MONOCARBABORANE ANION CHEMISTRY. SYNTHESES AND STRUCTURES WITHIN THE *closo* NINE-VERTEX SYSTEM

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It is a pleasure and a privilege to dedicate this paper to Professor Jaromír Plešek on the occasion of his 75th birthday, not only in recognition of his scientific contributions, particularly to polyhedral boron-containing cluster chemistry, but also because of much friendly, stimulating and educational discussion over the past several years.

Reaction of HCHO with $B_{10}H_{14}$ under aqueous alkaline conditions yields the *arachno* 10-vertex $[6\text{-}CB_9H_{14}]^-$ anion **2** (60%) which upon solid-state thermolysis as its Cs^+ salt yields the *closo* 9-vertex $[4\text{-}CB_8H_9]^-$ anion **1** (45%). MeCHO reacts similarly to give the *C*-methylated *arachno* $[6\text{-Me-}6\text{-}CB_9H_{13}]^-$ anion **4** (37%) which upon thermolysis gives the *closo* $[4\text{-Me-}4\text{-}CB_8H_8]^-$ anion **3** (72%). PhCHO with $B_{10}H_{14}$ under alkaline conditions gives the *nido* 10-vertex $[6\text{-Ph-}6\text{-}CB_9H_{11}]^-$ anion **6** (85%) which upon thermolysis of its $[NEt_4]^+$ salt gives the *closo* $[4\text{-Ph-}4\text{-}CB_8H_8]^-$ anion **5** (73%). In a preliminary iodination investigation, unsubstituted *closo* anion **1** with elemental I_2 in CH_2Cl_2 gives approximately equimolar *closo* $[4\text{-}CB_8H_8\text{-}3\text{-}I]^-$ **12** and *closo* $[4\text{-}CB_8H_8\text{-}5\text{-}I]^-$ **13** (*ca* 60%) and smaller amounts of *closo* $[4\text{-}CB_8H_7\text{-}5,6\text{-}I_2]^-$ **14** (12%). The $[NEt_4]^+$ salts of **1**, **3** and **5** are characterised crystallographically, as is the $[PMePh_3]^+$ salt of **12**.

Keywords: Boranes; Carboranes; Monocarbaboranes; Thermolyses; Iodination; $[4\text{-}CB_8H_9]^-$.

The chemistry of the dicarbaboranes, *viz.* boron-containing cluster compounds that incorporate two carbon atoms in their clusters, is relatively well investigated[1,2]. By contrast, the chemistry of the corresponding monocarbaboranes, *viz.* species with only one carbon atom in their borane clusters, is relatively neglected[1]. Recently, however, *closo* monocarbaborane anions $[HCB_nH_n]^-$ have attracted an increasing attention because their very low basicities are most useful in the examination and exploitation of systems of high acidity[3,4]. In particular, the twelve-vertex *closo* $[HCB_{11}H_{11}]^-$ anion and its derivatives figure significantly in this latter regard[5–10]. Concomitantly, there is merit in the development of the chemistry of the other

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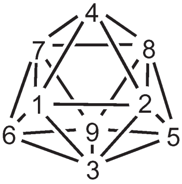
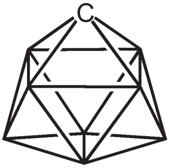
closo monocarbaborane $[HCB_nH_n]^-$ anions. Of these other closed species, the ten-vertex $[HCB_9H_9]^-$, eleven-vertex $[HC_{10}H_{10}]^-$ and twelve-vertex $[HCB_{11}H_{11}]^-$ *closo* anions have been recognised for some time[11–15], with the eight-vertex $[HCB_7H_7]^-$ congener reported more recently[17–19]. The nine-vertex $[HCB_8H_8]^-$ anion, however, has long constituted a gap in the $[HCB_nH_n]^-$ sequence. Here we now describe the preparation and characterisation of this last anion and some of its derivatives. The syntheses develop from the "Brellochs Reaction" of $B_{10}H_{14}$ with formaldehyde or higher aldehydes to give ten-vertex $\{CB_9\}$ species[20]. Cluster-dismantling reactions for the removal of one boron centre from the cluster thence permit the ready entry into the $\{CB_8\}$ systems described here. The numbering system of the closed eight-vertex skeleton is as in schematic cluster structure **I**. The new nine-vertex *closo* monocarbaboranes presented in this paper are all of the *closo*-4-carbanonaborane configuration **II**. Some preliminary aspects of some of the work have recently been communicated[21–23].



I



II

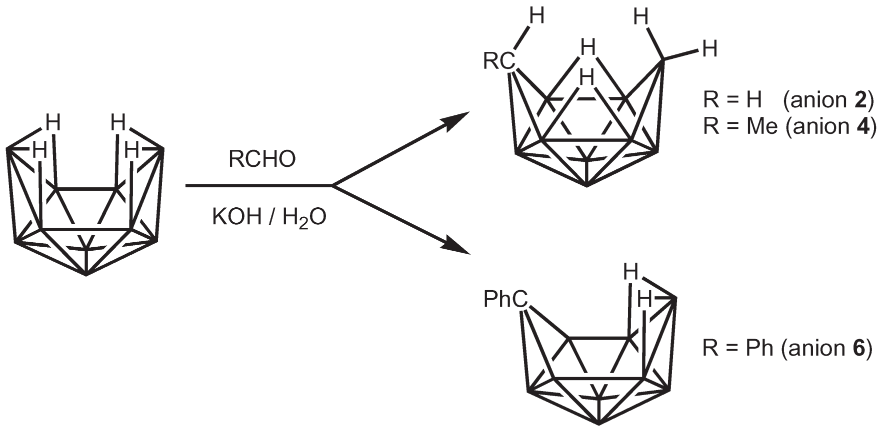
RESULTS AND DISCUSSION

The parent unsubstituted *closo* anion $[HCB_8H_8]^-$ (species **1**), alternatively described as $[$*closo*$\text{-}4\text{-}CB_8H_9]^-$, was prepared from the thermolysis of the $[$*arachno*$\text{-}6\text{-}CB_9H_{14}]^-$ anion (**2**). The corresponding *C*-methylated anion $[4\text{-}Me\text{-}$*closo*$\text{-}4\text{-}CB_8H_8]^-$ (species **3**) was similarly prepared from the $[6\text{-}Me\text{-}$*arachno*$\text{-}CB_9H_{13}]^-$ anion (**4**). The $[4\text{-}Ph\text{-}$*closo*$\text{-}4\text{-}CB_8H_8]^-$ anion (**5**) was prepared from the thermolysis of the $[6\text{-}Ph\text{-}$*nido*$\text{-}6\text{-}CB_9H_{11}]^-$ anion (**6**). The starting *arachno* and *nido* anions **2**, **4** and **6** were prepared by the reaction of the appropriate aldehydes with *nido*-$B_{10}H_{14}$ in aqueous alkaline solution (Scheme 1; note that, in the Schemes, unlettered vertices represent {BH(*exo*)} units).

