NINE- AND EIGHT-VERTEX POLYHEDRAL DICARBABORANE CHEMISTRY: NEW *arachno* AND *hypho* DICARBABORANES FROM *arachno*-4,5-$C_2B_7H_{13}$: ISOLATION AND CHARACTERIZATION OF THE [*arachno*-4,5-$C_2B_7H_{12}]^-$ AND [*hypho*-7,8-$C_2B_6H_{13}]^-$ ANIONS, AND OF THE NEUTRAL LIGAND DERIVATIVES *exo*-6-(MeNC)-*arachno*-4,5-$C_2B_7H_{11}$ AND *exo*-5-L-*hypho*-4,9-$C_2B_7H_{13}$ (L = NMe_3 and NEt_3)*

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Deprotonation of neutral *arachno*-4,5-$C_2B_7H_{13}$ (**1**) either with 1, 8-$(NMe_2)_2C_{10}H_6$ (proton sponge, PS) or with a mixture of aqueous K_2CO_3 and $[NMe_4]Cl$ leads to the isolation in high yield of the [*arachno*-4,5-$C_2B_7H_{12}]^-$ anion (**2**). Isostructural with this anion is the ligand derivative *exo*-6-(MeNC)-*arachno*-4,5-$C_2B_7H_{11}$ (**3**), which is prepared in 20% yield from the reaction between *arachno*-4,5-$C_2B_7H_{13}$ and MeNC in dichloromethane. Under comparable conditions compound **1** with tertiary amines gives the first representatives of the nine-vertex *hypho* family of dicarbaboranes, the ligand derivatives *exo*-5-(NR_3)-*hypho*-4,9-$C_2B_7H_{13}$ (**4a** and **4b**, where R = Me and Et, respectively) in moderate yields (20 – 55%), whereas the reaction between **1** and aqueous NaCN results in the selective removal of one boron vertex to yield the eight-vertex [*hypho*-7,8-$C_2B_6H_{13}]^-$ anion (**5**) in 61% yield. All compounds isolated were characterized by ^{11}B and ^1H NMR spectroscopy, with two-dimensional and selective decoupling techniques giving unambiguous assignments.

Our two groups have been interested for some time in the chemistry of nine-vertex dicarbaboranes[1–6] and in their metallated analogues[7–10], i.e. in polyhedral borane compounds that incorporate two carbon and seven boron atoms in the cluster framework. Of particular contemporary interest is the nine-vertex *arachno* species *arachno*-4,5-$C_2B_7H_{13}$ (compound **1**)[3–6,11,12], of which the nonmetallic chemistry has been only sparsely developed. The limited examples include (*a*) a preliminary account from one of

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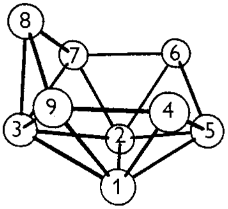
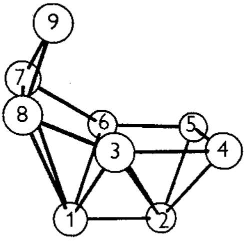
our groups on its selective dismantling to give the [*hypho*-7,8-$C_2B_6H_{13}$]$^-$ anion[13], and (*b*) a preliminary account on its conversion into the [*nido*-4,5-$C_2B_6H_9$]$^-$ anion via boron-vertex removal with acetonitrile[14] and a note on an X-ray diffraction study on the [*arachno*-5,6-$C_2B_7H_{12}$]$^-$ anion[15], which is formed by BH_3 . THF addition to [*nido*-4,5-$C_2B_6H_9$]$^-$. Now we report an extension of the chemistry of the *arachno*-4,5-$C_2B_7H_{13}$ dicarbaborane **1**, in particular its reactions with selected Lewis bases, together with experimental details of the preparation of the [*hypho*-7,8-$C_2B_6H_{13}$]$^-$ anion **5**. General cage structures and the numbering system for the nine-vertex *arachno* and *hypho,* and eight-vertex *hypho* compounds discussed in this work are in structures *I*, *II*, and *III*, respectively.



I



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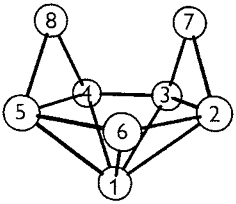


