Polyhedral Carbathiaborane Chemistry. Ten-vertex *nido* and *arachno*, Eleven-vertex *nido*, and Eight-vertex *hypho* Families of Carbathiaboranes

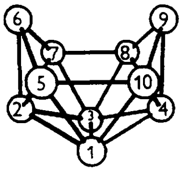
Josef Holub,[a] John D. Kennedy,*[,b] Tomáš Jelínek[a] and Bohumil Štíbr*[,a]
[a] *Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, 250 68 Řež, The Czech Republic*
[b] *School of Chemistry, University of Leeds, Leeds LS2 9JT, UK*

Treatment of *arachno*-4-CB_8H_{14} with sulfur and triethylamine in chloroform has produced the new ten-vertex carbathiaborane *arachno*-6,9-CSB_8H_{12}, which has been used for the preparation of a series of further carbathiaborane compounds. Deprotonation with sodium hydride or 1,8-bis(dimethylamino)-naphthalene generates the [*arachno*-6,9-$CSB_8H_{11}]^-$ anion. Thermolysis of the sodium salt of this anion, followed by acidification, results in comproportionation to give *nido*-7,9-CSB_9H_{11} and *arachno*-4,6-CSB_7H_{11}. Alternatively, oxidation by acetone yields the [*nido*-6,9-$CSB_8H_9]^-$ anion. Degradation of this latter anion with concentrated hydrochloric acid leads to *arachno*-4,6-CSB_7H_{11}. Deprotonation of this neutral carbathiaborane with sodium hydride in ether, followed by degradation by aqueous acetone of the [*arachno*-4,6-$CSB_7H_{10}]^-$ anion generated *in situ*, gives the [*hypho*-7,8-$CSB_6H_{11}]^-$ anion. This has been methylated by methyl iodide to afford neutral 8-Me-*hypho*-7,8-CSB_6H_{11}. The unambiguous cluster constitutions of all compounds isolated have been established by ^1H and ^{11}B NMR spectroscopy and mass spectrometry.

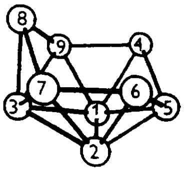
Mixed diheteroboranes have not been well examined. For example, carbathiaboranes, *i.e.* compounds containing heteroatomic {CH} and {S} vertices in the contiguous borane cluster moiety, have so far been only scarcely reported, and only nine-vertex *arachno*-4,6-CSB_7H_{11},[1] ten-vertex *arachno*-6,9-CSB_8H_{12},[2] and eleven-vertex 7-(NMe_3)-*nido*-7,8-CSB_9H_9[3] have been isolated and unequivocally characterized. Of these, we reported the preparation of the former two 'parent' (*i.e.* unsubstituted) model compounds,[1,2] and as a continuation of this work we now submit a full account of reactions from which the first examples of parent *arachno* and *nido* ten-vertex, *nido* eleven-vertex, and *hypho* eight-vertex carbathiaboranes have been isolated. The general structures and the numbering systems for the ten-vertex *nido* and *arachno*, nine-vertex *arachno*, eight-vertex *hypho*, and eleven-vertex *nido* compounds described in this paper are shown in structures **I**, **II**, **III** and **IV**, respectively. Note that transfers among cluster types will generally change the formal numbering of a particular atom, and also that, because of the IUPAC heteroatom hierarchy, in mixed heteroatom chemistry numbering changes can occur for the same structure type as a heteroatom is changed; also a cluster change can result in the enantiomer of the IUPAC-recommended numbering. Reference to Scheme 1 should minimize any confusion arising from this.

Results and Discussion

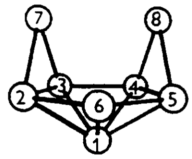
Syntheses.—In the optimization of a siting reaction outlined in a preliminary communication,[2] we have found that the reaction between nine-vertex *arachno*-4-CB_8H_{14} (compound **1** in Scheme 1) and elemental sulfur in chloroform in the presence of triethylamine (ambient temperature, 24 h) gives the ten-vertex carbathiaborane *arachno*-6,9-CSB_8H_{12} [compound **2**, path (*i*) in Scheme 1] as the main product in 48% yield. From the mechanistic viewpoint, this reaction seems to be in agreement with a straightforward insertion of the {S} vertex into the area identified by the B(6), B(7) and B(8) atoms in compound **1**.



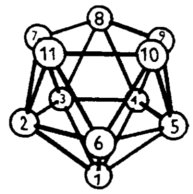
I



II



III



IV

We have found that compound **2** is a useful starting material for the preparation of those families of new thiacarbaborane compounds, outlined schematically in Scheme 1. Thus, deprotonation of **2** by proton sponge [1,8-$(Me_2N)_2C_{10}H_6$] in CD_3CN solution in an NMR tube leads to the *in situ* formation of the [*arachno*-6,9-$CSB_8H_{11}]^-$ anion [compound **3**, path (*ii*) in Scheme 1]. The same product is obtained as the $[PPh_4]^+$ salt by the deprotonation of **2** by sodium hydride in ether, followed by precipitation with aqueous $[PPh_4]Cl$. NMR spectroscopy (below) shows that the deprotonation entails the removal of a bridging proton [nominally H(7,8)] from structure **2**.

An interesting compound is generated from the *arachno* anion **3** ($[PPh_4]^+$ salt) by treatment with acetone at room temperature for 24 h, followed by chromatographic purification of the resulting product on silica gel using dichloromethane as liquid phase. The main product of the reaction was identified by

NMR spectroscopy as the $[PPh_4]^+$ salt of [*nido*-6,9-$CSB_8H_9]^-$ [compound **4**, path (*iii*) in Scheme 1]. This results from the oxidation of the *arachno* anion **3** by acetone (room temperature, yield 38%) with a presumed stoichiometry as in equation (1).

$$[CSB_8H_{11}]^- + Me_2CO \longrightarrow [CSB_8H_9]^- + Me_2CHOH \quad (1)$$

This reaction represents a second example of a straightforward *arachno* to *nido* transformation in ten-vertex boron cluster compounds that is effected by acetone. The only other reported case, as far as we are aware, is the high-yield formation of 8-(NMe_3)-9-Me-*nido*-6-CB_9H_{10} from 8-(NMe_3)-9-Me-*arachno*-6-CB_9H_{12} in the monocarbadecaborane system.[4]

Another carbaborane analogy, now to the ten-vertex *nido* two-carbon system, is the one-boron degradation reaction of the *nido* anion **4** with concentrated hydrochloric acid. This results in the formation of the previously reported[1] nine-vertex carbathiaborane *arachno*-4,6-CSB_7H_{11} [compound **5**, path (*iv*) in Scheme 1] in 55% yield. The reaction [presumed stoichiometry as in equation (2)] is not inconsistent with a

$$[CSB_8H_9]^- + H_3O^+ + 2H_2O \longrightarrow CSB_7H_{11} + B(OH)_3 + H_2 \quad (2)$$

hydrolytic elimination of the {B(10)} vertex (adjacent to sulfur) from compound **4**, Scheme 1, with S(9) moving to fill the space, with a concomitant cleavage of the S(9)–B(8) connectivity (numbering as in **4**). Alternatively C(6) moves analogously at the other end of the molecule. This process is mechanistically analogous to the degradation by hydrochloric acid of the isostructural dicarbaborane analogue of **4**, the [*nido*-6,9-$C_2B_8H_{10}]^{2-}$ dianion, giving *arachno*-4,6-$C_2B_7H_{13}$.[5]