Thus, dissolution of $B_{10}H_{14}$ in aqueous KOH solution, followed by reaction with formaldehyde, HCHO, at room temperature for 6 h, followed in turn by extraction with ether, evaporation, dissolution in water, and precipitation with CsCl, resulted in the isolation of the ten-vertex [*arachno*-6-CB_9H_{14}]$^-$ anion (**2**) in 60% yield as its Cs^+ salt. This anion **2** is previously well-characterised[24]. The reaction with acetaldehyde, MeCHO, occurs similarly, but much more slowly, taking several days for completion at room temperature. Precipitation from the reaction mixture using [NEt_4]Cl resulted in the isolation of the [6-Me-*arachno*-6-CB_9H_{13}]$^-$ anion (**4**) as its [NEt_4]$^+$ salt in yields of *ca* 30%. The lower yield compared to the HCHO reaction may result from competition from alkaline degradation of the polyhedral borane cluster over the longer reaction time. An overall stoichiometry may be written down as in Eq. (*1*), where R is H (for anion **2**) or Me (for anion **4**). Structural representations are shown in Scheme 1.

$$B_{10}H_{14} + 2\ [OH]^- + H_2O + RCHO \rightarrow [RCB_9H_{13}]^- + [B(OH)_4]^- + H_2 \qquad (1)$$

A closely related reaction occurs with the aromatic congener benzaldehyde, PhCHO. This reaction occurs more rapidly than the MeCHO reaction, being complete overnight. Precipitation from the reaction solution using [NEt_4]Cl, however, now gives the *nido* ten-vertex [6-Ph-*nido*-6-CB_9H_{11}]$^-$ anion (**6**) (Scheme 1), rather than the *arachno* species [6-Ph-*arachno*-6-CB_9H_{13}]$^-$ that would otherwise be expected from analogy with the formations of the *arachno* anions **2** and **4**. The stoichiometry is of course very similar (Eq. (*2*)). Yields have not been consistent over several preparations, and have varied between 64 and 94%. The highest yields have been obtained with freshly distilled benzaldehyde.



SCHEME 1

$$B_{10}H_{14} + 2\ [OH]^- + H_2O + PhCHO \rightarrow [PhCB_9H_{11}]^- + [B(OH)_4]^- + 2\ H_2 \qquad (2)$$

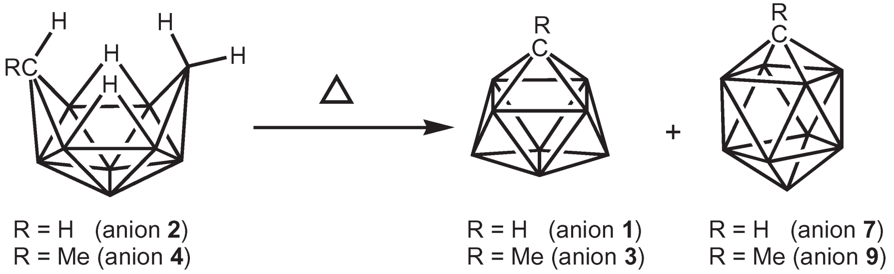
Our initial interest in these particular monocarbaborane systems was for the possible generation of corresponding ten-vertex *closo* species $[RCB_9H_9]^-$. We surmised that thermolyses of the *arachno* and *nido* ten-vertex anions might yield these *closo* ten-vertex species by the successive loss of dihydrogen as in Eqs (*3*) and (*4*).

$$\textit{arachno}\text{-}[RCB_9H_{13}]^- \rightarrow \textit{nido}\text{-}[RCB_9H_{11}]^- + H_2 \qquad (3)$$

$$\textit{nido}\text{-}[RCB_9H_{11}]^- \rightarrow \textit{closo}\text{-}[RCB_9H_9]^- + H_2 \qquad (4)$$

In this regard, we found that thermolysis of the Cs^+ salt of the [*arachno*-6-$CB_9H_{14}]^-$ anion (**2**) at 220 °C (Scheme 2, where R = H) did in fact yield the ten-vertex *closo* species $[CB_9H_{10}]^-$ (anion **7**) according to this supposition, but only as a minor product, isolatable in *ca* 8% yield as its $[PMePh_3]^+$ salt (Eqs (*3*) and (*4*), where R = H). NMR spectroscopy showed that a second minor product, in *ca* 3% yield, was the intermediate ten-vertex *nido* species [*nido*-6-$CB_9H_{12}]^-$ (anion **8**) (Eq. (*3*) only, where R = H). Unexpectedly, however, the predominant product was not a ten-vertex species, but the nine-vertex [*closo*-4-$CB_8H_9]^-$ anion (**1**), isolatable in *ca* 45% yield as its $[PMePh_3]^+$ salt.

The $[PMePh_3]^+$ salts of the two major components **1** and **7** were separated and purified by column chromatography. A good separation can also be effected by fractional crystallisation of the $[NEt_4]^+$ salts from hot ethanol, or of the Cs^+ salts from hot water. Formally, the ten-vertex-to-nine-vertex transi-



SCHEME 2

tion results from the loss of the elements of a $\{BH_3\}$ unit, for which stoichiometries may be written down as in Eqs (*5*) and (*6*), where R = H, but it is not clear what significance this may have mechanistically.

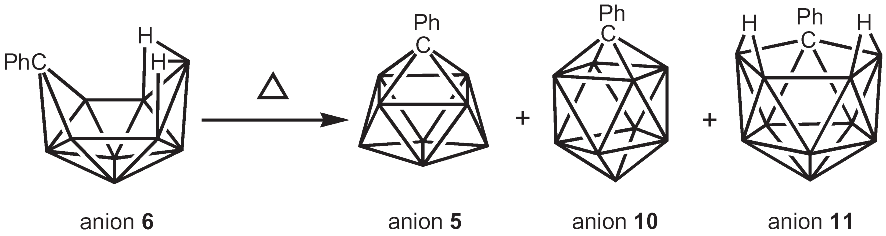
$$\textit{arachno}\text{-}[RCB_9H_{13}]^- \rightarrow \textit{closo}\text{-}[RCB_8H_8]^- + \{BH_3\} + H_2 \qquad (5)$$

$$\textit{nido}\text{-}[RCB_9H_{11}]^- \rightarrow \textit{closo}\text{-}[RCB_8H_8]^- + \{BH_3\} \qquad (6)$$

It should be noted at this point that Holub, Štíbr and co-workers have reported an alternative, and perhaps more elegant, route to the anion **1**[25]. This route involves the conversion of the [*arachno*-6-CB_9H_{14}]$^-$ anion (**2**) to nine-vertex neutral *arachno*-4-CB_8H_{14} and thence to neutral *nido*-1-CB_8H_{12}, followed by oxidation with elemental iodine in the presence of NEt_3 to give the $[CB_8H_9]^-$ anion (**1**) as product in *ca* 75% yield.