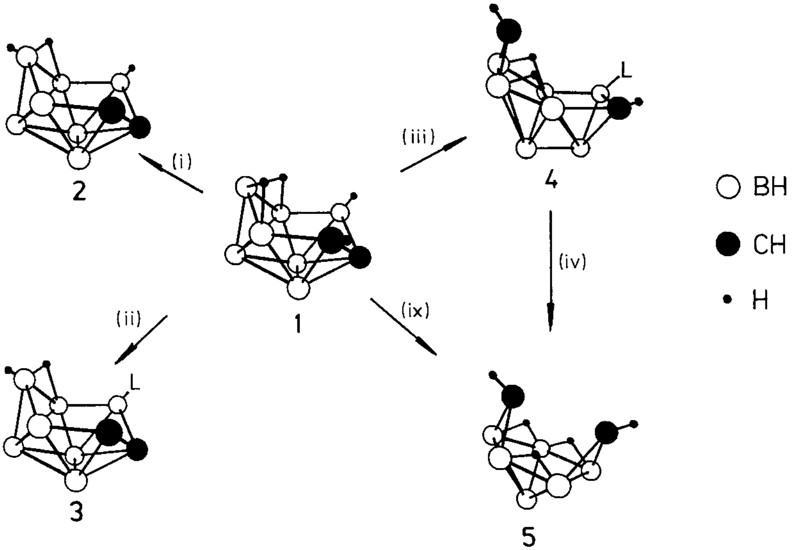
III

RESULTS AND DISCUSSION

Syntheses

NMR spectroscopy shows that deprotonation in situ of *arachno*-4,5-$C_2B_7H_{13}$ (compound **1** in Scheme 1) by proton sponge in CD_2Cl_2 solution (Table I below) leads to the quantitative formation of the [*arachno*-4,5-$C_2B_7H_{12}$]$^-$ anion **2** [structure **2** and path (i) in Scheme 1]. The same anion (with $[NMe_4]^+$ as countercation) is isolable in 92% yield by the treatment of a hexane solution of **1** with an aqueous mixture of potassium carbonate and tetramethylammonium chloride at room temperature for ten minutes. Comparison of structures **1** and **2** suggests that the formation of anion **2** is consistent with the the removal of the *endo* H(4) proton from structure **1**, associated with a minor shift of the original μH(8,9) bridging hydrogen into the *endo* H(8) site.

Structurally similar to anion **2**, and of the same Wadian electron count[16–19], is the ligand adduct *exo*-6-(MeNC)-*arachno*-4,5-$C_2B_7H_{11}$ (**3**). This is formed by the treatment of dicarbaborane **1** with methyl isocyanide in dichloromethane at ambient temperature for 20 h [path (ii) in Scheme 1], and can be isolated by column chromatography on



SCHEME 1

silica in ca 20% yield as a relatively stable, white crystalline solid. Its constitution is proposed on the basis of NMR measurements and mass spectroscopy as discussed below. It is reasonable to assume that the formation of **3** is consistent with the attack by methyl isocyanide at the B(6) position in structure **1** with concomitant loss of dihydrogen, as in Eq. (*A*).

$$\underset{\mathbf{1}}{C_2B_7H_{13}} \quad + \quad MeNC \longrightarrow \underset{\mathbf{3}}{C_2B_7H_{11} \cdot MeNC} \quad + \quad H_2 \qquad (A)$$

In contrast to the preceding reaction, tertiary amines, such as trimethylamine and triethylamine, react with carbaborane **1** at ambient temperature in dichloromethane under the formation of white crystalline compounds identified as *exo*-5-L-*hypho*-4,9-$C_2B_7H_{13}$ [path (iii) and structure **4** in Scheme 1; **4a** for L = NMe_3 and **4b** for L = NEt_3; yields 41 and 55%, respectively] by NMR spectroscopy and mass spectrometry as discussed below. The formation of these first examples of the quite stable nine-vertex *hypho* dicarbaboranes of structure **4** is in agreement with the fast formation of the $[LH]^+$ [*arachno*-4,5-$C_2B_7H_{12}]^-$ salt [structure **2** and path (i) in Scheme 1) in the initial stage of the reaction, followed by slow addition of a proton and L addition into structure **2**, as in Eq. (*B*).

$$\underset{\mathbf{1}}{C_2B_7H_{13}} \quad + \quad L \longrightarrow \underset{\mathbf{2}}{[LH]^+ \, [C_2B_7H_{12}]^-} \longrightarrow \underset{\mathbf{4}}{C_2B_7H_{13} \, . \, L} \qquad (B)$$

As seen from Scheme 1, these processes are not inconsistent with (*a*) the formation of the B(6)–L bond, together with (*b*) a rearrangement of the carbon vertex into the area identified by atoms B(8) and B(9) in structure **2**; this would be accompanied with the fission of the C(4)–C(5) and C(4)–B(1) connectivities to form the new *hypho*-type cluster **4**.