This cluster dismantling process can be continued: thus deprotonation of the nine-vertex carbathiaborane **5** by sodium hydride in ether yields the sodium salt. Evaporation of the ether and reaction *in situ* with aqueous acetone under reflux for 5 h, followed by addition of aqueous $[PPh_4]Cl$, then leads to the isolation of the [*hypho*-7,8-$CSB_6H_{11}]^-$ anion [compound **6**, path (*v*) in Scheme 1] in 65% yield as the $[PPh_4]^+$ salt, as outlined in equation (3). The reaction stoichiometry of this

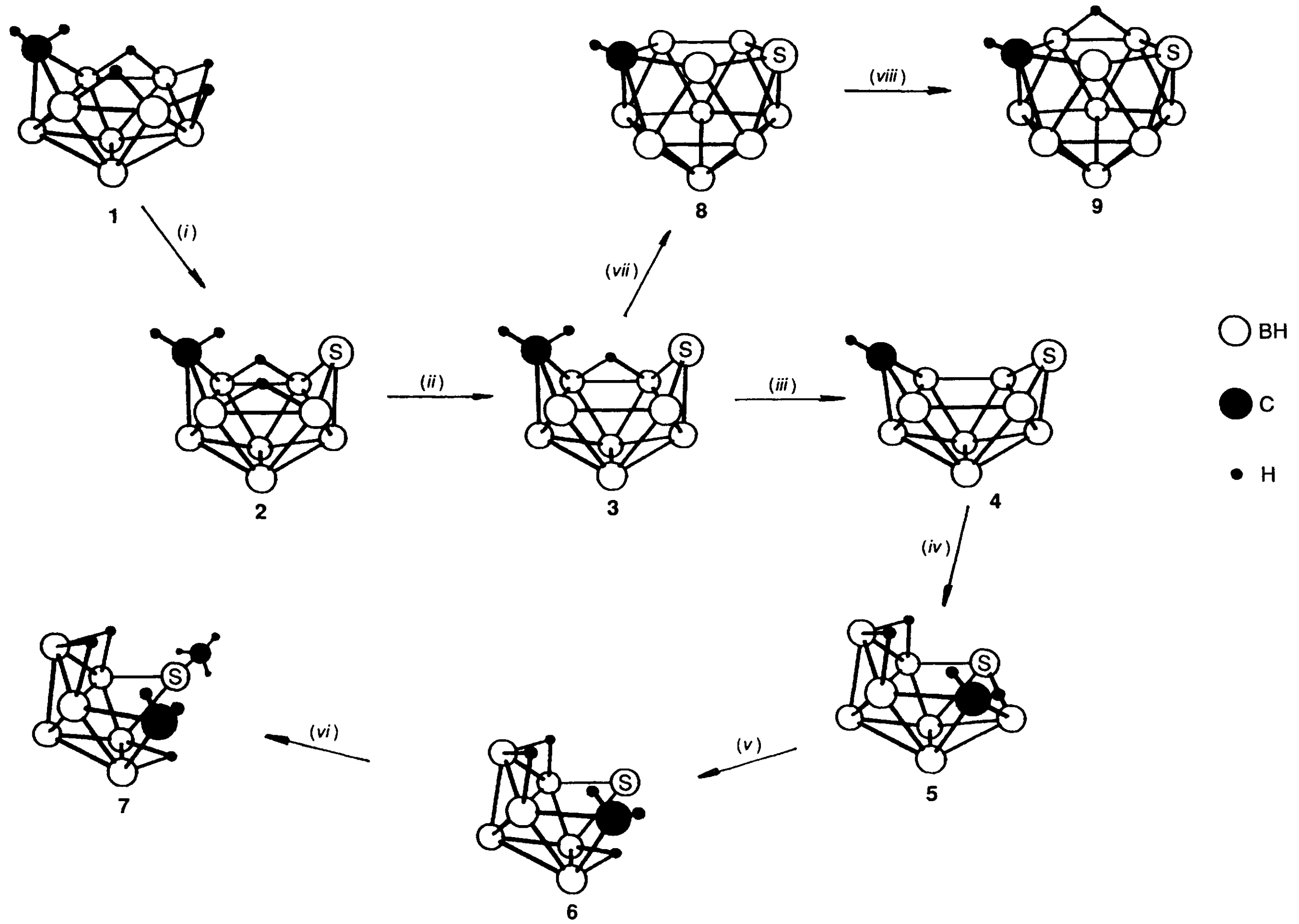
$$[CSB_7H_{10}]^- + Me_2CO + 3H_2O \longrightarrow [CSB_6H_{11}]^- + Me_2CHOH + B(OH)_3 \quad (3)$$

equation is consistent with an acetone-induced degradation of the {B(5)} vertex in compound **5** and this entirely parallels the previously reported[6] reaction between *arachno*-4,6-$S_2B_7H_9$[1] (an isostructural analogue of **5**) and acetone to give the dithia analogue of **6**, the [*hypho*-$S_2B_6H_9]^-$ anion.

The reaction between the *hypho* anion **6** and methyl iodide in thf (thf = tetrahydrofuran) at ambient temperature results in the methylation of the sulfur atom to obtain the neutral compound 8-Me-*hypho*-7,8-CSB_6H_{11} [compound **7**, path (*vi*) in Scheme 1] in 75% yield, equation (4). This reaction also has

$$[CSB_6H_{11}]^- + MeI \longrightarrow MeCSB_6H_{11} + I^- \quad (4)$$

similarities to previous[6] dithiaborane work, being analogous to the reported methylation of the [*hypho*-$S_2B_6H_9]^-$ anion.