The equivalent thermolysis at 220 °C of the $[NEt_4]^+$ salt of the [6-Me-*arachno*-6-CB_9H_{13}]$^-$ anion (**4**) gave a somewhat cleaner reaction, with the $[NEt_4]^+$ salt of the nine-vertex [4-Me-*closo*-4-CB_8H_8]$^-$ anion (**3**) being isolatable in the higher yield of 72% (Eqs (*5*) and (*6*), where R = Me). The only other identifiable product was the $[NEt_4]^+$ salt of the ten-vertex [1-Me-*closo*-1-CB_9H_9]$^-$ anion (**9**), isolatable in *ca* 20% yield (Eqs (*3*) and (*4*), where R = Me). These products were again separated chromatographically.

Upon thermolysis at 200 °C, the $[NEt_4]^+$ salt of the [6-Ph-*nido*-6-CB_9H_{11}]$^-$ anion (**6**) behaves similarly (Scheme 3), yielding the $[NEt_4]^+$ salt of the nine-vertex [4-Ph-*closo*-4-CB_8H_8]$^-$ anion (**5**) as the predominant product at 73%, with trace quantities of the ten-vertex [1-Ph-*closo*-1-CB_9H_9]$^-$ (**10**) also being isolatable.



SCHEME 3

A second isolated minor product was the $[NEt_4]^+$ salt of the eleven-vertex $[7\text{-Ph-}\textit{nido}\text{-}7\text{-}CB_{10}H_{12}]^-$ anion (**11**). This last anion **11** could arise from additon of $\{BH_3\}$ as in Eq. (*7*), or from a more direct disproportionation as in Eq. (*8*). The three products were again separable chromatographically.

$$\{BH_3\} + \textit{nido}\text{-}[PhCB_9H_{11}]^- \ (\mathbf{6}) \rightarrow \textit{nido}\text{-}[PhCB_{10}H_{12}]^- \ (\mathbf{11}) + H_2 \qquad (7)$$

$$2\ \textit{nido}\text{-}[PhCB_9H_{11}]^- \ (\mathbf{6}) \rightarrow \textit{closo}\text{-}[PhCB_8H_8]^- \ (\mathbf{5}) +$$

$$+ \ \textit{nido}\text{-}[PhCB_{10}H_{12}]^- \ (\mathbf{11}) + H_2 \qquad (8)$$

The three new nine-vertex *closo* species **1**, **3** and **5** were characterised both by multielement NMR spectroscopy and by crystallography using single-crystal X-ray diffraction analyses of their (unsolvated) $[PMePh_3]^+$, $[NEt_4]^+$ and $[NEt_4]^+$ salts, respectively (Fig. 1 and Table I). Criteria of purity and compound integrity were clean NMR spectra consistent with the

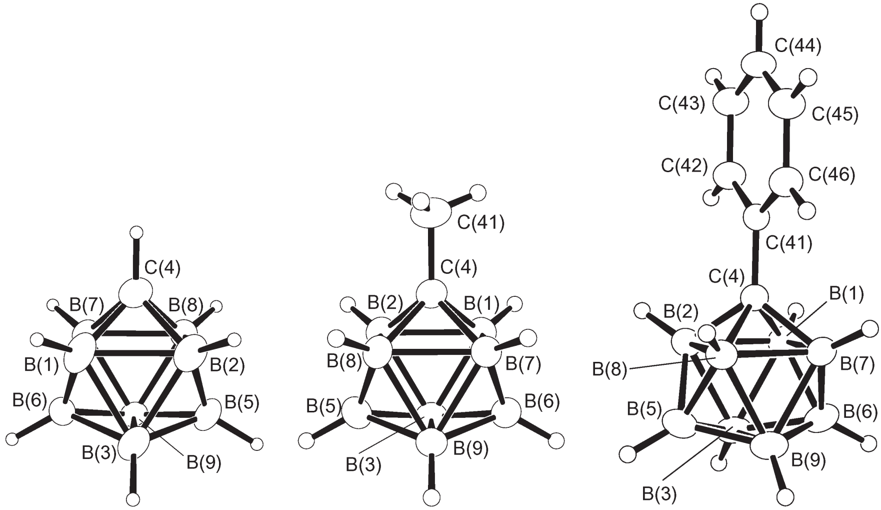


FIG. 1

Crystallographically determined molecular structures of (left) the $[\textit{closo}\text{-}4\text{-}CB_8H_9]^-$ anion (**1**), as determined in its $[PMePh_3]^+$ salt, (centre) the $[4\text{-Me-}\textit{closo}\text{-}4\text{-}CB_8H_8]^-$ anion (**3**), as determined in its $[NEt_4]^+$ salt, and (right) the $[4\text{-Ph-}\textit{closo}\text{-}4\text{-}CB_8H_8]^-$ anion (**5**), as determined in its $[NEt_4]^+$ salt. The crystal structure for the salt of anion **1** had two independent $[PMePh_3]^+[CB_8H_9]^-$ units per unit cell; one $[CB_8H_9]^-$ anion was disordered, the other not: the anion depicted here is the undisordered one. For selected interatomic dimensions see Table I all-atom molecular structures determined from the crystallographic work. The basic closed skeletons have the classical tricapped trigonal prismatic structure of the [*closo*-B_9H_9]$^{2-}$ anion[26], but with a carbon atom in a four-connectivity position, formally the 4-position in a IUPAC numbering scheme (Fig. 1 and schematic structures **I** and **II**). Detailed intercomparisons of selected interatomic dimensions among anions **1**, **3** and **5** can be made by reference to Table I. It should be noted that the crystal structure

TABLE I
Selected crystallographically determined interatomic distances (in Å) and angles (in °) for the [*closo*-4-CB_8H_9]$^-$ anion (**1**)[a], the [4-Me-*closo*-4-CB_8H_8]$^-$ anion (**3**), the [4-Ph-*closo*-4-CB_8H_8]$^-$ anion (**5**) and the [*closo*-4-CB_8H_8-3-I]$^-$ anion (**12**)[b]