Mechanistically somewhat similar to reaction (*B*) seems to be the reaction between the dicarbaborane **1** and the cyanide anion in a water–hexane mixture at room tempera-

TABLE I
NMR parameters for [*arachno*-4,5-$C_2B_7H_{12}$]$^-$ [PSH]$^+$ (**2**) and 6-(MeNC)-*arachno*-4,5-$C_2B_7H_{11}$ (**3**) in CD_2Cl_2 solution at 294 – 297 K

Assignment[a]	Compound **2**			Compound **3**		
	$\delta(^{11}B)^a$	$^1J(^{11}B$-$^1H)$	$\delta(^1H)^{b,c}$	$\delta(^{11}B)^a$	$^1J(^{11}B$-$^1H)$	$\delta(^1H)^b$
BH(9)	9.0	139	3.41	6.2	143	3.29
BH(2)	–2.2	147	2.66	–2.2	152	2.74
BH(7)	–19.1	135	1.67	–14.0	146	2.31
BH(8)	–29.1	110[d]	1.20[e] 0.89[f]	–30.9	112[d]	1.70
BH(6)	–40.2	117[g]	0.04[e] –0.81[f]	–48.9	139	–0.41[f] 3.61[h]
BH(3)	–41.7	132	0.29	–44.4	132	0.39
BH(1)	–45.0	163	0.16	–45.2	149	0.36
CH(4)	–	–	3.17	–	–	3.12
CH(5)	–	–	3.43	–	–	3.52
µH(7,8)	–	–	–4.50	–	–	–3.33

[a] Assignment on the basis of [^{11}B-^{11}B]-COSY experiments under conditions of complete {^1H(broadband noise)} decoupling; observed cross-peaks for compound **2**: 1-2 s, 1-3 s, 2-3 s, 2-6 m, 2-7 s, 3-7 w?, 3-8 s, 3-9 s; s = stronger, m = intermediate, w = weak, and ? = uncertain; compound **3** shows similar [^{11}B-^{11}B]-COSY patterns, except that the 2-6 cross-peak is missing. [b] Assignments by ^1H-{^{11}B(selective)} measurements. [c] [^1H-^1H]-COSY spectra measured under conditions of complete {^{11}B(broadband)} decoupling; observed cross-peaks for anion **2**: 1-5 s, 1-3 s?, 2-3 s, 2-5 s?, 2-*exo*-6 s, 3-7 m, 3-*exo*-8 s, 3-9 s, 4-5 s?, 4-9 s?, 5-*exo*-6 m, *exo*-6-*endo*-6 s, *exo*-6-7 s, *exo*-8-*endo*-8 s, *endo*-8-9 m. [d] Broad triplet structure due to coupling to µH. [e] *exo*-Hydrogen. [f] *endo*-Hydrogen. [g] Sharp triplet. [h] Singlet of the MeNC methyl group (3 H).

ture, followed by precipitation by tetramethylammonium chloride, to yield [*hypho*-7,8-$C_2B_6H_{13}]^-$ $[NMe_4]^+$ [structure **5**, path (ix) in Scheme 1]. This was isolated in 61% yield as a white solid which is stable under anaerobic conditions. The reaction may well proceed via an unstable [5-CN-*hypho*-4,9-$C_2B_7H_{13}]^-$ intermediate [structure **4** for L = CN^-, path (iii) in Scheme 1] which is converted into eight-vertex anion **5** by hydrolytic elimination of the B(5) atom without any significant rearrangement of cage atoms [path (iv) in Scheme 1]. This mechanism is in agreement with a deuterium-tracer study in which carbaborane **1**, deuterated in the μ,μ′,3,*exo*-6, *endo*-6,7, and 8 positions[6], was employed as a starting substrate. ^{11}B NMR spectroscopy on the *hypho* anion **5** thence obtained showed that it was fully deuterated at the B(1) site and partially (ca 50%) at the B(6) and B(2,5) positions, with no sign of deuteration of the B(3,4) atoms. Anion **5** is the first eight-vertex *hypho* species to be reported[13]; following this, more recently the structurally similar *hypho* 7, 8-diheteroboranes $[S_2B_6H_9]^-$, $[CSB_6H_{11}]^-$, and NSB_6H_{11} have been defined[20–22].

NMR Measurements and Structural Considerations

The results of [^{11}B-^{11}B]-COSY (ref.[23]), [^{1}H-^{1}H]-COSY (ref.[24]) (for **4b** and **2**), and ^{1}H-{^{11}B(selective)} NMR experiments[25] permitted the assignments of all the ^{11}B and ^{1}H resonances for the new compounds **2**, **3**, **4a**, **4b**, and **5**, and also yielded some information on possible bonding interactions among cage vertices. The measured NMR parameters for compounds **1** – **5** are given in Tables I – III, and selected features, together with other data for comparison, are presented in Figs 1 and 2.