Scheme 1 (*i*) NEt_3–S–$CHCl_3$, 24 h, room temperature (r.t.); (*ii*) 1,8-$(Me_2N)_2C_{10}H_6$–CD_3CN, 15 min, r.t. or NaH–Et_2O, 1 h, r.t.; (*iii*) Me_2CO–$CHCl_3$, 24 h, r.t.; (*iv*) concentrated HCl–hexane, 30 min, r.t.; (*v*) NaH–Et_2O, Me_2CO–H_2O, 5 h, reflux; (*vi*) MeI–thf, 2 h, r.t.; (*vii*) 30 min, 120–200 °C; (*viii*) CF_3CO_2H–CH_2Cl_2

Another interesting reaction in this series of compounds is the thermal decomposition of the *arachno* anion **3**, of which a main reaction path seems to be a comproportionation into a mixture of the eleven-vertex carbathiaborane anion [*nido*-7,9-CSB_9H_{10}] [compound **8**, path (*vii*) in Scheme 1] and the nine-vertex anion [*arachno*-4,6-$CSB_7H_{10}]^-$ as in stoichiometric equation (5). Owing to the difficulties in the separation, the

$$2[CSB_8H_{11}] \longrightarrow [CSB_9H_{10}]^- + [CSB_7H_{10}]^- + H_2 \quad (5)$$

anionic mixture arising from reaction (5) was not resolved into its components. However, acidification by trifluoroacetic acid in the presence of dichloromethane generates a mixture of the two corresponding neutral carbathiaboranes *nido*-7,9-CSB_9H_{11} [compound **9**, path (*viii*) in Scheme 1] and *arachno*-4,6-CSB_7H_{11} **5**, which can be separated by preparative thin layer chromatography (TLC) on silica, using hexane as the liquid phase, to isolate compounds **9** and **5** in yields 63% and 17%, respectively. The monitoring by NMR of the *in situ* reaction between compound **9** and proton sponge in $CDCl_3$ reveals the unambiguous formation of the pure anion **8** *via* proton abstraction of the bridging H(10, 11) atom in compound **9**. An alternative approach to the synthesis of anion **8** in the form of the $[PPh_4]^+$ salt is the deprotonation of **9** by sodium hydride in ether [the reverse of path (*viii*) in Scheme 1], followed by the precipitation from aqueous solution of the sodium salt by $[PPh_4]Cl$.

NMR Spectroscopy and Structural Considerations.—All compounds were identified by NMR spectroscopy allied with mass spectrometry to confirm the molecular formulae. Boron-11 and ^1H NMR spectroscopy, making use of [^{11}B–^{11}B]-correlation spectroscopy (COSY)[7] and [^1H–^1H]-COSY[8] and ^1H-{^{11}B(selective)}[9] techniques, resulted in the assignment of all the ^{11}B and ^1H resonances to their individual cluster positions for all compounds **2**–**9**. A comparison of cluster shielding patterns with those of the structurally related carbaborane or non-mixed heteroborane analogues is therefore possible.

Measured NMR data for the ten-vertex *arachno* carbathiaboranes 6,9-CSB_8H_{12} **2** and [6,9-$CSB_8H_{11}]^-$ **3** are in Table 1. The chemical shifts are as summarized in preliminary notes[2,10,11] and will be discussed more thoroughly elsewhere in the context of the whole family of *arachno* 6,9-diheterodecaboranes $EE'B_8H_{10}$, where E and E' are variously from the series of isolobal[12] units $\{BH_2\}^-$, $\{CH_2\}$, $\{NH\}$, $\{S\}$, *etc.* The most interesting aspect, common to other carbathiaboranes, is that there are general and specific ^{11}B deshieldings associated with the incorporation of $\{S\}$ units in the cluster instead of $\{CH_2\}$.

Of interest are also the changes upon deprotonation of **2** to give the anionic diheteroborane **3**. As seen from Fig. 1 (bottom diagram), removal of one bridging proton [taken for this discussion as H(7,8) rather than H(5,10)] from compound **2** in the formation of the asymmetric [*arachno*-6,9-$CSB_8H_{11}]^-$ anion **3** brings about a marked shielding increase for all ^{11}B nuclei except for the B(3) atom. The most marked shielding changes (+15 to +17 ppm) are for the B(2), B(4), and B(1) positions. By contrast, the B(3) site is deshielded by *ca.* 7 ppm when compared to the neutral compound **2**; this however is in accord with the loss of the β-positioned neighbouring B(7)–H–B(8) bridging proton, according to general cluster shielding patterns, as summarized, for example, in ref. 13.

Measured ^{11}B and ^1H NMR parameters of the ten-vertex [*nido*-6,9-$CSB_8H_9]^-$ anion **4** are in Table 2, and Fig. 2 (bottom part) compares ^{11}B shielding properties of this anion with those of the only known isostructural analogue of **4**, the dianion [*nido*-6,9-$C_2B_8H_{10}]^{2-}$ (refs. 5 and 15). Both compounds are unique in the ten-vertex main-group heteroborane *nido* system in that they do not have bridging hydrogen atoms. The comparison shows that the overall character of the spectrum has been preserved by notional replacement of one {CH} cluster unit by the isolobal[12] {S} vertex in the dicarbaborane dianion. The most marked feature is again a strong downfield shift (−18 to −20 ppm) of the resonances of the $^{11}B(8,10)$ and $^{11}B(2)$ nuclei which are adjacent and antipodal[13] to the S(9) atom, respectively. Similar adjacent/antipodal effects are seen in the corresponding *arachno* systems discussed elsewhere.[2,16]

Measured ^{11}B and ^1H NMR parameters of the eight-vertex [*hypho*-7,8-$CSB_6H_{11}]^-$ anion **6** and of its neutral S-*exo*-methyl derivative 8-Me-*hypho*-7,8-CSB_6H_{11} **7** are in Table 3. Fig. 3 (bottom part) compares ^{11}B shielding properties of this anion

Table 1 Assigned ^{11}B and ^1H NMR parameters for *arachno*-6,9-CSB_8H_{12} **2** in $CDCl_3$ and [*arachno*-6,9-$CSB_8H_{11}]^-$ **3** in CD_3CN at 294–297 K

Compound **2**						Compound **3**				
Assignment[a]	δ(^{11}B)	J(^{11}B–^1H)/Hz	Observed [^{11}B–^{11}B]-COSY correlations[b]	δ(^1H)[c]	Observed [^1H–^1H]-COSY correlations[d]	Assignment[a]	δ(^{11}B)	J(^{11}B–^1H)/Hz	Observed [^{11}B–^{11}B]-COSY correlations[b]	δ(^1H)[c]
2	+10.7	162	1,3s 5,7s	+3.30	1,3s 5,7s *exo*6s *endo*6s	2	−3.3	137	1s 3s 5m 7m	+2.38
4	+6.1	177	1,3s 8,10s	+3.37	1,3s 8,10w	4	−10.0	158	1s 3s	+2.48
8,10	−12.6	156/47	1,3s 4s	+2.56	1,3s 4w,	8	−18.7[e]	*ca.* 131/64[e]	3s 7m	+1.38[f]
					μ-5,10; 7,8	10	−16.0	144	1s 5m	+2.56
5,7	−21.6	155/56	1,3s 2s	+1.99	1,3s 2w	5	−24.5	138/46	1s 2m 10m	+1.72
					μ-5,10; 7,8	7	−18.7[e]	*ca.* 131/64[e]	2m 3s 8m	+1.44[f]
1,3	−34.1	151	2s 4s 5,7s 8,10s	+1.29	2s 4s 5,7s	1	−51.2	141	2s 3s 4s 5s 10s	
					8,10s μ-5,10; 7,8s	3	−26.7	137	1s 2s 4s 7s 8s	+1.29
6	[CH]	—	—	+1.11 (*exo*)	2s *endo*6s	6	[CH]	—	—	−0.07 (*exo*)
		—	—	+0.26 (*endo*)	2s *exo*6s μ-5,10; 7,8s			—	—	−0.44 (*endo*)
μ-5,10; 7,8	—	—	—	−1.14	5,7s 8,10s *endo*6s	μ-5,10	—	—	—	−1.03

[a] Assignment by [^{11}B–^{11}B]-COSY and [^1H–^1H]-COSY experiments. [b] Measured with {^1H(broadband)} decoupling; s = strong, m = medium, w = weak. [c] Assignment by ^1H-{^{11}B(selective)} experiments. [d] Measured with ^1H-{^{11}B(broadband)} decoupling. [e] Coincidental signals overlap. [f] Experiments do not distinguish between H(7) and H(8) assignments.

