POLYHEDRAL MONOCARBABORANE CHEMISTRY. A REVIEW OF RECENT DEVELOPMENTS AMONG *C*-ARYL MONOCARBABORANE SYSTEMS

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It is an honour and a pleasure to be able to contribute to this volume dedicated to Professor Jaromír Plešek, not only in recognition of his 75th birthday, but also in recognition of his considerable experimental contributions and intellectual insights into polyhedral boron-containing cluster chemistry, and in recognition of many friendly discussions over the years on chemistry and on the philosophies of science and of life.

The Brellochs Reactions, of *nido*-$B_{10}H_{14}$ with aromatic aldehydes to give [6-Ar-*nido*-6-CB_9H_{11}]$^-$ anions in high yield, now permits excellent entries into *C*-aryl monocarbaborane chemistry, which is reviewed. From [6-Ar-*nido*-6-CB_9H_{11}]$^-$, one-step cluster-closure, cluster-Aufbau, or cluster-dismantling reactions yield [1-Ph-closo-1-$CB_{11}H_{11}$]$^-$, [7-Ph-*nido*-7-$CB_{10}H_{12}$]$^-$, [1-Ph-*closo*-1-CB_9H_9]$^-$, [2-Ph-*closo*-2-CB_9H_9]$^-$, [4-*closo*-4-PhCB_8H_8]$^-$ and [6-Ph-*arachno*-6-CB_8H_{13}]. Second-step reactions involving these products yield [2-Ph-*closo*-2-$CB_{10}H_{10}$]$^-$, [6-Ph-*nido*-6-CB_8H_{11}], [1-Ph-*closo*-1-CB_7H_7]$^-$ and [4-Ph-*closo*-4-CB_8H_8]$^-$, as well as alternative routes to [1-Ph-*closo*-1-$CB_{11}H_{11}$]$^-$ and [1-Ph-*closo*-1-CB_9H_9]$^-$. This readier access to this exten-

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sive suite of *C*-aryl monocarbaboranes permits a readier examination of their derivative chemistry. Monohalogenated and poly-halogenated species [1-Ph-*closo*-1-$CB_9H_{9-n}X_n]^-$ and [1-Ph-*closo*-1-$CB_{11}H_{11-n}X_n]^-$ have been formed as well as (SMe_2)-substituted {CB_{11}} and {CB_{10}} systems. Coupling reactions with *para*-substituted $[XC_6H_4CB_{11}H_{10}X]^-$ systems give rod-like anions, and with poly-iodinated $[PhCB_{11}H_5I_6]^-$ and $[PhCB_9H_4I_5]^-$ give the globular $[PhCB_{11}H_5Ar_5I]^-$ and $[PhCB_9H_4Ar_4I]^-$ anions. Additional interesting species include $[PhCB_{11}H_{10}CH=CHCH_3]^-$, $[PhCB_{11}H_{10}SMe(CH_2)_4OH]^-$ and $[PhCB_9H_8\text{-}6\text{-}OH]^-$. A review with 49 references.

Keywords: Boranes; Carboranes; Monocarbaboranes; Brellochs Reaction; Aldehydes; Rearrangements; Arenes; Cluster-closure reactions.