The ^{11}B NMR spectrum of the nine-vertex *arachno* dicarbaborane anion **2** (see Table I and Fig. 1) consists of five doublets and two triplets, each of relative intensity 1, thus indicating seven different boron environments with two {BH_2} vertices. The ^{1}H NMR spectrum of **2** shows two singlets of relative areas 1 : 1, assigned to two different cluster {CH} groups and one broad high-field singlet of intensity 1 indicating the presence of one bridging hydrogen atom. All the [^{11}B-^{11}B]-COSY interactions expected for structure **2** are observed, except for that between the resonances of the bridge-connected atoms B(7) and B(8). However, the corresponding [^{1}H-^{1}H]-COSY measurements unequivocally showed the presence of a hydrogen bridge localised between sites 7 and 8 and also the positioning of the two pairs of {BH_2} groups and {CH} units, in agreement with structure **2**. Interestingly, intercomparison of the ^{11}B NMR data for **2** with those for the neutral dicarbaborane **1** (Fig. 1, bottom part) demonstrates very marked changes in the sequencing and positioning of individual resonances. These changes arise because the two species are not isostructural, in that a different arrangement of the open-face hydrogen atoms occurs on deprotonation of **1** to give **2**. Anion **2** is isomeric to the recently reported[15] [*arachno*-5,6-$C_2B_7H_{12}]^-$ anion, the first dicarbaborane analogue of n-B_9H_{15}.

Similar NMR patterns to those for **2** were also obtained for the *arachno* nine-vertex ligand derivative **3** (see Table I and Fig. 1), except that the triplet of the {B(6)H_2} unit is now missing because of the substitution by the *exo*-MeNC ligand. Intercomparison of the ^{11}B NMR data for **2** and **3** (Fig. 1, bottom part) reveals striking NMR similarities

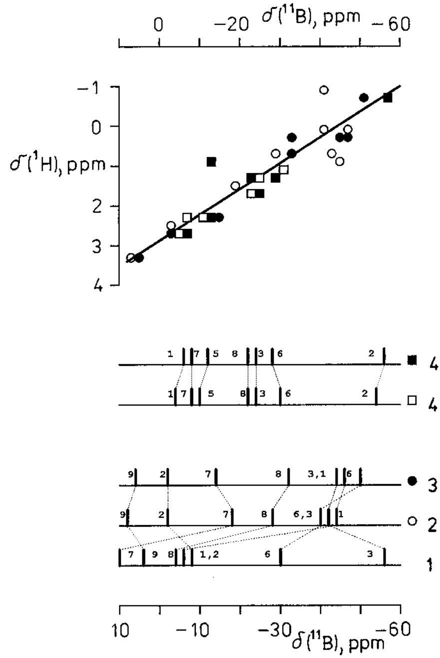


FIG. 1
NMR data for *arachno*-4,5-$C_2B_7H_{13}$ (**1**) together with those for the [*arachno*-4,5-$C_2B_7H_{12}$]$^-$ anion (**2**, ❍) and for the neutral compounds *exo*-6-(MeNC)-*arachno*-4,5-$C_2B_7H_{11}$ (**3**, ●), and *exo*-5-L-*hypho*-4,9-$C_2B_7H_{13}$ (L = NMe_3 and NEt_3; **4a**, ❐ and **4b**, ■) for comparison. The top diagram plots δ(^{1}H) versus δ(^{11}B) for *exo*-BH units for compounds **2** and **3**, and for **4a** and **4b**. The line drawn for the *arachno* compounds **2** and **3** has a slope δ(^{1}H)/δ(^{11}B) 1 : 15, intercept +2.9 in δ(^{1}H) and that for the *hypho* compounds **4a** and **4b** (hatched line) has a slope 1 : 17 and intercept +3.0 in δ(^{1}H). The bottom diagrams are stick representations of the chemical shifts and relative intensities in the ^{11}B spectra of all compounds

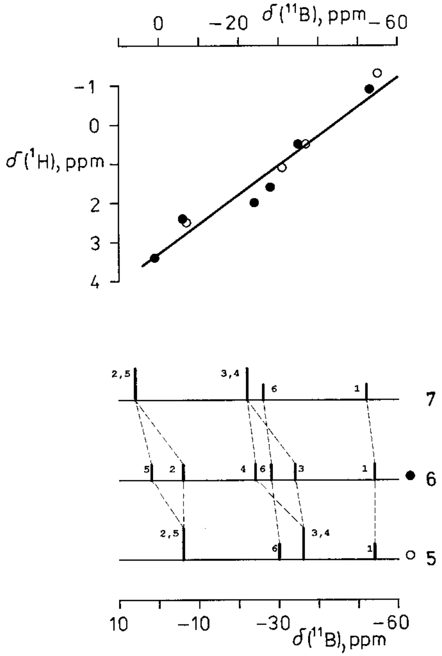


FIG. 2
NMR data for the [*hypho*-7,8-$C_2B_6H_{13}$]$^-$ anion (**5**, ❍) together with those for the *hypho* eight-vertex anions [*hypho*-7,8-CSB_6H_{11}]$^-$ (**6**, ●) and [*hypho*-7,8-$S_2B_6H_9$]$^-$ **7** for comparison. The top diagram δ(^{1}H) versus δ(^{11}B) for *exo*-BH units for compounds **5** and **6**, data for **7** are not available[20]. The line drawn has a slope δ(^{1}H)/δ(^{11}B) 1 : 13, intercept +3.1 in δ(^{1}H). The bottom diagrams are stick representations of the chemical shifts and relative intensities in the ^{11}B spectra of all three compounds

between both compounds. This is expected because, unlike the **1**–**2** pair, they are isostructural. The only major difference is that the resonance of the substituted B(6) atom occurs at high field in **3** because of the high shielding effect of the MeNC ligand[26,27].