Table 2 Assigned ^{11}B and ^{1}H NMR parameters for the $[PPh_4]^+$ salt of [*nido*-6,9-CSB_8H_9]$^-$ **4** in $CDCl_3$ at 294–297 K

Assignment[a]	$\delta(^{11}B)$	$J(^{11}B-^{1}H)$/ Hz	Observed $[^{11}B-^{11}B]$-COSY correlations[b]	$\delta(^{1}H)$[c]
8, 10	+13.2	149	1, 3s 5, 7s	+3.51
1, 3	−1.9	136	2s 4s 5, 7s 8, 10s	+2.62
5, 7	−3.6	132	1, 3s 2s	+2.71
2	−11.1	147	1, 3s 5, 7s	+1.48
4	−32.7	166	1, 3s 8, 10w	+0.52
6	[CH]	—	—	+6.66

[a] Assignment by $[^{11}B-^{11}B]$-COSY experiments. [b] Measured with $\{^{1}H$(broadband)$\}$ decoupling; s = strong, w = weak. [c] Assignment by $^{1}H-\{^{11}B$(selective)$\}$ experiments.

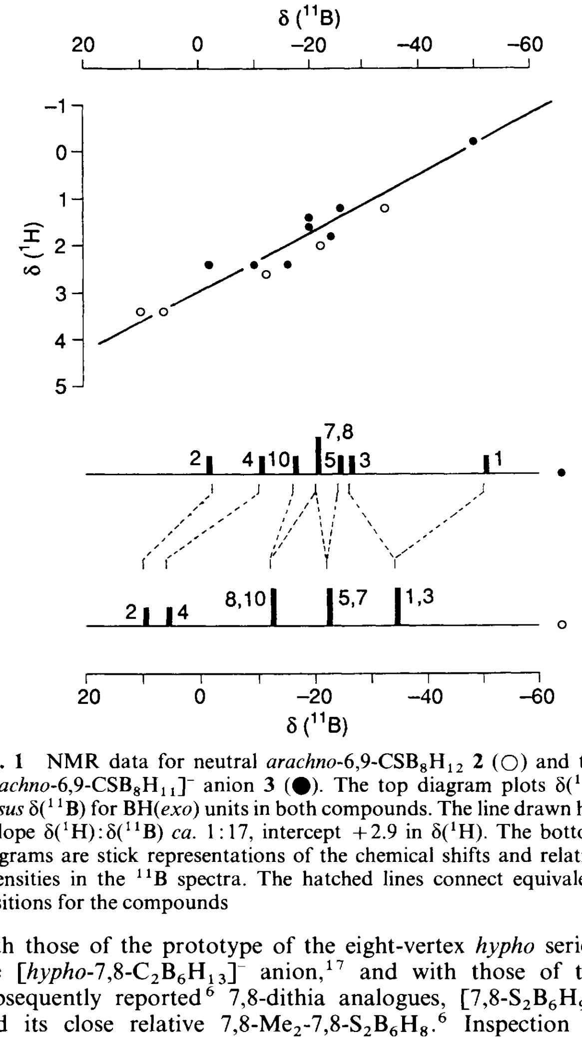


Fig. 1 NMR data for neutral *arachno*-6,9-CSB_8H_{12} **2** (○) and the [*arachno*-6,9-CSB_8H_{11}]$^-$ anion **3** (●). The top diagram plots $\delta(^{1}H)$ *versus* $\delta(^{11}B)$ for BH(*exo*) units in both compounds. The line drawn has a slope $\delta(^{1}H):\delta(^{11}B)$ *ca.* 1:17, intercept +2.9 in $\delta(^{1}H)$. The bottom diagrams are stick representations of the chemical shifts and relative intensities in the ^{11}B spectra. The hatched lines connect equivalent positions for the compounds

with those of the prototype of the eight-vertex *hypho* series, the [*hypho*-7,8-$C_2B_6H_{13}$]$^-$ anion,[17] and with those of the subsequently reported[6] 7,8-dithia analogues, [7,8-$S_2B_6H_9$]$^-$ and its close relative 7,8-Me_2-7,8-$S_2B_6H_8$.[6] Inspection of Fig. 3 readily reveals that, compared to the dicarbaborane [$C_2B_6H_{13}$]$^-$, there is a general trend for deshielding of all boron positions, and that this deshielding is most marked for the boron positions adjacent to the sulfur centre. Taking individual shifts of comparable positions into account, the increments Δδ [where $\Delta\delta = \delta(E^1 = E^2 = CH_2) - \delta(E^1 = CH_2; E^2 = S)$ and $\delta(E^1 = CH_2) - \delta(E^1 = E^2 = S)$] are essentially of additive character on going through the anionic [*hypho*-7,8-$E^1E^2B_6H_9$]$^-$ series from [$C_2B_6H_{13}$]$^-$ to [$S_2B_6H_9$]$^-$ by the sequential replacement of $\{CH_2\}$ vertices by {S}. As also seen from Fig. 3, the corresponding ^{11}B patterns for the methylated species **7** and the dimethylated compound 7,8-Me_2-7,8-$S_2B_6H_8$ are also very similar, although the last compound, although isoelectronic, is not isostructural with the others because it has one fewer bridging-hydrogen atom.[6]

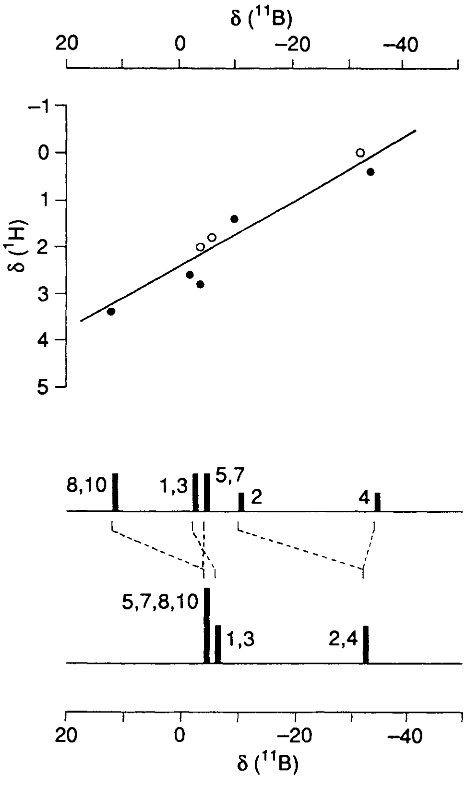


Fig. 2 NMR data for [*nido*-6,9-CSB_8H_9]$^-$ **4** (●) together with those for the isostructural [*nido*-6,9-$C_2B_8H_{10}$]$^{2-}$ anion (○) (data from ref. 14) for comparison. The top diagram plots $\delta(^{1}H)$ *versus* $\delta(^{11}B)$ for BH(*exo*) units for the two compounds. The line drawn has a slope $\delta(^{1}H):\delta(^{11}B)$ *ca.* 1:19, intercept +2.6 in $\delta(^{1}H)$. The bottom diagrams are stick representations of the chemical shifts and relative intensities in the ^{11}B spectra of these compounds. The hatched lines connect equivalent positions in the compounds