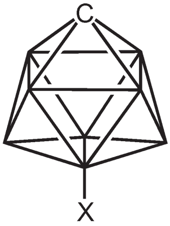
Dimension	**1**[a,c]	**3**	**5**	**12a**[b,c]	**12b**[b,c]
C(4)–C(organyl)	–	1.511(2)	1.490(2)	–	–
C(4)–B(1)	1.635(5)	1.615(2)	1.623(2)	1.603(8)	1.603(8)
C(4)–B(2)	1.628(5)	1.619(2)	1.622(2)	1.663(11)	1.631(10)
C(4)–B(7)	1.646(4)	1.617(2)	1.620(2)	1.630(8)	1.648(8)
C(4)–B(8)	1.642(5)	1.616(2)	1.623(2)	1.647(10)	1.630(9)
B(1)–B(2)	2.004(5)	1.965(2)	1.975(3)	1.931(9)	1.931(9)
B(7)–B(8)	1.930(4)	1.975(2)	1.971(3)	1.959(10)	1.969(9)
B(1)–B(7)	1.768(5)	1.788(2)	1.788(2)	1.880(5)	1.880(5)
B(2)–B(8)	1.786(5)	1.784(2)	1.792(2)	1.807(12)	1.787(11)
B(3)–B(9)	1.800(5)	1.796(2)	1.792(3)	1.900(5)	1.900(5)
B(1)–C(4)–B(7)	65.2(2)	67.20(8)	66.9(1)	71.1(3)	71.1(3)
B(2)–C(4)–B(8)	66.2(2)	66.95(8)	67.0(1)	66.2(5)	66.4(5)
B(1)–C(4)–B(2)	75.8(2)	74.81(9)	75.0(1)	72.5(4)	72.5(4)
B(7)–C(4)–B(8)	71.9(2)	75.31(8)	74.8(1)	73.4(5)	73.8(5)

[a] The crystal structure for the unsubstituted anion **1** has two independent [$PMePh_3$]$^+$ [CB_8H_9]$^-$ units per unit cell. One anion is disordered, the other not: data in this Table are for the undisordered one, although their overall accuracy will be affected by the disorder in the other anion. [b] In the crystal structure, the anion **12** exhibits a quasi-two-fold disorder: dimensions for each of the two contributing units are given; the nature of the disorder is such that some vectors are common to both molecules. [c] Although both anion species **1** and **12** are unequivocally identified by the crystallographic work, the derived dimensions are insufficiently accurate for fine structural intercomparisons because of the disorder within the crystals.

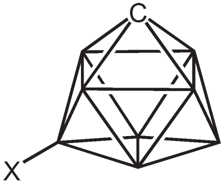
for the unsubstituted anion **1** had two independent $[PMePh_3]^+[CB_8H_9]^-$ units per unit cell. One $[CB_8H_9]^-$ anion was disordered, the other not. The anion chosen for Fig. 1, and for the data presented in Table I is the undisordered one. For this undisordered anion, it can be seen from Table I that, compared to the *C*-substituted anions **3** and **5**, there is a much greater variation between distances that would be expected to be equivalent if the molecule adhered to the C_{2v} symmetry to which the solid-state structure approximates. This may reflect aspects of crystallographic consequences of the disorder. In all three species, and as with the [*closo*-$B_9H_9]^{2-}$ anion[26], the edges of the central trigonal prism at *ca* 2.00 Å are at the longer end of what are regarded as typical interboron cluster bonding distances; this phenomenon was addressed by O'Neill and Wade some two decades ago for the [*closo*-$B_9H_9]^{2-}$ model[27]. In comparing among the three anions **1**, **3** and **5**, there appears to be a small difference between the C(4)(cage)–C(organyl) distances for the *C*-methyl species **3** and the *C*-phenyl species **5**, with values of 1.511(2) and 1.490(2) Å for **3** and **5**, respectively, but there is no crystallographically significant differential effect observable in the intracluster boron–carbon distances involving the C(4) atom, which range from 1.615(2)–1.619(2) Å for **3** and 1.620(3)–1.623(2) Å for **5**. The corresponding intracluster boron–carbon distances for the unsubstituted parent anion **1** appear to be somewhat longer, at 1.628(5)–1.646(5) Å, but because of the consequences of disorder in the crystal structure as mentioned above, these derived distances are not reliable for purposes of such a fine comparison.

In view of the long-standing and currently reburgeoning interest and activity in the halogenations of *closo* $[HCB_nH_n]^-$ anions in general[3,4,18,28–32], we have also conducted a preliminary investigation of the iodination of the unsubstituted [*closo*-4-$CB_8H_9]^-$ anion **1**. It is convenient to report on this iodination in this present paper. Thus, in a siting experiment, we have examined the reaction of the anion **1** with 1.5 equivalents of elemental diodine so that preliminary aspects of both monoiodination and diodination could be assessed. Rapid decolouration of the iodine occurred in CH_2Cl_2 solution, and chromatography yielded a mixture of the [*closo*-4-CB_8H_8-3-I]$^-$ anion (**12**) (schematic cluster structure **III**) and its isomer the [*closo*-4-CB_8H_8-5-I]$^-$ anion (**13**) (schematic cluster structure **IV**) in a combined yield of *ca* 60%, and a pure sample of the *closo*-[4-CB_8H_7-5,6-$I_2]^-$ anion (**14**) in *ca* 12% yield (schematic cluster structure **V**), all isolated as their $[PMePh_3]^+$ salts. They were identified as such by NMR spectroscopy, and, in the case of the 3-monoiodinated isomer **12**, by a single crystal X-ray diffraction analysis of its $[PMePh_3]^+$ salt (Fig. 2). Repeated chromatography and fractional crystallisations have so far failed to yield pure bulk samples of the

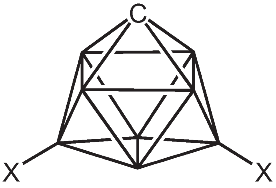
[PMePh$_3$][*closo*-4-CB$_8$H$_8$-3-I] and [PMePh$_3$][*closo*-4-CB$_8$H$_8$-5-I] isomers, best purities that we have been able to obtain being *ca* 20 : 80 and *ca* 75 : 25 mixtures, but one crystallisation attempt yielded a few crystals of the [PMePh$_3$][*closo*-4-CB$_8$H$_8$-3-I] isomer suitable for the single-crystal work, confirming the substitutent position on anion **12**, and thence, by comparative NMR spectroscopy, the substituent sites on anions **13** and **14** also. Within the mixtures, assignments of NMR resonances, both to individual compounds and to specific positions within each compound, were readily established by ^{11}B and ^{1}H homonuclear and heteronuclear correlation experiments as well as by relative intensity considerations.



III



IV



V

The distribution of the iodination in these products is interesting. The predominant isolated products were the 3-iodo, 5-iodo and 5,6-diodo species (anions **12**, **13** and **14**, schematics **III**, **IV** and **V**, respectively). Their