The results of [^{11}B-^{11}B]-COSY measurements on the new-type of *hypho* nine-vertex compounds **4a** and **4b** exhibited all the $^{1}J(^{11}B$-$^{11}B)$ cross-peaks among seven different resonances (see Table II and Fig. 1, bottom part), except for those between the bridge-connected pairs B(3)–B(8) and B(6)–B(7), and between the B(7) and B(8) pair connected to the {C(9)H_2}vertex. The corresponding [^{1}H-^{1}H]-COSY experiment on **4b** revealed similar features, and also confirmed the bonding interaction of the {C(4)H_2}

TABLE II

NMR parameters for 5-L-*hypho*-4,9-$C_2B_7H_{13}$ compounds **4a** and **4b** in $CDCl_3$ solution at 294 – 297 K

Assignment[a]	Compound **4a**			Compound **4b**		
	$\delta(^{11}B)$[a]	$^{1}J(^{11}B$-$^{1}H)$	$\delta(^{1}H)$[b]	$\delta(^{11}B)$[a]	$^{1}J(^{11}B$-$^{1}H)$	$\delta(^{1}H)$[b,c]
BH(1)	–2.0	144	2.90	–3.2	144	2.77
BH(7)	–8.0	141	2.38	–8.3	140[d]	2.28
BH(5)	–10.1	138	1.28[e,f]	–11.4	137	1.08[e,f]
BH(8)	–23.6	152	1.43	–24.0	162[d]	1.30[d]
BH(3)	–24.9	145/60	1.91	–25.2	155/30	1.83
BH(6)	–29.7	136/50	1.24	–28.1	140/52	1.30[d]
BH(2)	–54.7	139	–0.50	–55.5	140	–0.63
CH(9)	–	–	0.07[g]	–	–	–0.10[g]
			–2.86[f]			–2.93[f]
CH(4)	–	–	–0.31[f]	–	–	0.42[g]
			–0.31[g]			–0.24[f]
μH(3,8)	–	–	–2.04	–	–	–2.14
μH(6,7)	–	–	–2.17	–	–	–2.22

[a] Assignment on the basis of [^{11}B-^{11}B]-COSY experiments under conditions of complete {^{1}H(broadband noise)} decoupling; observed cross-peaks for compound **4a**: 1-2 s, 1-3 s, 1-5 s, 1-6 s, 2-3 s, 2-6 s, 2-7 m, 2-8 s, 3-8 s?, 5-6 s; s = stronger, m = intermediate, w = weaker, and ? = uncertain; compound **4b** shows the same [^{11}B-^{11}B]-COSY patterns. [b] Assignments by ^{1}H-{^{11}B(selective)} measurements. [c] [^{1}H-^{1}H]-COSY spectra measured under conditions of complete {^{11}B(broadband)} decoupling; observed cross-peaks for compound **4b**: 1-2 s, 1-3 w, 1-5 m, 1-*exo*-4 s, 1-*endo*-4 s, 2-3 s, 2-6 s, 2-7 s, 2-8 s, 2-μH(6,7) m, 2-*exo*-9 s, 2-*endo*-9 m, 3-μH(3,8) s, 3-*exo*-4 s, *exo*-4-μH(3,8), *exo*-4-*endo*-4 s, *endo*-4-5 s, *endo*-4-μH(3,8) w, 5-6 ?, 5-μH(6,7) m, 6-μH(6,7) m, 7-μH(6,7) m, 7-*exo*-9 s, 7-*endo*-9 m, 8-*exo*-9 s, 7-*endo*-9 m, *exo*-9-*endo*-9 s, *endo*-9-μH(3,8) m, *endo*-9-μH(6,7) m. [d] Approximate value due to peak overlap. [e] Additional signals of *exo*-5-NMe_3 at $\delta(^{1}H)$ +4.1(s, 9 H) and $\delta(^{13}C)$ + 54.77 (q, 3 C). Signals of *exo*-5-NEt_3 at $\delta(^{1}H)$ 1.28 (t, 3 H) and 3.05 (m, 2 H). [f] *endo*-Hydrogen. [g] *exo*-Hydrogen.