Measured ^{11}B and ^{1}H NMR parameters of the eleven-vertex [*nido*-7,9-CSB_9H_{10}]$^-$ anion **8** and of its protonation product, the neutral species *nido*-7,9-CSB_9H_{11} **9**, are in Table 4. Graphical intercomparisons of the ^{11}B shielding parameters of these compounds, together with those for the isoelectronic parent dicarbaborane analogue, the [7,9-$C_2B_9H_{12}$]$^-$ anion[15,18] are in Fig. 4. Inspection of Fig. 4 (bottom part) reveals close ^{11}B shielding parallels between this symmetric dicarbaborane anion and its isostructural and isoelectronic asymmetric carbathiaborane analogue *nido*-7,9-CSB_9H_{11} **9**. As in the other cluster types discussed in this paper, the presence of the S(9) atom induces a significant downfield shift of the whole spectrum, this effect once more being most pronounced for positions adjacent to the sulfur atom. As also seen from the same figure, bridge deprotonation of **9** to form the anion **8** induces significant ^{11}B shielding at all boron positions, except for $^{11}B(6)$ which is by contrast strongly deshielded in comparison with compound **9**, in agreement with previously recognized cluster constituent nuclear shielding tendency patterns.[13]

Experimental

General.—Diethyl ether was distilled from sodium diphenylketyl, dichloromethane and chloroform from P_4O_{10}, and benzene and hexane from calcium hydride, prior to use. Other substances were of analytical or reagent grade and were used as purchased. Analytical thin-layer chromatography (TLC) was performed using Silufol sheets (Kavalier, silica gel on Al foil) (detection by I_2 vapour, followed by 2% aqueous $AgNO_3$ spray). Preparative TLC was carried out using silica gel (Fluka, type GF 254) as the stationary phase on plates of dimensions

Table 3 Assigned ^{11}B and ^{1}H NMR parameters for the $[PPh_4]^+$ salt of [*hypho*-7,8-CSB_6H_{11}]$^-$ **6** and 8-Me-*hypho*-7,8-CSB_6H_{11} **7** in $CDCl_3$ at 294–297 K

	Compound **6**				Compound **7**			
Assignment[a]	δ(^{11}B)	J(^{11}B–^{1}H)/Hz	δ(^{1}H)[b]	Observed [^{1}H–^{1}H]-COSY correlations[c]	δ(^{11}B)	J(^{11}B–^{1}H)/Hz	Observed [^{11}B–^{11}B]-COSY correlations[d]	δ(^{1}H)[b]
5	+2.0	147	+3.45	1w 4? 6s μ-5,6m	−1.3	*ca.* 134[e]	1s 6s	+3.22
2	−3.1	131	+2.45	1w 6s μ-2, 6s *exo*/*endo* 7s	−2.7	—[e]	1s 3s 6s	+2.62
4	−23.9	141[f]	+1.91	1w 5? μ-3,4s	−19.9	156/44[f]	1s 3m	+2.45
6	−29.4	142[g]	+1.41	1? 2s 5s μ-2,6s μ-5,6s	−25.8	155[f]	1s 2s 5s	+2.16
3	−33.2	126/46[h]	+0.57	1w μ-3, 4s *exo*7s *endo*7w	−31.6	136/48[f]	1s 2m 4m	+1.07
1	−54.8	134	−0.81	2w 3w 4w 5w 6?	−59.7	144	2s 3s 4s 5s 6s	−0.80
7	[CH]	—	−0.16 (*exo*)	2s 3s *endo*7s	[CH]	—	—	+0.57 (*exo*)
		—	−1.74 (*endo*)	2s 3w μ-2,6s μ-5,6s *exo*7s		—	—	−2.12[e] (*endo*)
3,4	—	—	−0.67	3s 4s μ-2,6s μ-5,6s	—	—	—	−0.12
2,6	—	—	−1.27	2s 6s μ-3,4s μ-5,6s *exo*/*endo*7s	—	—	—	−1.20
5,6	—	—	−2.51	5m 6s μ-3,4s μ-2,6s *endo*7s	—	—	—	−2.12[e]

[a] Assignment by [^{11}B–^{11}B]-COSY and [^{1}H–^{1}H]-COSY experiments and inter-comparison. [b] Assignment by ^{1}H-{^{11}B(selective)} experiments. [c] Measured with ^{1}H-{^{11}B(broadband)} decoupling; s = strong, m = medium, w = weak. [d] Measured with ^{11}B-{^{1}H(broadband)} decoupling. [e] Coincidental signal overlap. [f] μ-H splitting also present. [g] Additional fine splitting (quartet). [h] Doublet of doublets.

Table 4 Assigned ^{11}B and ^{1}H NMR parameters for [*nido*-7,9-CSB_9H_{10}]$^-$ **8** in CD_3CN and *nido*-7,9-CSB_9H_{11} in $CDCl_3$ at 294–297 K

	Compound **8**				Compound **9**				
Tentative assignment[a]	δ(^{11}B)	J(^{11}B–^{1}H)/Hz	Observed [^{11}B–^{11}B]-COSY correlations[b]	δ(^{1}H)[c]	Assignment[a]	δ(^{11}B)	J(^{11}B–^{1}H)/Hz	Observed [^{11}B–^{11}B-COSY correlations[b]	d(^{1}H)[c]
10	−5.6	—[d]	11s	+1.98	5	+11.4	165	1s 4m 6s 10s	+3.33
5	−8.9	159	1s 6s	+1.78	2	+6.3	177	1m 3w? 6s 11m	+3.28
6	−10.9	135	1m 2w 5m	+1.94	8	−1.5	162	3w 4w	+2.86
2	−13.8	134	1m 6w	+1.45	11	−12.1	156	2m 6s	+2.35
4	−15.0	149	1s 3m	+1.77	4	−13.1	*ca.* 146[e]	1s 3s 5m 8w	+2.34
8	−15.3[f]	149	—	+1.68	10	−14.1	*ca.* 159[e]	5s 6s	+2.04
3	−18.1	*ca.* 170[g]	1m 4m	+1.77	3	−15.3	*ca.* 165[e]	1s 2w? 4s 8w	+2.49
11	−18.1	*ca.* 170[g]	10s	+1.08	1	−27.0	159	2m 3s 4s 5s 6s?	+1.38
1	−42.4	141	2s 3m 4s 5s 6m	+0.66	6	−28.0	162	1s? 2s 5s 10s 11s	+2.05
7	—			+1.40?	7	—	—	—	+2.98
					10, 11	—	—	—	−1.29

[a] Assignment by [^{11}B–^{11}B]-COSY experiments and by the assumption that the ^{11}B shielding for atoms adjacent to S will be less than for those adjacent to C. [b] Measured with ^{11}B-{^{1}H(broadband)} decoupling; s = strong, m = medium, w = weak. [c] Assignment by ^{1}H-{^{11}B(selective)} experiments. [d] Large coupling ^{1}J(^{11}B–^{11}B) 48 Hz. [e] Signal overlap. [f] Very sharp resonance. [g] Value uncertain due to peak overlap.