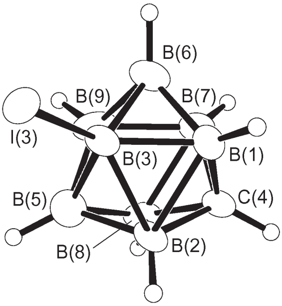


FIG. 2

Crystallographically determined molecular structure of the [*closo*-4-CB$_8$H$_8$-3-I]$^-$ anion (**12**), as determined in its [PMePh$_3$]$^+$ salt. The crystallographic solution revealed a quasi-two-fold disorder of the anion: only one of the two components, molecule **12a**, is shown here; dimensions of the other component are very similar (Table I). Distances from the iodinated atom B(3) for molecule **12a** are as follows: to I(3) 2.181(3), to B(1) 1.848(5), to B(2) 1.898(10), to B(5) 1.731(9), to B(6) 1.674(4) and to B(9) 1.900(5) Å, although see footnote *c* to Table I. For other selected interatomic dimensions see Table I combined isolated yield was high, and NMR spectroscopy of the initially isolated crude product mixtures showed only trace quantities of other (possibly iodinated) products species. In particular, the NMR work suggested no significant amounts of additional products iodinated at B(3) or its equivalent B(9) position, which, by analogy with the 3-monoiodo species **12**, would exhibit singlet ^{11}B resonances with $\delta(^{11}\mathrm{B})$ values in the higher field region at *ca* –25 ppm. This suggests that a symmetrical diodination at the B(3) and B(9) positions, or a mixed diiodination at adjacent B(3) and B(5) sites, is not favoured, implying interesting differential activation processes or cluster rearrangement. That the B(1), B(2), B(7) and B(8) sites adjacent to the carbon position were not halogenated, but that the distal B(3), B(5) and B(6) positions were, is in accord with halogenation behaviour of the well-examined ten-vertex [*closo*-$CB_9H_{10}]^-$ and the twelve-vertex [*closo*-$CB_{11}H_{12}]^-$ systems[4,6,28,32], and is also consistent with what little work has been reported on the eight-vertex [*closo*-$CB_7H_8]^-$ system[18]. Of these distal positions in the nine-vertex $\{CB_8\}$ system reported here, the higher predominance of substitution at the B(5) and B(6) sites of cluster-connectivity four, rather than at the five-connectivity B(3) and B(9) sites, suggests a differential activation that differs from the activity sequencing observed for halogenations in the [*closo*-$CB_9H_{10}]^-$ system, in which it is the distal five-connectivity sites that are halogenated before the distal four-connectivity site[29]. These differences may reflect differences in the internal cluster electronics. That the only diiodinated product in the nine-vertex $\{CB_8\}$ system is thence the 5,6-disubstituted species **14** suggests a strong selective activation by the halogenated B(5) site for the second halogenation that is not mirrored by an equivalent activation when the initially halogenated site is B(3). Again this may be compared to the $\{CB_9\}$ system[29]. It will clearly be of interest further to examine these and related phenomena. Halogenated anions of the *closo* monocarbaborane families are of high current interest in their own right as “least coordinating anions” for the examination of systems of high acidity[3,4], and halogenated species are potentially very useful as intermediate “building blocks” for further derivative chemistry[32].

EXPERIMENTAL

General

Reactions were carried out under N_2 unless otherwise mentioned, with subsequent manipulations and separations in air. Column chromatography was carried out using silica 60 (mesh 70–230 (0.06–0.20 mm); Lancaster Synthesis). The progress of the column chromatographic elution was monitored by analytical TLC using silica gel G on aluminium foil (Silufol

(Kavalier, Prague)), components being detected by exposure to iodine vapour followed by aqueous Ag[NO_3] spray. Analytic TLC R_F values are quoted for the same solvent as used for the column elutions specified in each case. Criteria of purity and compound integrity were clean NMR spectra consistent with all-atom molecular structures determined from the single-crystal X-ray diffraction analysis of representative compounds.

Nuclear Magnetic Resonance Spectroscopy

NMR spectroscopy was performed at *ca* 5.9 and 11.75 T (fields corresponding to 250 and 500 MHz ^{1}H frequencies, respectively) using commercially available instrumentation and using techniques and procedures as adequately described and enunciated elsewhere[33–41]. Chemical shifts δ are given in ppm relative to Ξ = 100 MHz for δ(^{1}H) (±0.05 ppm) (nominally TMS), and to Ξ = 32.083972 MHz for δ(^{11}B) (±0.5 ppm) (nominally Et_2OBF_3 in $CDCl_3$)[37]; Ξ is as defined by McFarlane[42]. Data were recorded at 294–300 K, and cluster boron hydride data are presented in the order: {assignment, δ(^{11}B)/ppm [δ(^{1}H)/ppm of directly attached *exo* hydrogen atom in square brackets] splitting arising from $^1J(^{11}B\text{-}^1H)$/Hz}, unless specifed otherwise. The splittings arising from $^1J(^{11}B\text{-}^1H)$ are taken from unenhanced ^{11}B spectra with digital resolution 6 Hz.

Reaction $B_{10}H_{14}$ with HCHO;
Isolation of the Cs^+ Salt of the [*arachno*-6-CB_9H_{14}]$^-$ Anion (**2**)

$B_{10}H_{14}$ (1.4 g, 1.13 mmol) was dissolved in aqueous KOH (10% w/v solution; 45 ml). After 30 min, aqueous HCHO (38%, stabilised with 12% MeOH; 3.6 ml) was added. The resulting solution was stirred at room temperature for 6 h. The reaction mixture was then extracted with Et_2O (2 × 30 ml), and the combined Et_2O layers added to water (10 ml). The ether was then evaporated off, and the resulting aqueous solution filtered and then treated with aqueous CsCl (3.0 g in 10 ml of water). The resulting white precipitate was filtered off and recrystallised from hot water (*ca* 20 ml), filtered, and dried *in vacuo*, yielding the Cs^+ salt of the [*arachno*-6-CB_9H_{14}]$^-$ anion (**2**) (1.37 g, 60% yield), characterised by comparison with literature data[24].

Reaction $B_{10}H_{14}$ with MeCHO;
Isolation of the [NEt_4]$^+$ Salt of the [6-Me-*arachno*-6-CB_9H_{13}]$^-$ Anion (**4**)

$B_{10}H_{14}$ (1.24 g, 1.00 mmol) was dissolved in aqueous KOH (10% w/v solution; 45 ml). After 1 h, excess MeCHO (1.5 ml) was added, and the mixture stirred overnight. Next day a second portion of MeCHO (1.5 ml) was added, and the solution was stirred for a further 2 days. Monitoring by ^{11}B and ^{1}H NMR spectroscopy showed a slow diminution of the starting borane material, and successive portions of MeCHO (1.5 ml) were added at 2-day intervals. After 14 days the reaction was complete: the resulting solution was then filtered, and volatile organic residues removed from the filtrate *in vacuo*. The resulting aqueous solution was then treated with aqueous [NEt_4]Cl (2.5 g in 20 ml water). The resulting white precipitate was filtered off, washed with water and recrystallized from hot EtOH (*ca* 20 ml) to give the product, characterised as the [NEt_4]$^+$ salt of the [6-Me-*arachno*-6-CB_9H_{13}]$^-$ anion (**4**) (1.01 g, 37.5% yield). NMR ($(CD_3)_2CO$): BH(4) –2.9 [*ca* +2.20] 135, BH(2) –6.9 [*ca* +1.90] 145, BH(5,7) –9.5 [+2.12 and μH] 150, B(9) –22.9 [+0.93 (*exo*), –0.76 (*endo*)] apparent splitting *ca* 110 (triplet), BH(8,10) –28.8 [+0.78 and μH] 134, and BH(1,3) –39.3 [+0.38] 139; δ(^{1}H)(Me) +1.18 (singlet), μH(5,10;7,8) –3.73.