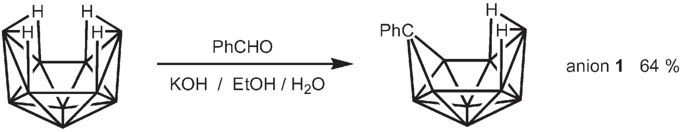
1. INTRODUCTION

Boron and carbon are adjacent in the periodic table. Both form extensive series of hydrides. Because of their polyhedral cluster nature that is fundamentally different to the chain and ring structures of the well known hydrides of carbon, the boranes, *viz*. the hydrides of boron, and their derivatives, have been well examined. Elements other than boron can also be incorporated into the borane cluster structures. The resulting metallaborane, heteroborane and metallaheterocarbaborane chemistries, both realised and potential, are also extensive. Of these last, the known chemistry of the dicarbaboranes – boron-hydride cluster species that also contain two carbon atoms in the polyhedral units – exceeds that of the boron hydrides themselves[1,2]. By contrast, the middle ground of the monocarbaboranes – borane cluster compounds that contain just one carbon atom as cluster constituent – is very sparely investigated compared to its two more richly represented flanking fields of the boranes on one hand and the dicarbaboranes on the other[1]. Reasons for this include that entry into dicarbaborane chemistry *via* the addition of alkynes to decaborane is relatively easy. By contrast, entries into monocarbaborane chemistry have been more difficult, relying principally on one-carbon dismantling reactions from dicarbaboranes, or on cyanide or organyl cyanide addition to borane residues to give *C*-aminated monocarbaboranes which then generally must involve subsequent *C*-deamination protocols for further monocarbaborane chemistry.

The Brellochs Reactions[3], of *nido*-decaborane with formaldehyde to give the [*arachno*-6-$CB_9H_{14}]^-$ anion, with aliphatic aldehydes to give the [6-R-*arachno*-6-$CB_9H_{13}]^-$ anions, and with aromatic aldehydes to give the [6-Ar-*nido*-6-$CB_9H_{11}]^-$ anions, all in high yield, now permit excellent entries into monocarbaborane chemistry[4–7], which, in this review, we exemplify with the *C*-aryl monocarbaborane system. It is convenient to start the summary with the ten-vertex {CB_9} system, since entry to this area is *via* the ten-vertex [6-Ar-*nido*-6-CB_9H_{11}]$^-$ anions that are derived directly from $B_{10}H_{14}$ *via* reaction with aryl aldehydes.

2. TEN-VERTEX *nido* AND *closo* SPECIES

Although the reactions of formaldehyde and aliphatic aldehydes with $B_{10}H_{14}$ in aqueous alkaline solution yield the *arachno* ten-vertex anions [6-CB_9H_{14}]$^-$ and [6-R-6-CB_9H_{13}]$^-$, respectively[4,8], the corresponding reaction with benzaldehyde gives the *nido* [6-Ph-6-CB_9H_{11}]$^-$ anion **1** (Eq. (*1*) below), rather than an *arachno* product[5,6,8]. The structural transformation is represented in Scheme 1. Note that, in the Schemes in this article, unlabelled polyhedral vertices generally represent {BH(*exo*)} units; occasionally, also, carbon-atom vertices are represented by solid black circles.



SCHEME 1

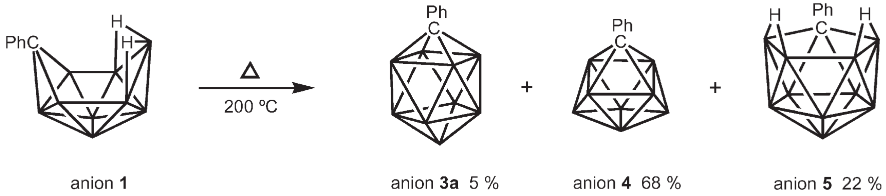
It is thought that the reaction may proceed *via* the nine-vertex [*arachno*-B_9H_{14}]$^-$ anion (Eq. (*2*)), which is well known to derive from *nido*-$B_{10}H_{14}$ under alcoholic aqueous alkaline conditions. Because of the relative infancy the exploitation of the Brellochs Reaction, a more detailed study of this aspect of the reaction chemistry remains as yet incomplete.

$$B_{10}H_{14} + PhCHO + 2\,H_2O + 2\,[OH]^- \rightarrow [PhCB_9H_{11}]^-\,(\mathbf{1}) + [B(OH)_4]^- + H_2 \qquad (1)$$

$$[B_9H_{14}]^- + PhCHO \rightarrow [PhCB_9H_{11}]^-\,(\mathbf{1}) + H_2O + H_2 \qquad (2)$$