200 × 200 × 1 mm, made on glass formers from aqueous slurries followed by drying in air at 80 °C.

Physical Measurements.—NMR spectroscopy was performed as described in other recent papers from our laboratories,[15–19] using the general approach as most recently summarized in ref. 20. Chemical shifts (δ) are given in ppm to high frequency (low field) of Ξ 32.083 971 MHz (nominally $BF_3{\cdot}OEt_2$) for ^{11}B (quoted ±0.5 ppm) and Ξ 100 MHz ($SiMe_4$) for ^{1}H (quoted ±0.05 ppm), Ξ being defined as in ref. 21. Coupling constants are given in Hz, ±8 Hz. Mass spectra were recorded in the electron-impact mode (70 eV ionisation) using JEOL HP-5985 equipment.

Preparations.—*arachno*-6,9-CSB_8H_{12} **2**. To a solution of *arachno*-4-CB_8H_{14} (5 g, 43.9 mmol) in chloroform (100 cm^3) was added elemental sulfur (1.6 g, 50.0 mmol), and then triethylamine (6.5 cm^3, 46.3 mmol) was added dropwise under stirring for 30 min at room temperature. The stirring was continued for 24 h and the reaction mixture was then decomposed carefully (gas evolution) with water (*ca.* 50 cm^3) and the chloroform layer separated and evaporated to dryness. The solid residue was separated by chromatography on a silica gel column (*ca.* 30 × 2.5 cm) using hexane as the liquid phase. The fraction of R_f 0.28 (as measured by TLC) was collected and evaporated to dryness and the residual solid was sublimed *in vacuo* (oil pump) at 50–80 °C. The white sublimate [3.0 g, 47%; m.p. 179–181 °C; *m*/*z* 144 (M^+, with most intense peak at *m*/*z* 140)] was identified as *arachno*-6,9-CSB_8H_{12} **2** by mass spectrometry and by NMR spectroscopy as described above.

[*arachno*-6,9-CSB_8H_{11}]$^-$ **3**. (*a*) *Salt of monoprotonated* 1,8-$(Me_2N)_2C_{10}H_6$ *in solution.* In an NMR tube (5 mm outer diameter), *arachno*-6,9-CSB_8H_{12} **2** (20 mg, 140 μmol) was dissolved in CD_3CN (*ca.* 0.5 cm^3) and 1,8-$(Me_2N)_2C_{10}H_6$ (30 mg, 140 μmol) was added with shaking. After *ca.* 15 min NMR spectroscopy identified the [*arachno*-6,9-CSB_8H_{11}]$^-$ anion **3** as the only boron-containing component of the reaction mixture.

(*b*) *Tetraphenylphosphonium salt.* A solution of *arachno*-6,9-CSB_8H_{12} **2** (420 mg, 2.91 mmol) in diethyl ether (5 cm^3) was added dropwise to a stirred suspension of sodium hydride (72 mg, 3 mmol) in diethyl ether (20 cm^3). The stirring was continued for 1 h at room temperature, the mixture filtered *in vacuo* using standard Schlenk apparatus, and a solution of

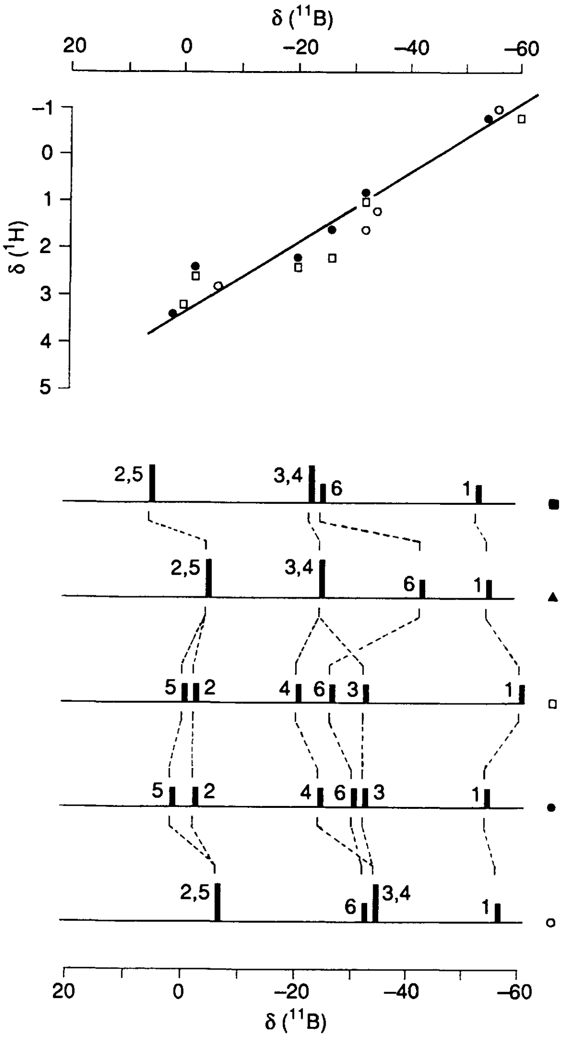


Fig. 3 NMR data for the $[PPh_4]^+$ salt of [*hypho*-7,8-$CSB_6H_{11}]^-$ **6** (●) together with those for 8-Me-*hypho*-7,8-CSB_6H_{11} **7** (□), [*hypho*-7,8-$C_2B_6H_{13}]^-$ (○) (data from ref. 17), [*hypho*-7,8-$S_2B_6H_9]^-$ (■) (data from ref. 6), and 7,8-Me_2-*hypho*-7,8-$S_2B_6H_8$ (▲) (data from ref. 6) for comparison. The top diagram plots $\delta(^1H)$ *versus* $\delta(^{11}B)$ for BH(*exo*) units for some of these compounds. The line drawn has a slope $\delta(^1H):\delta(^{11}B)$ *ca.* 1:15, intercept +3.0 in $\delta(^1H)$. The bottom diagrams are stick representations of the chemical shifts and relative intensities in the ^{11}B spectra of all the compounds. The hatched lines connect equivalent positions in the compounds

$[PPh_4]Cl$ (1.20 g, 3.2 mmol) in water (20 cm^3) added to the filtrate. The diethyl ether was removed by evaporation and the precipitate was filtered off, washed with water (*ca.* 5 cm^3) and diethyl ether (*ca.* 5 cm^3), and vacuum dried to give a white solid. This was identified as $[PPh_4]^+$[*arachno*-6,9-$CSB_8H_{11}]^-$ (yield 1.24 g, 88%) by NMR spectroscopy as described above.