Reaction $B_{10}H_{14}$ with PhCHO; Isolation of the $[NEt_4]^+$ Salt of the [6-Ph-*nido*-6-$CB_9H_{11}]^-$ Anion (**6**)

$B_{10}H_{14}$ (1.29 g, 1.04 mmol) was added to stirred aqueous KOH (10% w/v solution; 45 ml). After 1 h a solution of PhCHO (freshly distilled; 3.6 g, 3.4 mmol) in EtOH (20 ml) was added. The reaction mixture was then stirred at room temperature for 4 h, and then a second portion of PhCHO (1.2 g) in EtOH (5 ml) was added, and the solution stirred overnight. The organic solvents were removed from the resulting mixture *in vacuo*, and the resulting aqueous solution filtered. A solution of $[NEt_4]^+Cl^-$ (2.5 g) in water (20 ml) was added. The resulting white precipitate was filtered off, washed with water, and recrystallised from hot EtOH (*ca* 20 ml), to yield the $[NEt_4]^+$ salt of the [6-Ph-*nido*-6-$CB_9H_{11}]^-$ anion (**6**) (2.90 g, 85% yield). NMR ($(CD_3)_2CO$): BH(1,3) +1.4 [+3.34] 136, BH(9) –2.5 [+2.92 and μH] 156, BH(5,7) –4.7 [+2.48] 137, B(8,10) –12.2 [+2.00 and μH] 136, BH(2) –25.8 [+0.63] 149, and BH(4) –38.0 [+0.42] 141; δ(^{1}H)(Ph) +6.97 to +7.34 (multiplets), μH(8,9;9,10) –3.33.

Thermolysis of the Cs^+ Salt of the [*arachno*-6-$CB_9H_{14}]^-$ Anion (**2**); Isolation of the $[PMePh_3]^+$ Salt of the [*closo*-4-$CB_8H_9]^-$ Anion (**1**)

A solid sample of the Cs^+ salt of the [*arachno*-6-$CB_9H_{14}]^-$ anion (**2**) (550 mg, 2.15 mmol; prepared as above) was heated under vacuum at 220 °C for 3 h. After cooling, the solid residue was treated with Me_2CO (20 ml), the mixture filtered, and the Me_2CO then evaporated from the filtrate *in vacuo*. The viscous residue was dissolved in water (30 ml) and treated with $[PMePh_3]Cl$ (2.5 g). The resulting white precipitate was filtered off and dried *in vacuo*. NMR spectroscopy showed that this precipitate contained a mixture of three anions: the [*closo*-1-$CB_9H_{10}]^-$ anion (**7**), the [*nido*-6-$CB_9H_{12}]^-$ anion (**8**), and an initially unknown species subsequently identified as the [*closo*-4-$CB_8H_9]^-$ anion (**1**)[21], in molar ratio 3 : 1 : 10, respectively. The precipitate was chromatographed on silica gel (2.5 × 30 cm column) using MeCN–CH_2Cl_2 (1 : 15) as liquid phase. The two principal fractions were of R_F 0.21 and 0.18. These were filtered and evaporated, yielding the $[PMePh_3]^+$ salts of the known [*closo*-1-$CB_9H_{10}]^-$ anion (**7**) (R_F 0.21; 100 mg, 8.5% yield), identified as such by NMR spectroscopy, and the $[PMePh_3]^+$ salt of the new [*closo*-4-$CB_8H_9]^-$ anion (**1**) (R_F 0.21; 550 mg, 45.2% yield). NMR (CD_3CN): BH(5,6) +12.9 [+4.35] 145, BH(1,2,7,8) –14.4 [+1.16] 150, BH(3,9) –20.3 [+0.60] 135; δ(^{1}H)(CH) +4.10 (broad singlet). Crystals of the $[PMePh_3]^+$ salt of the [*closo*-4-$CB_8H_9]^-$ anion (**1**) suitable for the single-crystal X-ray diffraction analysis were prepared by diffusion of hexane into a solution in CH_2Cl_2.

Thermolysis of the $[NEt_4]^+$ Salt of the [6-Me-*arachno*-6-$CB_9H_{13}]^-$ Anion (**4**); Isolation of the $[NEt_4]^+$ Salt of the [4-Me-*closo*-4-$CB_8H_8]^-$ Anion (**3**)

A solid sample of the $[NEt_4]^+$ salt of the [6-Me-*arachno*-6-$CB_9H_{13}]^-$ anion (**4**) (prepared as above; 300 mg 1.10 mmol) was heated at 220 °C under vacuum for 4 h. After cooling, the resulting solid residue was treated with MeCN (15 ml), the mixture filtered, and the filtrate evaporated *in vacuo*. The viscous residue was then chromatographed on silica gel (2.5 × 30 cm) using MeCN–CH_2Cl_2 (1 : 10) as liquid phase, yielding two fractions, with R_F 0.22 and 0.19. These were filtered and evaporated, yielding the $[NEt_4]^+$ salts of the [1-Me-*closo*-1-$CB_9H_9]^-$

anion (**9**) (R_F 0.22; 60 mg, 21%), identified by NMR spectroscopy, and of the new [4-Me-*closo*-4-CB_8H_8]$^-$ anion (**3**) (R_F 0.22; 200 mg, 72%). NMR (CD_3CN): BH(5,6) +11.4 [+4.22] 145, BH(1,2,7,8) –10.8 [+1.44] 147, BH(3,9) –17.4 [+0.75] 131; δ(^{1}H)(Me) +2.47 (singlet). Crystals of the latter salt, suitable for the single-crystal X-ray diffraction analysis, were prepared by diffusion of hexane into a solution in CH_2Cl_2.

Thermolysis of the [NEt_4]$^+$ Salt of the [*nido*-6-Ph-6-CB_9H_{11}]$^-$ Anion (**6**); Isolation of the [NEt_4]$^+$ Salt of the [4-Ph-*closo*-4-CB_8H_8]$^-$ Anion (**5**)

A solid sample of the [NEt_4]$^+$ salt of [6-Ph-*nido*-6-CB_9H_{11}]$^-$ anion (**6**) (prepared as above; 300 mg, 900 μmol) was heated under vacuum at 200 °C for 2 h. After cooling, the resulting solid residue was treated with MeCN (15 ml), filtered, and the filtrate evaporated *in vacuo*. The residue was taken up in minimum CH_2Cl_2 and chromatographed on silica gel (2.5 × 30 cm) using MeCN–CH_2Cl_2 (1 : 10) as liquid phase, yielding three fractions of R_F 0.25, 0.20 and 0.15. The first two of these fractions were identified as the [NEt_4]$^+$ salts of the [1-Ph-*closo*-1-CB_9H_9]$^-$ anion (**10**) (R_F 0.25; *ca* 10 mg) and the [7-Ph-*nido*-7-$CB_{10}H_{12}$]$^-$ anion (**11**) (R_F 0.20; 50 mg). The third was characterised as the new [4-Ph-*closo*-4-CB_8H_8]$^-$ anion (**5**) (R_F 0.15; 210 mg, 73% yield). NMR (CD_3CN): BH(5,6) +13.38 [+4.44] 148, BH(1,2,7,8) –10.80 [+1.71] 151, BH(3,9) –17.23 [+0.88] 131; δ(^{1}H)(Ph) +7.32 to +7.93 (multiplets). Crystals of this last salt, suitable for the single-crystal X-ray diffraction analysis, were prepared by diffusion of hexane into a solution in CH_2Cl_2.