The reaction proceeds essentially quantitatively and the anion **1** may be isolated as its [NEt_4]$^+$ salt in yields of 64–94%. The species is characterised crystallographically (Fig. 1)[9,10]. The *para*-tolyl analogue, the [6-(*p*-Tol)-*nido*-6-CB_9H_{11}]$^-$ anion **1a**, has also been isolated, prepared similarly from the reaction of *para*-tolylaldehyde in 65% yield[9]. Another potentially important variant is the *para*-bromophenyl species [1-(*p*-BrC_6H_4)-*closo*-1-CB_9H_{11}]$^-$ (anion **2**), also prepared similarly, now from the reaction with *para*-bromo-benzaldehyde in 69% yield. Anion **2** has use as a building-block precursor for the construction of larger molecular architectures (see, for example, species **30** and **31** in Sections 8 and 10 below).

Solid-state thermolysis of the $[NEt_4]^+$ salt of **1** does not result in simple cluster closure to give a ten-vertex *closo* $[1\text{-Ph-}1\text{-}CB_9H_9]^-$ anion **3a**[5,10]. Rather, disproportionation occurs to give a mixture of the nine-vertex *closo* anion $[4\text{-Ph-}4\text{-}CB_8H_8]^-$ (species **4**; Section 3 below) (68%), and the eleven-vertex *nido* anion $[7\text{-Ph-}7\text{-}CB_{10}H_{12}]^-$ (species **5**; Section 5 below) (22%), with only small quantities of the [1-Ph-*closo*-1-$CB_9H_9]^-$ anion **3a** (*ca* 5%). The structural transformations are represented in Scheme 2.



SCHEME 2

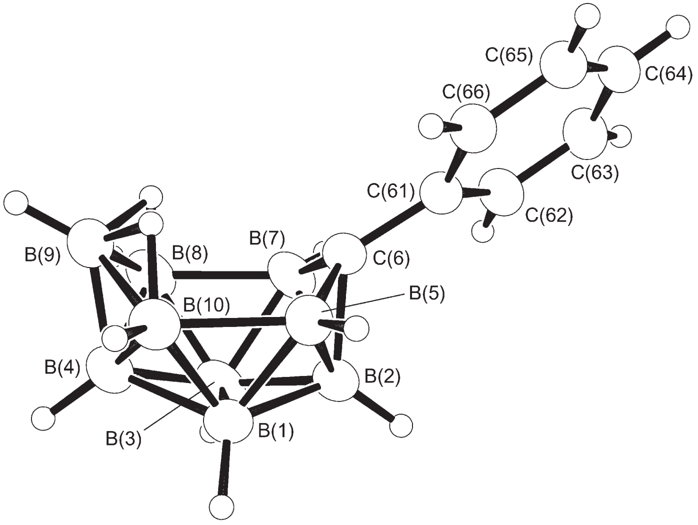


FIG. 1
Crystallographically determined molecular structure of the [6-Ph-*nido*-6-$CB_9H_{11}]^-$ anion **1** as its $[NEt_4]^+$ salt [CCDC 184220]. The C(6)–C(phenyl) distance is 1.492(2) Å, other distances to C(6) being 1.704(2) from B(2), 1.536(2) from B(5) and 1.539(2) Å from B(7)

Larger amounts of ten-vertex **3a** (*ca* 25%) are formed in the reaction between the *nido* anion **1** and [$BH_3(NEt_3)$] without solvent at 210 °C (Scheme 3), but the product is admixed with the twelve-vertex *closo* species [1-Ph-1-$CB_{11}H_{11}$]$^-$ (species **6**; Section 6 below) (*ca* 50%); the two anions **3** and **6** may be separated by fractional crystallisation of their Cs^+ salts. A more convenient preparation of **3a** derives from the heating of the $[NEt_4]^+$ salt of **1** with elemental sodium in tetrahydrofuran solution[9]. The role of the sodium in this ostensibly simple dihydrogen elimination is not clear. The $[NEt_4]^+$ salt of **3a** (74%) may thence be readily separated by converting any remaining starting material anion **1** to the neutral nine-vertex *arachno* derivative [4-Ph-4-CB_8H_{13}] (compound **7**; Section 3 below) (18%) by treatment with the oxidising agent $FeCl_3$ in acidic solution[7]. The [1-Ph-*closo*-1-CB_9H_9]$^-$ anion **3a** has been characterised as its $[NEt_4]^+$ salt (Fig. 2)[9].