[*nido*-6,9-$CSB_8H_9]^-$ **4**. A solution of $[PPh_4]^+$[*arachno*-6,9-$CSB_8H_{11}]^-$ (198 mg, 410 μmmol) in chloroform (15 cm^3) was treated with acetone (10 cm^3) for 24 h at ambient temperature. The solvents were removed by evaporation and the residue was purified by column chromatography on a silica gel column (*ca.* 1.5 x 30 cm), using dichloromethane as the liquid phase. The fraction of R_f 0.25 was evaporated to a volume of *ca.* 2 cm^3, overlaid carefully with hexane (*ca.* 4 cm^3) and left to crystallize for 4 d. The yellow crystals thus obtained were dried *in vacuo* and identified as $[PPh_4]^+$[*nido*-6,9-$CSB_8H_9]^-$ (yield 75 mg, 38%) by NMR spectroscopy as described above.

Degradation of [*nido*-6,9-$CSB_8H_9]^-$ **4** *to arachno*-4,6-CSB_7H_{11} **5**. Hexane (10 cm^3) was added to the solid $[PPh_4]^+$-

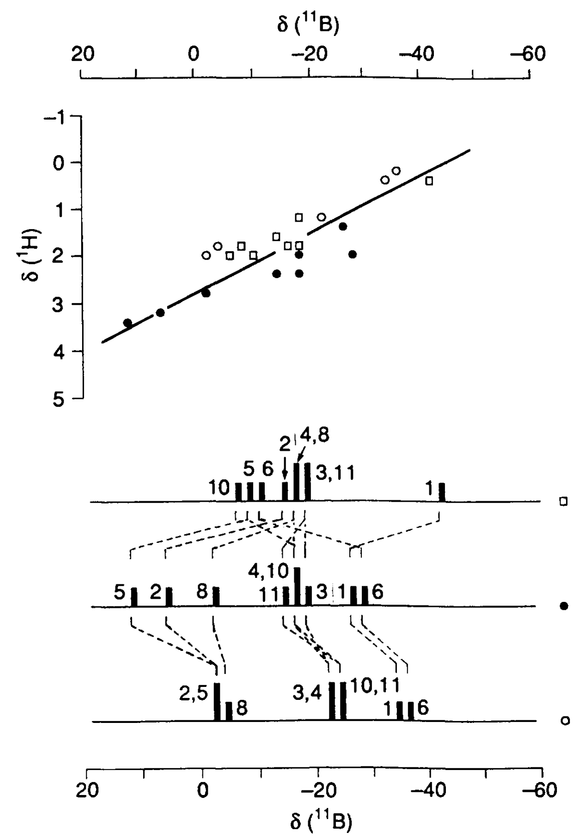


Fig. 4 NMR data for *nido*-7,9-CSB_9H_{11} **9** (●) together with those for the $[PPh_4]^+$ salt of [*nido*-7,9-$CSB_9H_{10}]^-$ **8** (□) and the isoelectronic [*nido*-7,9-$C_2B_9H_{12}]^-$ anion (○) (data from ref. 15) for comparison. The top diagram plots $\delta(^1H)$ *versus* $\delta(^{11}B)$ for BH(*exo*) units for all of these compounds. The line drawn has a slope $\delta(^1H):\delta(^{11}B)$ *ca.* 1:21, intercept +2.9 in $\delta(^1H)$. The bottom diagrams are stick representations of the chemical shifts and relative intensities in the ^{11}B spectra of all the compounds. The hatched lines connect equivalent positions in the compounds

[*nido*-6,9-$CSB_8H_9]^-$ (100 mg, 210 μmmol), followed by dropwise addition of concentrated hydrochloric acid (1 cm^3) at room temperature. After hydrogen evolution had ceased (*ca.* 30 min), the hexane layer was separated, evaporated to dryness, and the solid residue sublimed at 60–70 °C *in vacuo* (oil pump) to obtain a white solid (15 mg, 55%) identified as *arachno*-4,6-CSB_7H_{11} **5**[1] by NMR spectroscopy and mass spectrometry.

[*hypho*-7,8-$CSB_6H_{11}]^-$ **6**. A solution of *arachno*-4,6-CSB_7H_{11} **5** (1.0 g, 7.57 mmol) in diethyl ether (10 cm^3) was added dropwise to a stirred suspension of sodium hydride (192 mg, 8 mmol) in diethyl ether (10 cm^3) at ambient temperature. Stirring was continued for a further 2 h and the mixture was then filtered. The filtrate was evaporated to a syrupy consistency, the residue treated with a mixture of acetone (30 cm^3) and water (2 cm^3), and then heated at reflux for *ca.* 5 h. After cooling to room temperature, water (30 cm^3) was added and the acetone removed by evaporation (rotary evaporator, bath at 20 °C). The aqueous solution thus obtained was precipitated by the addition of a solution of $[PPh_4]Cl$ (3.0 g, 8.02 mmol) in water (30 cm^3), the white precipitate isolated by filtration, washed with water (*ca.* 10 cm^3) and dried *in vacuo* to give $[PPh_4]^+$-[*hypho*-7,8-$CSB_6H_{11}]^-$ (2.26 g, 65%), which was identified by NMR spectroscopy as described above. An analytical product was obtained by crystallization from a concentrated dichloromethane solution that had been overlaid with a two-fold volume of hexane.

8-Me-*hypho*-7,8-CSB_6H_{11} **7**. Excess methyl iodide (1 cm^3, 16.05 mmol) was added to a solution of $[PPh_4]^+$[*hypho*-7,8-$CSB_6H_{11}]^-$ (1.0 g, 2.17 mmol) in thf (20 cm^3) and the mixture was left to stand for 2 h at ambient temperature, filtered to remove the precipitated $[\mathrm{PPh_4}]\mathrm{I}$, and the filtrate was evaporated to dryness. The residual solid was purified by chromatography on a silica gel column (*ca.* 2.5 × 30 cm) using a mixture of chloroform and hexane (1:2 v/v) as the liquid phase. The fraction of R_f 0.60 (in benzene) was collected, evaporated to dryness and the solid material sublimed *in vacuo* (oil pump) at *ca.* 50 °C (oil bath) to isolate a white sublimate [220 mg, 75%; m.p. 32 °C; *m/e* 136 (M^+, with the most intense peak at *m/z* 135)] which was identified as 8-Me-*hypho*-7,8-$\mathrm{CSB_6H_{11}}$ **7** by mass spectrometry and by NMR spectroscopy as described above.