unit with the adjacent BH(1)–BH(3)–BH(5) atom group and that of the {C(9)H_2} unit with the BH(2), BH(7), and BH(8) atom group, in agreement with structure **4**. These measurements also confirm the presence of two different bridging hydrogen atoms, localised between atoms B(3) and B(8), and between B(6) and B(7). Additionally, there are two triplets of equal intensity in the ^{13}C NMR spectrum of **4a** (see notes to Table II), confirming the presence of two different {CH_2} groups. The ^{11}B shielding properties of compounds **4a** and **4b** (upper two traces in Fig. 1, bottom part) show the close NMR similarities that are expected between these two isostructural compounds. The lower diagram in Fig. 1, by contrast, reflects the completely different structural features between the ligand derivatives of *hypho* type **4** and *arachno* type **3**. The cluster structure adopted by the new compounds **4**, of general structure *II*, is formally derived by the removal of three adjacent vertices from the twelve-vertex structure as in Scheme 2. It constitutes a new type of nine-vertex *hypho* cage system which is isomeric to that adopted by the previously reported compounds $S_2CB_6H_{10}$ and $S_2B_7H_{11}$ (ref.[20]).

The ^{11}B and ^{1}H chemical shift data, along with the observed [^{11}B-^{11}B]-COSY and [^{1}H-^{1}H]-COSY interactions, for the *hypho* eight-vertex anion **5** (see Table III and Fig. 2) are in agreement with the proposed symmetrical structure **5**. All cross-peaks expected among the resonances of the individual *exo*-BH units for structure **5** are observed, except for the [^{1}H-^{1}H]-COSY correlation between the resonances assigned to the {BH(2,5)} and {BH(3,4)} vertices. The [^{1}H-^{1}H]-COSY spectrum also confirms unam-

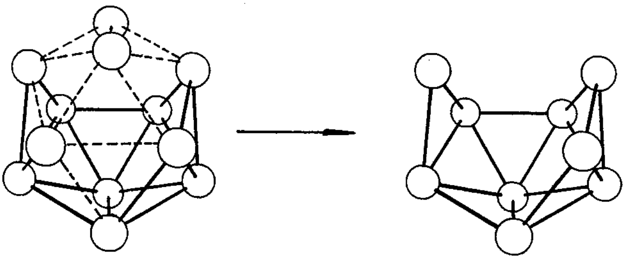
TABLE III

NMR parameters for [*hypho*-7,8-$C_2B_6H_{13}$]$^-$ [NMe_4]$^+$ (**5**) in CD_3CN solution at 294 – 297 K

Assignment[a]	δ(^{11}B)[a]	^{1}J(^{11}B-^{1}H)	δ(^{1}H)[b,c]
BH(2,5)	–5.6	125	2.40
BH(6)	–30.8	145	1.12
BH(3,4)	–33.0[d]	122/54	0.59
BH(1)	–55.0	125	–1.22
CH(7,8)	–	–	–0.43[e,f]
			–2.46[g]
μH(3,4) = μ_1	–	–	–1.87
μH(2,6/5,6) = μ_2	–	–	–2.69

[a] Assignment on the basis of [^{11}B-^{11}B]-COSY experiments under conditions of complete {^{1}H(broadband noise)} decoupling; observed cross-peaks: 1-2,5 s, 1-3,4 s, 1-6 s, 2,5-6 m, 3,4-2,5 w; s = stronger, m = intermediate, w = weaker. [b] Assignments by ^{1}H-{^{11}B(selective)} measurements. [c] [^{1}H-^{1}H]-COSY spectra measured under conditions of complete {^{11}B(broadband)} decoupling; observed cross-peaks: 1-2,5 m, 1-3,4 s, 1-6 s, 1-μ2w, 1-*endo*-7, 8 s, 2,5-6 w, 2,5-*exo*-7,8 s, 2,5-*endo*-7,8 m, 3,4-μ1 s, 3,4-*endo*-7,8 s, 6-μ2 s, *exo*-7,8-*endo*-7,8 s, *endo*-7,8-μ1 s, *endo*-7,8-μ2 s. [d] Doublet of quartets. [e] Quartet structure. [f] *exo*-Hydrogen. [g] *endo*-Hydrogen.

biguously the attachment of the two identical $\{C(7)H_2\}$ and $\{C(8)H_2\}$ units to the hexaboron core in structure **5**. Figure 2 (bottom diagrams) compares the ^{11}B shielding patterns of anion **5** with the corresponding parameters for the isostructural eight-vertex *hypho* species $[7,8\text{-}CSB_6H_{11}]^-$ (**6**) (ref.[21]) and $[S_2B_6H_9]^-$ (**7**) (ref.[20]) and illustrates a trend for the downfield shift of all resonances by successive replacement of the $\{CH_2\}$ units in **5** by the isolobal[28,29] {S} cluster unit.