Iodination of the [*closo*-4-CB_8H_9]$^-$ Anion (**1**)

A sample of the [$PMePh_3$]$^+$ salt of the [*closo*-4-CB_8H_9]$^-$ anion (**1**) (prepared as above; 150 mg, 39 μmol) was dissolved in CH_2Cl_2 (10 ml). Elemental I_2 (150 mg, 59 μmol) was added to this stirred solution in three portions, at a rate compatible with the decolourisation of the iodine. The mixture was then stirred overnight, and then directly chromatographed on silica gel (2.5 × 30 cm) using MeCN–CH_2Cl_2 (1 : 15) as liquid phase, yielding two fractions. The first fraction of R_F 0.22 was characterised as the [$PMePh_3$]$^+$ salt of the [*closo*-4-CB_8H_7-5,6-I_2]$^-$ anion (**14**) (30 mg, 12.2% yield). The second fraction was a mixture of the [$PMePh_3$]$^+$ salts of two monoiodo isomers (120 mg, 60 % yield), the [*closo*-4-CB_8H_8-3-I]$^-$ anion (**12**) and the [*closo*-4-CB_8H_8-5-I]$^-$ anion (**13**), in molar ratio *ca* 1 : 1 as gauged by integrated ^{11}B NMR spectroscopy. Evaporation followed by repeated chromatography and fractional crystallisation has not provided clean isomeric samples. Best results have been from CH_2Cl_2/Et_2O, resulting in samples of each that are mutually contaminated to the extent of about 20% with the other isomer. All three anions were clearly defined by NMR spectroscopy, and, in the case of the 3-iodinated species **12**, by a single-crystal X-ray diffraction analysis; for this last, a few crystals of the [$PMePh_3$]$^+$ salt of the [*closo*-4-CB_8H_8-3-I]$^-$ anion (**12**) suitable for the single-crystal X-ray diffraction analysis were found in one crystalline sample prepared by diffusion of hexane into a solution in CH_2Cl_2 of a *ca* 25 : 75 mixture of the [$PMePh_3$]$^+$ salts of **12** and **13**. NMR data for these three [$PMePh_3$]$^+$ salts are as follows (CD_3CN): For the 3-iodo anion **12**, BH(5,6) +12.7 [+4.41] 146, BH(1,2) –11.9 [+1.72] 160, BH(7,8) –14.8 [+1.31] 153, BH(9) –19.2 [+1.04] 146, BI(3) –25.8 [I-substituted]; δ(^{1}H)(CH) +4.06 (broad singlet). For the 5-iodo anion **13**, BH(6) +11.9 [+4.32] 137, BI(5) +6.7 (I-substituted], BH(1,7) and BH(2,8) –11.3 and –11.4 [+1.31] and [+1.77] both *ca* 154, BH(3,9) –16.7 [+0.91] 144; δ(^{1}H)(CH) +4.21 (broad singlet). For the 5,6-diiodo anion **14**, BI(5,6) +4.9 [I-substituted], BH(1,2,7,8) –8.7 [+1.94] 150, BH(3,9) –13.7 [+1.52] 138; δ(^{1}H)(CH) +4.38 (broad singlet).

Single-Crystal X-Ray Diffraction Data

The crystallography for the $[PMePh_3]^+$ salt of anion **1**, $[PMePh_3]$[*closo*-4-CB_8H_9], and for the $[NEt_4]^+$ salt of anion **5**, $[NEt_4]$[4-Ph-*closo*-4-CB_8H_8], have been adequately dealt with in the preliminary notes of refs[21,22]. The previously unreported crystal data for the $[NEt_4]^+$ salt of anion **3**, $[NEt_4]$[4-Me-*closo*-4-CB_8H_8], and of the $[PMePh_3]^+$ salt of anion **12**, $[PMePh_3]$[*closo*-4-CB_8H_8-3-I] are as follows: For the salt of anion **3**, $C_{10}H_{31}B_8N$: M = 251.84, orthorhombic (from CH_2Cl_2/C_6H_{14}), space group $P2_12_12_1$, a = 9.4861(1) Å, b = 12.2523(2) Å, c = 14.6915(2) Å, U = 1 707.54(4) $Å^3$, D_{calc} = 0.98 Mg m^{-3}, Z = 4, MoKα, λ = 0.71073 Å, μ = 0.048 mm^{-1}, T = 150(2) K, R_1 = 0.0354 for 3 226 reflections with $I > 2\sigma(I)$, and wR_2 = 0.1027 for all 3 331 unique reflections. For the salt of anion **12**, $C_{20}H_{26}B_8IP$, M = 510.76, monoclinic (from CH_2Cl_2/C_6H_{14}), space group $P2_1/c$, a = 12.9690(2) Å, b = 10.9782(2) Å, c = 16.8985(3) Å, β = 90.145(1)°, U = 2405.94(7) $Å^3$, D_{calc} = 1.41 Mg m^{-3}, Z = 8, MoKα, λ = 0.71073 Å, μ = 1.403 mm^{-1}, T = 150(2) K, R_1 = 0.0379 for 4 277 reflections with $I > 2\sigma(I)$, and wR_2 = 0.1038 for all 4 725 unique reflections. For both compounds, methods and programs were standard[43–46].

CCDC 159456 (salt of **1**), CCDC 184137 (12a), CCDC 164853 (salt of **5**) and CCDC 184138 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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REFERENCES

1. Štíbr B.: *Chem. Rev. (Washington, D. C.)* **1992**, *92*, 25.
2. Bregadze V. I.: *Chem. Rev. (Washington, D. C.)* **1992**, *92*, 209.
3. Strauss S. H.: *Chem. Rev. (Washington, D. C.)* **1993**, *93*, 927.
4. Reed C. A.: *Acc. Chem. Res.* **1998**, *31*, 133.
5. Xie Z., Tsang C-W., Xue F., Mak T. C. W.: *J. Organomet. Chem.* **1999**, *577*, 197.
6. Ivanov S. V., Ivanova S. M., Miller S. M., Anderson O. P., Solntsev K. A., Strauss S. H.: *Inorg. Chim. Acta* **1999**, *289*, 76.
7. Peymann T., Herzog A., Knobler C. B., Hawthorne M. F.: *Angew. Chem., Int. Ed.* **1999**, *38*, 1062.
8. Morris J. H., Henderson K. W., Ol'shevskaya V. A.: *J. Chem. Soc., Dalton Trans.* **1998**, 1951.
9. Douglas A. G., Janoušek Z., Kaszynski P., Young V. G.: *Inorg. Chem.* **1998**, *37*, 6361.
10. See, for example: Stasko D., Reed C.A.: *J. Am. Chem. Soc.* **2002**, *124*, 1148; and references therein.
11. Onak T., Drake R. P., Dunks G. B.: *J. Am. Chem. Soc.* **1965**, *87*, 2505.
12. Prince S. R., Schaeffer R.: *Chem. Commun.* **1968**, 451.
13. Onak T., Matschei P., Groszek E.: *J. Chem. Soc. A* **1969**, 1990.

