H_{13}$). In such cases, an ^{1}H–^{1}H two-dimmensional NMR study and/or a good agreement with all pertinent rules and experiences[30] are necessary.

EXPERIMENTAL

NMR spectra were measured using a Varian XL-200 NMR spectrometer (^{11}B: 64·184 MHz, ^{1}H: 200 MHz, ^{13}C: 50·309 MHz). The locked spectra of *I* were recorded in $CDCl_3$, those of *VI* in CD_3COCD_3. Referencing was to an external $BF_3.O(C_2H_5)_2$ for ^{11}B and internal tetramethylsilane for H.

For 2D ^{11}B–^{11}B spectra, the COSY pulse sequence was used to generate the t_1, t_2 matrix (512 × 512). The spectra were obtained utilizing standard Varian XL-200 software "HOMCOR". Acquisition parameters: acquisition time AT 0·047 s, relaxation delay D1 0·2 s, sweep width SW 5 000 Hz, number of transitions NT 32. The resulting COSY spectra were line-narrowed (using resolution enhancement RE 0·003 and the apodization function AF 0·01), symmetrized, and recorded using a Nicolet Zeta 1 553 plotter.

The T_1 values were measured with accuracy ±10% using the 180°-τ-90° pulse sequence at 23°C. Ten values from 1 to 200 ms were used. For differentiating the overlapped signals, intensities of selected peaks from the line-narrowed spectra (RE 0·003, AF 0·012) were analyzed by the exponential least-squares routine.

Preparation of [1,5,6,10-D_4-7,8-$C_2B_9H_8$]$^-$ (*VIb*)

To a solution of 3·7 g (25 mmol) of 8,9,10,12-D_4-1,2-$C_2B_{10}H_8$ in 50 ml of methanol, solid KOH (8·4 g, 150 mmol) was added. The mixture was refluxed for 4 h, cooled and 50 ml of water was added. Methanol was evaporated in vacuo and the remaining aqueous solution was extracted with diethyl ether (2 × 30 ml). The solid remnant was dissolved in 30 ml of water, the solution was filtered and 6·5 g (25 mmol) of CsI was added to the clear filtrate. The separated precipitate was collected by filtration, washed with a small amount of cold water and recrystallized from 50 ml of hot water. The yield was 6·0 g (89%) of *VIb*. ^{11}B NMR (CD_3COCD_3): −11·30 d (B-9, B-11); −16·90 s (B-5, B-6); −17·73 d (B-3); −22·30 d (B-2, B-4); −33·35 s (B-10); −38·22 s (B-1).

Preparation of [μ,9,11-D_3-7,8-$C_2B_9H_9$]$^-$ K^+ (*VIc*)

A 1M solution (20 ml) of [7,8-$C_2B_9H_{12}$] K ref.[31] was evaporated to dryness in vacuo. The solid remnant was dissolved in 20 ml of 6M-DCl in D_2O. The solution was set aside for 8 hours at room temperature and then it was used for further reactions. ^{11}B NMR of the dried $(CH_3)_4N^+$ [μ,9,11-D_3-7,8-$C_2B_9H_9$]$^-$ precipitate (CD_3COCD_3): −11·37 s (B-9,B-11); −16·85 d (B-5, B-6); −17·73 d (B-3); −22·27 d (B-2, B-4); −33·17 d (B-10); −37·96 d (B-1).

Preparation of $[\mu,1,5,6,9,10,11\text{-}D_7\text{-}7,8\text{-}C_2B_9H_5]^-$ (*VId*)

The solid remnant prepared as in *VIc*, was dissolved in 30 ml of 6M-DCl in D_2O, and the solution was refluxed for 8 h in an inert atmosphere. The final solution was used for the preparation of *Id*. A small sample was precipitated in the form of $(CH_3)_4N^+[\mu,1,5,6,9,10,11\text{-}D_7\text{-}7,8\text{-}C_2B_9H_5]^-$, and dried in vacuo. ^{11}B NMR (CD_3COCD_3): −11·45 s (B-9, B-11); −16·91 s (B-5, B-6); −17·73 d (B-3); −22·32 d (B-2, B-4); −33·36 s (B-10); −38·23 s (B-1).

Degradation of the deuterated $[7,8\text{-}C_2B_9H_{12}]^-$ anions *VIb*–*VId* to the deuterated 4,5-$C_2B_7H_{13}$ carboranes *Ib*–*Id* and *If*

An 1M aqueous solution of the $[7,8\text{-}C_2B_9H_{12-x}D_x]^-$ salt (15 ml) was overlayered with 50 ml of hexane, and diluted HCl (1 : 3, 30 ml) or 6M-DCl in D_2O (30 ml) was added. To this mixture, 6 ml of 38% CH_2O or CD_2O in D_2O was added and stirring was continued for further 4 h. The hexane layer was then separated, dried over $CaCl_2$ and filtered. The clear filtrate was evaporated in vacuo and a solid remnant was sublimed at 60°/1·3 Pa. Yields 40–60%. ^{11}B NMR of *Ib*–*Id*, *If* see in Table I.

Preparation of $\mu,\mu',6\text{-}endo\text{-}D_3\text{-}4,5\text{-}C_2B_7H_{10}$ (*Ie*)

A solution of 0·5 g (4·4 mmol) of 4,5-$C_2B_7H_{13}$ in 30 ml of hexane was underlayered with 30 ml of 6M-DCl in D_2O and the mixture obtained was stirred for 4 h in an inert atmosphere at room temperature. The hexane layer was then separated, dried over $CaCl_2$, filtered, hexane was evaporated in vacuo and the solid residue was sublimed at 60°/1·3 Pa. Yield 0·45 g (90%) of *Ie*. ^{11}B NMR in $CDCl_3$ of *Ie* see in Table I.

Preparation of CD_2O

Paraformaldehyde (9·0 g 0·3 mol) was refluxed in 50 ml of 6M-DCl/D_2O for 48 h in an inert atmosphere, the resulting mixture was cooled to room temperature and filtered. The obtained solution was used for the preparation of *If* in the above degradation.

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