SCHEME 2

The upper diagrams in Figs 1 and 2 reveal an approximately linear correlation between the ^{11}B and ^{1}H chemical shifts for the *exo*-{BH} units in compounds **2**, **3**, **4**, and **5**, with some data points for the *endo*-{BH} vertices beyond the general correlation line as is more generally observed (see, for example, refs[24,25]). The lines drawn have slopes ca 1 : 16 (for *arachno* nine-vertex **2** and **3** and for *hypho* nine-vertex **4**), and 1 : 13 (for *hypho* eight-vertex **5**) with intercepts +2.9, and +3.1 in $\delta(^1H)$, respectively.

CONCLUSION

The addition of two-electron donor molecules to the "electro-deficient" clusters is a classical reaction of polyhedral boron-containing compounds. Although *arachno*-4,5-$C_2B_7H_{13}$ has been known for many years[1,4–6,11,12], suprisingly it has not been investigated for this behaviour. The work reported now establishes conditions for such additions to $C_2B_7H_{13}$, which, depending on the two-electron donor, are (*a*) accompanied by dihydrogen loss to give previously unreported *arachno*-$C_2B_7H_{11}$. L species, or (*b*) dihydrogen is retained to give the nine-vertex *hypho*-$C_2B_7H_{13}$. L species, also previously unreported. Under more severe conditions (*c*) cluster dismantling occurs to give the interesting and sparsely investigated eight-vertex *hypho* species $[C_2B_6H_{13}]^-$. These reaction products have a number of novel features that we are currently developing further. For example, intermediate and higher boranes and heteroboranes in the *hypho* category are rare. Aspects of our ongoing work are directed at the application of these procedures with other two-electron donors, at the investigation of analogous conditions for *arachno* → *hypho* cluster opening in the intermediate and higher borane and heteroborane systems, and at exploiting the reasonable yields to utilize these new species as starting substrates for further chemistry, for example metalladicarbaborane formation.

EXPERIMENTAL

General

Unless otherwise stated, all reactions were carried out under dry nitrogen, though some operations, such as column chromatography on **2**, **3**, and **4**, were performed in air. Dichloromethane and hexane were distilled from calcium hydride prior to use. Other substances and solvents were of reagent grade used and were used as purchased. Analytical thin-layer chromatography (TLC) was performed using Silufol sheets (Kavalier, The Czech Republic, silica gel on Al foil, detection by I_2 vapour, followed by 2% aqueous $AgNO_3$ spray). Column chromatography was effected using silica gel of standard quality (L 100/400, Lachema, The Czech Republic). The starting *arachno*-4,5-$C_2B_7H_{13}$ dicarbaborane (**1**) was made by the literature method[4].

Physical Measurements

Melting points were determined on a Kofler-type apparatus and are uncorrected. NMR spectroscopy was performed as described in other recent papers from our laboratories[30,31], with chemical shifts δ being given in ppm to high frequency (low field) of Ξ 32.083971 MHz (nominally F_3B . OEt_2) for ^{11}B (quoted ±0.5 ppm) and Ξ 100 MHz ($SiMe_4$) for ^1H (quoted ±0.05 ppm), Ξ being defined as in ref.[32]. Coupling constants $^1J(^{11}B\text{-}^1H)$ are given in Hz ± 8. Mass spectra were recorded on the 70 eV electron-impact mode, using a ion trap benchtop GC/MS system (Magnum, Finnigan MAT, U.S.A.) supplied with “heated unlet” option (Spectronex Basel, Switzerland) and on a V.G. Autospec instrument.

[*arachno*-4,5-$C_2B_7H_{12}$]$^-$ [NMe_4]$^+$ (**2**)

A solution of carborane **1** (500 mg; 5 mmol) in hexane (20 cm^3) was shaken for 10 min with a mixture of 5% aqueous sodium carbonate (20 cm^3) and tetramethylammonium chloride (550 mg; 5 mmol). The white precipitate thus formed was filtered off, washed with water (20 cm^3) and benzene (20 cm^3) and dried in vacuo to a constant weight to give 856 mg (92%) of a white salt which was identified as [*arachno*-4,5-$C_2B_7H_{12}$]$^-$ [NMe_4]$^+$ (**2**) by NMR spectroscopy as described above. The anion **2** can also be generated in situ by adding an approximately twofold molar equivalent of proton sponge to a solution of the dicarbaborane **1** in an NMR tube: it is identified by NMR spectroscopy after approximately 10 min.

exo-6-(MeNC)-*arachno*-4,5-$C_2B_7H_{11}$ (**3**)