14. Knoth W. H.: *J. Am. Chem. Soc.* **1967**, *89*, 1274.
15. Knoth W. H.: *Inorg. Chem.* **1971**, *10*, 598.
16. Knoth W. H.: *Inorg. Chem.* **1973**, *12*, 785.
17. Plešek J., Jelínek T., Štíbr B., Heřmánek S.: *J. Chem. Soc., Chem. Commun.* **1988**, 348.
18. Jelínek T., Štíbr B., Plešek J., Kennedy J. D., Thornton-Pett M.: *J. Chem. Soc., Dalton Trans.* **1995**, 431.
19. a) Franken A., Kilner C. A., Thornton-Pett M., Kennedy J. D.: *J. Organomet. Chem.* **2002**, in press, paper JOM 11359; b) Franken A., Ormsby D. L., Kilner C. A., Clegg W., Thornton-Pett M., Kennedy J. D.: *J. Chem. Soc., Dalton Trans.* **2002**, 2807.
20. a) Brellochs B.: *Abstracts Tenth International Meeting on Boron Chemistry (IMEBORON X), Durham, England, July 11–16, 1999*, Abstract No. CA-18, p. 82; b) Brellochs B. in: *Contemporary Boron Chemistry* (M. G. Davidson, A. K. Hughes, T. B. Marder and Wade K., Eds), p. 212. Royal Society of Chemistry, Cambridge (England) 2000.
21. Jelínek T., Štíbr B., Holub J., Bakardjiev M., Hnyk D., Ormsby D. L., Kilner C. A., Thornton-Pett M., Schanz H.-J., Wrackmeyer B., Kennedy J. D.: *Chem. Commun.* **2001**, 1756.
22. Jelínek T., Kilner C. A., Thornton-Pett M., Kennedy J. D.: *Chem. Commun.* **2001**, 1790.
23. Jelínek T., Štíbr B., Holub J., Bakardjiev M., Thornton-Pett M., Kennedy J. D., Tok O. L., Milius W., Wrackmeyer B.: *Abstracts Second European Symposium on Boron Chemistry, EUROBORON 2, Dinard, France, September 2–7, 2001*, Abstract No. P 19.
24. Fontaine X. L. R., Kennedy J. D., Thornton-Pett M., Nestor K., Štíbr B., Jelínek T., Baše K.: *J. Chem. Soc., Dalton Trans.* **1990**, 2887.
25. Jelínek T., Kaněrová I., Holub J., Štíbr B., Tok O., Wrackmeyer B.: Manuscript in preparation, as cited in ref.[21]. See now also: Štíbr B., Wrackmeyer B.: *J. Organomet. Chem.* **2002**, in press, and references therein.
26. Guggenberger J.: *Inorg. Chem.* **1968**, *7*, 2260.
27. O'Neill M. E., Wade K.: *Polyhedron* **1983**, *2*, 963.
28. Jelínek T., Plešek J., Heřmánek S., Štíbr B.: *Collect. Czech. Chem. Commun.* **1986**, *51*, 819.
29. See, for example: Ivanov S. V., Rockwell J. J., Miller S. M., Anderson O. P., Solntsev K. A., Strauss S. H.: *Inorg. Chem.* **1996**, *35*, 7882; and references therein.
30. See, for example: a) Tsang C. W., Yang Q., Tung-po Sze E., Mak T. C. W., Chan D. T. W., Xie Z.: *Inorg. Chem.* **2001**, *39*, 3582; b) Tsang C. W., Yang Q., Tung-po Sze E., Mak T. C. W., Chan D. T. W., Xie Z.: *Inorg. Chem.* **2001**, *39*, 5851; and references therein.
31. See, for example: Stasko D., Reed C. A.: *J. Am. Chem. Soc.* **2002**, *124*, 1148; and references therein.
32. See, for example: Franken A., Kilner C. A., Thornton-Pett M., Kennedy J. D.: *Collect. Czech. Chem. Commun.* **2002**, *67*, 869.
33. See, for example: Kennedy J. D. in: *Multinuclear NMR* (J. Mason, Ed.), Chap. 8, p. 221. Plenum, New York and London 1987; and references therein.
34. Kennedy J. D., Staves J.: *Z. Naturforsch. B* **1979**, *34*, 808.
35. a) Venable T. L., Hutton W. C., Grimes R. N.: *J. Am. Chem. Soc.* **1982**, *104*, 4716; b) Venable T. L., Hutton W. C., Grimes R. N.: *J. Am. Chem. Soc.* **1984**, *106*, 29.
36. Fontaine X. L. R., Kennedy J. D.: *J. Chem. Soc., Chem. Commun.* **1986**, 779.
37. Fontaine X. L. R., Kennedy J. D.: *J. Chem. Soc., Dalton Trans.* **1987**, 1573.
38. See, for example: Beckett M. A., Bown M., Fontaine X. L. R., Greenwood N. N., Kennedy J. D., Thornton-Pett M.: *J. Chem. Soc., Dalton Trans.* **1988**, 1969; and references therein.

39. See, for example: Ferguson G., Kennedy J. D., Fontaine X. L. R., Faridoon, Spalding T. R.: *J. Chem. Soc., Dalton Trans*. **1988**, 2555; and references therein.
40. See, for example: Reed D.: *Chem. Soc. Rev*. **1993**, *22*, 109; and references therein.
41. See, for example: Heřmánek S.: *Inorg. Chim. Acta* **1999**, *289*, 20; and references therein.
42. McFarlane W.: *Proc. R. Soc. London, Ser*. A **1968**, *306*, 185.
43. Otwinowski Z., Minor W.: *Methods Enzymol*. **1997**, *276*, 307.
44. *COLLECT: Data Collection Strategy Program*. Nonius 1999.
45. Sheldrick G. M.: *Acta Crystallogr., Sect. A: Fundam. Crystallogr.* **1990**, *46*, 467.
46. Sheldrick G. M.: *SHELX97, Program System for X-Ray Stucture Refinement*. University of Göttingen, Göttingen 1997.