A cleaner, essentially quantitative, yield of anion **3a** is obtained by thermal isomerisation from its [2-Ph-*closo*-2-CB_9H_9]$^-$ isomer **3b** (isolated yield of $[NEt_4]^+$ salt of **3a** 94%)[9b,10]. Species **3b** is obtained from the *nido* precursor **1** *via* oxidation with elemental I_2 in aqueous alkaline solution (92%).

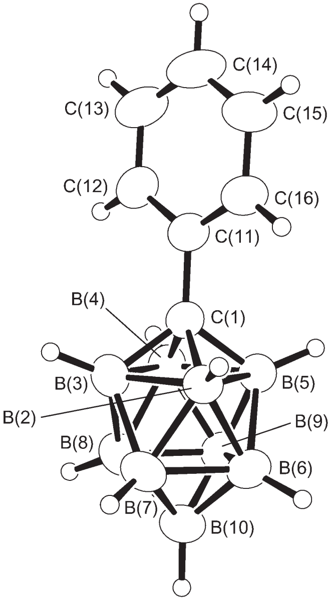
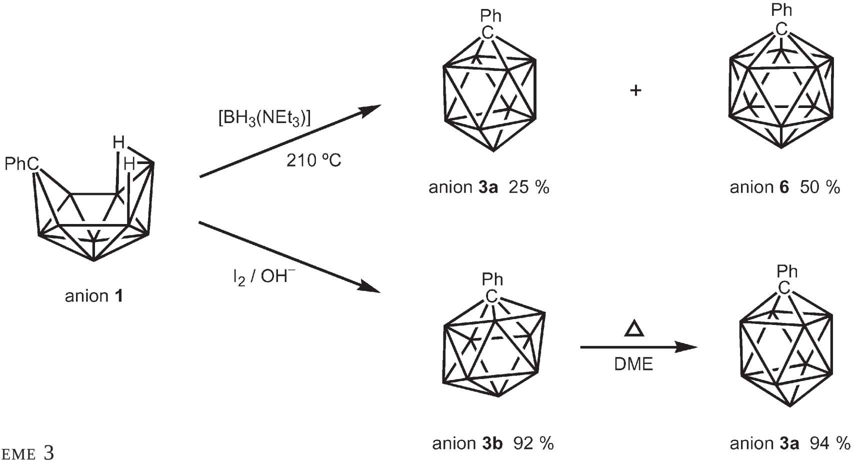


FIG. 2

Crystallographically determined molecular structure of the [1-Ph-*closo*-1-CB_9H_9]$^-$ anion **3a** as its $[NEt_4]^+$ salt [CCDC 164851]. The C(1)–C(phenyl) distance is 1.503(4) Å, the distance to C(1) from the four adjacent boron atoms being 1.613(4), 1.606(4), 1.598(5) and 1.606(4) Å



SCHEME 3

This is also characterised crystallographically as its $[NEt_4]^+$ salt (Fig. 3). It is of interest because positional isomerism of the heteroatom is otherwise unknown in main-group monoheteroboranes (although well established in transition-element metallaborane chemistry)[12,13]. Additional interest arises because halogenation of **3b** followed by isomerisation extends the