Methyl isocyanide (500 mg; 12.1 mmol) was added to a solution of the dicarbaborane **1** (350 mg; 3.25 mmol) in dichloromethane (10 cm^3) and the mixture was left to stand for 24 h at ambient temperature (dihydrogen evolution). The mixture was then reduced in volume to ca 10 cm^3 and transferred onto a silica gel column (30 × 2.5 cm). Elution with a mixture of dichloromethane and hexane (1 : 1, v/v) developed the main fraction of R_F 0.15 (CH_2Cl_2–hexane 1 : 1), which was evaporated to dryness. The residue was crystallized from a concentrated dichloromethane solution that was overlayered by a twofold amount of hexane, to give white crystals [100 mg; 20%; m.p. ca 120 °C (decomp.)]. These were identified as *exo*-6-(MeNC)-*arachno*-4,5-$C_2B_7H_{11}$ (**3**) by NMR spectroscopy as described above, and by mass spectrometry: *m/z* 153; for $^{12}C_4{}^1H_{14}{}^{11}B_7{}^{14}N^+$ calculated: 153; the most significant fragmentation envelopes had *m/z* 112 ($^{12}C_2{}^{11}B_7{}^1H_{11}{}^+$), *m/z* 55 ($^{12}C_2{}^1H_6{}^{11}B^{14}N^+$), and *m/z* 41 $^{12}C_2{}^1H_3{}^{14}N^+$).

exo-5-(NMe_3)-*hypho*-4,9-$C_2B_7H_{13}$ (**4a**)

A solution of dicarbaborane **1** (400 mg; 3.5 mmol) in dichloromethane (30 cm^3) was added to a 10% solution of trimethylamine in dichloromethane (5 cm^3), and the mixture was stirred for 24 h at ambient temperature. The dichloromethane was then removed by evaporation and the crude residue separated by column chromatography (silica gel, 2 × 25 cm), using benzene as the liquid phase. The major fraction (R_F 0.38, CH_2Cl_2) was evaporated to give crude **4a** (250 mg; 41%) as a white solid. An analytical sample was recrystallized from a concentrated dichloromethane solution that was overlayered by a twofold amount of hexane and identified by NMR spectroscopy (see Table II) and mass spectrometry: *m/z* 173; for $^{12}C_5{}^1H_{22}{}^{11}B_7{}^{14}N^+$ calculated: 173; significant fragmentation envelopes at *m/z* 110 ($^{12}C_2{}^1H_9{}^{11}B_7{}^+$), *m/z* 72 ($^{12}C_3{}^1H_{12}{}^{11}B^{14}N^+$), and *m/z* 59 ($^{12}C_3{}^1H_9{}^{14}N^+$).

exo-5-(NEt_3)-*hypho*-4,9-$C_2B_7H_{13}$ (**4b**)

Triethylamine (0.5 cm^3; 3.61 mmol) was added to a solution of dicarbaborane **1** (400 mg; 3.50 mmol) in dichloromethane (20 cm^3) and the mixture was left to stand for 2 days at ambient temperature. The mixture was then reduced in volume to ca 10 cm^3 and transferred onto a silica gel column (ca 30 × 2.5 cm). Elution with dichloromethane developed the main fraction of R_F 0.53, which was evaporated to dryness and crystallized from a concentrated dichloromethane solution that was overlayered by a twofold amount of hexane, to give white crystals [412 mg; 55%; m.p. ca 107 °C (decomp.)]. These were identified as *exo*-5-(NEt_3)-*hypho*-4,9-$C_2B_7H_{13}$ (**4b**) by NMR spectroscopy as described above and by mass spectrometry: *m/z* 215; for $^{12}C_8{}^1H_{28}{}^{11}B_7{}^{14}N^+$ calculated: 215; significant fragmentation envelopes at *m/z* 115 ($^{12}C_6{}^1H_{18}{}^{11}B^{14}N^+$), *m/z* 110 ($^{12}C_2{}^1H_9{}^{11}B_7{}^+$), and *m/z* 101 ($^{12}C_6{}^1H_{15}{}^4N^+$)].

[*hypho*-7,8-$C_2B_6H_{13}$]$^-$ [NMe_4]$^+$ (**5**)

A solution of dicarbaborane **1** (1.2 g; 10.6 mmol) in hexane (60 cm^3) was stirred with a solution of sodium cyanide (2.5 g; 51 mmol) in water (60 cm^3) and the mixture was left to stand for 2 h at ambient temperature (dihydrogen evolution). The hexane layer was separated off and precipitation induced from the aqueous solution by the addition of aqueous 1 M Me_4NCl (15 cm^3). The resulting white precipitate was filtered using a Schlenk-type apparatus, washed with water (ca 30 cm^3), dried in vacuo, and recrystallised from a minimum amount of an acetone–ethanol mixture (1 : 1, v/v) to obtain a white microcrystalline salt (0.9 g; 61%), identified as [*hypho*-7,8-$C_2B_6H_{13}$]$^-$ [NMe_4]$^+$ (**5**) by NMR spectroscopy as described above. The product is stable under dry nitrogen for several months, but spontaneously ignites when exposed to air.

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