nido-7,9-$\mathrm{CSB_9H_{11}}$ **9**. A solution of *arachno*-6,9-$\mathrm{CSB_8H_{12}}$ **2** (184 mg, 1.28 mmol) in diethyl ether (10 $\mathrm{cm^3}$) was added dropwise to a stirred suspension of sodium hydride (48 mg, 2 mmol) in the same volume of diethyl ether over a period of *ca.* 30 min at ambient temperature. The stirring was continued for an additional 2 h, the mixture was then filtered *in vacuo* using Schlenk apparatus, and the filtrate evaporated to dryness *in vacuo* at room temperature. The residue was then heated at 120–200 °C for *ca.* 30 min *in vacuo* (oil pump) under a sublimation finger at 0 °C to recover *arachno*-6,9-$\mathrm{CSB_8H_{12}}$ **2** (39 mg, 21%; identified by NMR spectroscopy and mass spectrometry). Dichloromethane (10 $\mathrm{cm^3}$) was added to the sublimation residue and the mixture was treated with $\mathrm{CF_3CO_2H}$ (*ca.* 0.5 $\mathrm{cm^3}$, dropwise under intense shaking). The dichloromethane layer was then separated, concentrated to a volume of *ca.* 2 $\mathrm{cm^3}$, and applied to a preparative TLC plate. Development with hexane gave two fractions (R_f 0.40 and 0.30) which were isolated by extraction with dichloromethane, followed by evaporation and sublimation of the solid residues at *ca.* 50–60 °C (oil bath) (oil pump vacuum). The white sublimates were identified as *nido*-7,9-$\mathrm{CSB_9H_{11}}$ **9** [123 mg, 63%; *m/z* 154 (M^+)] and *arachno*-4,6-$\mathrm{CSB_7H_{11}}$[1] **5** (28 mg, 17%), respectively, by mass spectrometry and by NMR spectroscopy as described above.

$[$*nido*-7,9-$\mathrm{CSB_9H_{10}}]^-$ **8**. (*a*) *Salt of monoprotonated* 1,8-$\mathrm{(Me_2N)_2C_{10}H_6}$. In an NMR tube, *nido*-7,9-$\mathrm{CSB_9H_{11}}$ **9** (20 mg, 140 µmmol) was dissolved in dichloromethane (*ca.* 0.5 $\mathrm{cm^3}$) and 1,8-$\mathrm{(Me_2N)_2C_{10}H_6}$ (30 mg, 140 µmmol) was added with shaking. After *ca.* 15 min NMR spectroscopy identified the $[$*nido*-7,9-$\mathrm{CSB_9H_{10}}]^-$ anion **8** as the only boron-containing component of the reaction mixture.

(*b*) *Tetraphenylphosphonium salt.* A solution of *nido*-7,9-$\mathrm{CSB_9H_{11}}$ **9** (152 mg, 1 mmol) in diethyl ether (5 $\mathrm{cm^3}$) was added dropwise to a stirred suspension of sodium hydride (24 mg, 1 mmol) in diethyl ether (10 $\mathrm{cm^3}$). Stirring was continued for 1 h at room temperature, the mixture filtered using Schlenk apparatus, and a solution of $[\mathrm{PPh_4}]\mathrm{Cl}$ (375 mg, 1 mmol) in water (10 $\mathrm{cm^3}$) added to the filtrate. The diethyl ether was removed by evaporation and the precipitate was filtered off, washed with water (*ca.* 5 $\mathrm{cm^3}$) and diethyl ether (*ca.* 5 $\mathrm{cm^3}$), and vacuum dried to give a white solid. This was identified as $[\mathrm{PPh_4}]^+[$*nido*-7,9-$\mathrm{CSB_9H_{10}}]^-$ (456 mg, 93%) by NMR spectroscopy as described above.

Acknowledgements

Contribution No. 33 from Řež–Leeds Anglo–Czech Polyhedral Collaboration (A. C. P. C.). The authors thank Drs. J. Fusek and F. Mareš for NMR measurements, Dr. J. Plešek for helpful discussions, and Dr. Z. Weidenhoffer for the mass spectra. We also thank the Royal Society, Borax Research Limited, the SERC, and the Academy of Sciences of the Czech Republic (grants No. 432 03 and 432 04) for support, and Dr. T. S. Griffin, Dr. R. A. Walker and Dr. D. M. Wagnerová for their helpful cooperation.

References

1 J. Plešek, S. Heřmánek and Z. Janoušek, *Collect. Czech. Chem. Commun.*, 1977, **42**, 785.
2 J. Holub, T. Jelínek, J. Plešek, B. Štíbr, S. Heřmánek and J. D. Kennedy, *J. Chem. Soc., Chem. Commun.*, 1991, 1389.
3 A. Arafat, G. D. Friesen and L. J. Todd, *Inorg. Chem.*, 1983, **22**, 3721.
4 J. Plešek, T. Jelínek, B. Štíbr and S. Heřmánek, *J. Chem. Soc. Chem. Commun.*, 1988, 348. J. Plešek, B. Štíbr, X. L. R. Fontaine, T. Jelínek, M. Thornton-Pett, S. Heřmánek and J. D. Kennedy, unpublished work.
5 B. Štíbr, J. Plešek and S. Heřmánek, *Collect. Czech. Chem. Commun.*, 1973, **38**, 335.
6 S. O. Kang and L. G. Sneddon, *J. Am. Chem. Soc.*, 1989, **111**, 3281.
7 W. C. Hutton, T. L. Venable and R. N. Grimes, *J. Am. Chem. Soc.*, 1984, **106**, 29.
8 X. L. R. Fontaine and J. D. Kennedy, *J. Chem. Soc., Chem. Commun.*, 1986, 779.
9 X. L. R. Fontaine and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.*, 1987, 1573.
10 B. Štíbr, J. D. Kennedy and T. Jelínek, *J. Chem. Soc., Chem. Commun.*, 1990, 1309.
11 T. Jelínek, J. D. Kennedy and B. Štíbr, *J. Chem. Soc., Chem. Commun.*, 1993, 1628.
12 R. Hoffman, *Science*, 1981, **211**, 995, and refs. therein.
13 S. Heřmánek, *Chem. Rev.*, 1992, **92**, 325, and refs. therein.
14 J. D. Kennedy, B. Štíbr, T. Jelínek, X. L. R. Fontaine and M. Thornton-Pett, *Collect. Czech. Chem. Commun.*, 1993, **58**, 2090.
15 J. Plešek, B. Štíbr, X. L. R. Fontaine, J. D. Kennedy, S. Heřmánek and T. Jelínek, *Collect. Czech. Chem. Commun.*, 1991, **56**, 1618.
16 K. Nestor, T. Jelínek, X. L. R. Fontaine, J. D. Kennedy, M. Thornton-Pett, K. Baše and B. Štíbr, *J. Chem. Soc., Dalton Trans.*, 1990, 2887.
17 T. Jelínek, J. Plešek, S. Heřmánek and B. Štíbr, *Main Group Met. Chem.*, 1987, **10**, 397.
18 M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owen, S. G. Schwerin, F. N. Tebbe and P. A. Wegner, *J. Am. Chem. Soc.*, 1968, **90**, 862.
19 J. D. Kennedy, X. L. R. Fontaine, M. McGrath and T. R. Spalding, *Magn. Reson. Chem.*, 1991, **29**, 711.
20 D. Reed, *Chem. Soc. Rev.*, 1993, 109.
21 W. McFarlane, *Proc. R. Soc. London, Ser. A*, 1986, **306**, 185.

Received 25*th October* 1993; *Paper* 3/06356I