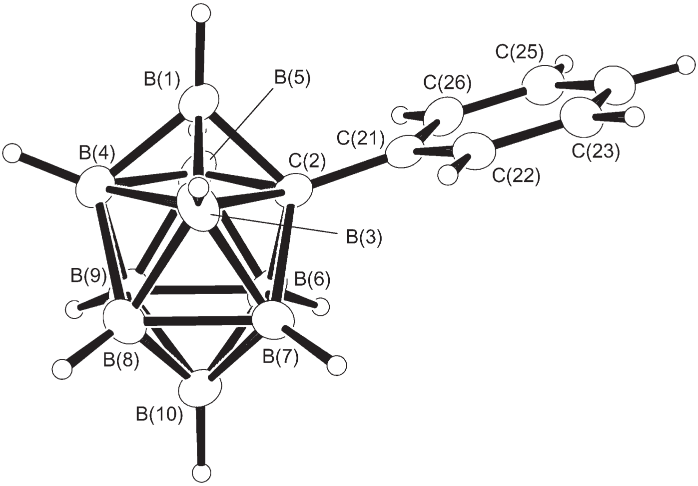


FIG. 3
Crystallographically determined molecular structure of the $[2\text{-Ph-}closo\text{-}2\text{-}CB_9H_9]^-$ anion **3b** as its $[NEt_4]^+$ salt [CCDC 184221]. The C(2)–C(phenyl) distance is 1.498(2) Å, other distances to C(2) being 1.636(3) from B(1), 1.761(3) from B(3), 1.766(3) from B(5), 1.752(3) from B(6) and 1.749(3) Å from B(9)

range of *B*-halogenated derivatives of the [1-Ph-*closo*-1-CB_9H_9]$^-$ congener **3a** (Section 7 below)[9].

The isomerisation of **3b** to **3a** probably proceeds *via* a double-diamond-square-diamond mechanism (DDSD) as discussed below for *B*-halogenated derivatives in Section 7.

3. NINE-VERTEX *arachno, nido* AND *closo* SPECIES

As mentioned above (*e.g.* Scheme 2), the nine-vertex anion [4-Ph-*closo*-4-CB_8H_8]$^-$ (species **4**) is formed in 68% yield from the thermolysis of the [6-Ph-*nido*-6-CB_9H_{11}]$^-$ anion **1**[5]. By-products consist of [7-Ph-*nido*-7-$CB_{10}H_{12}$]$^-$ (anion **5**) and [1-Ph-*closo*-1-CB_9H_9]$^-$ (anion **3a**). It may be that a cleaner higher-yield route to anion **4** could derive from an oxidative treatment of neutral [4-Ph-*arachno*-4-CB_8H_{13}] or neutral [1-Ph-*nido*-1-CB_8H_{11}] (compounds **7** and **8**, see below), but that has not yet been investigated. A drawing of the molecular structure of the [4-Ph-*closo*-4-CB_8H_8]$^-$ anion **4**, as determined crystallographically, is given in Fig. 4. In accord with general

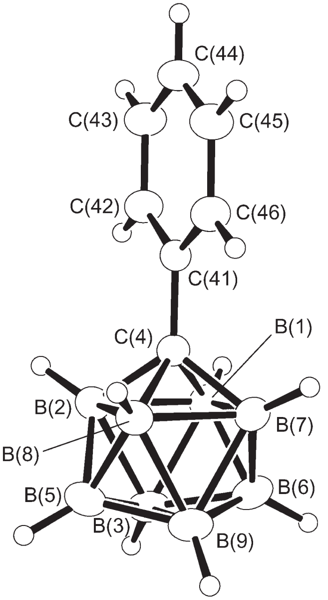
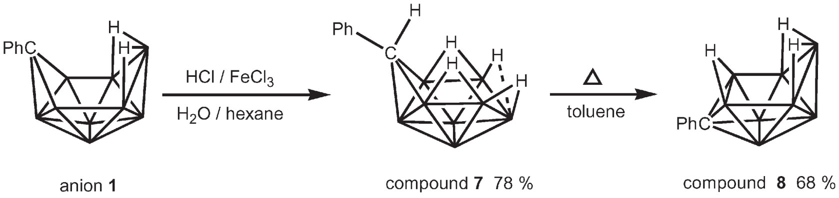


FIG. 4

Crystallographically determined molecular structure of the [4-Ph-*closo*-4-CB_8H_8]$^-$ anion **4** as its [NEt_4]$^+$ salt [CCDC 164852]. The C(4)–C(phenyl) distance is 1.490(2) Å, other distances to C(4) being 1.623(2) from B(1), 1.622(2) from B(2), 1.620(2) from B(7) and 1.623(2) Å from B(8) behaviour of carbaborane cluster species[14], the carbon atom takes a position of lower cluster-connectivity four. In contrast to the ten-vertex *closo* systems (anions **3a** and **3b** (Section 2 above)), but in accord with observations on the eight- and seven-vertex *closo* congeners **9** and **10** (Section 4 below), there is so far no evidence of the alternative [1-Ph-*closo*-1-$CB_8H_8]^-$ isomer which would have the carbon atom in a position of cluster-connectivity five.

The neutral nine-vertex species [4-Ph-*arachno*-4-CB_8H_{13}] (compound **7**) is obtained in 78% yield by treatment of the [6-Ph-*nido*-6-$CB_9H_{11}]^-$ anion **1** with the oxidising agent $FeCl_3$ in acidic solution (Eq. (*3*) and Scheme 4, left).



SCHEME 4

Compound **7** also arises in 22% yield from the reaction of [BH_3(thf)] with the *nido* [6-Ph-6-$CB_9H_{11}]^-$ anion **1**, followed by treatment with $FeCl_3$ [9]. The last reaction yields the eleven-vertex [7-Ph-*nido*-7-$CB_{10}H_{12}]^-$ anion **5** (Section 5 below) as the predominant product (40%). Compound **7** is a white solid, m.p. 74 °C, but has not been characterised crystallographically. NMR spectroscopy indicates a conventional nine-vertex *arachno* configuration, a conclusion supported by the results of DFT calculations (Fig. 5)[11a].

$$[PhCB_9H_{11}]^- (\mathbf{1}) + 2\,Fe^{3+} + 3\,H_2O \rightarrow [PhCB_8H_{13}]\,(\mathbf{7}) + [B(OH)_3] + 2\,Fe^{2+} + H^+ \quad (3)$$

The structure of its *nido* congener [1-Ph-*nido*-1-CB_8H_{11}] (compound **8**), a colourless oil, has similarly been established by DFT calculations in the absence of a structure derived from a single-crystal diffraction analysis (Fig. 6)[11a]. Compound **8** can be prepared in 78% yield by a simple thermolytic dehydrogenation of its *arachno* precursor **7** in refluxing toluene solution (Scheme 4, right). It has been long recognised that this type of nine-vertex *arachno* to *nido* conversion does not simply involve a connectivity closure across the open face, and therefore must also involve a skeletal rearrangement[1]; this is apparent from a comparison of the carbon positions

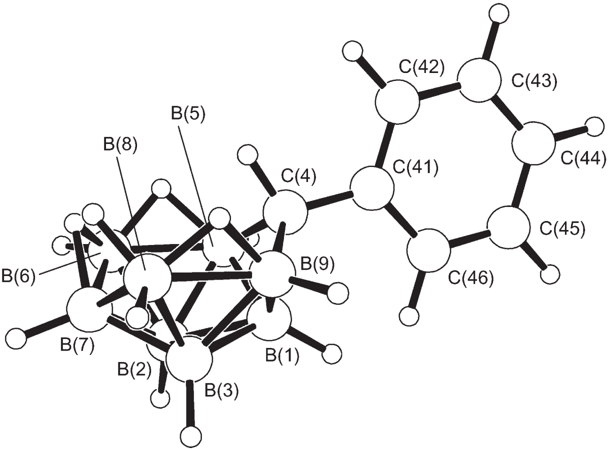


FIG. 5
Molecular structure of neutral [4-Ph-*arachno*-4-CB_8H_{13}] (compound **7**) as derived from DFT calculations at the B3LYP/6-31G* level. The C(4)–C(phenyl) distance is 1.450 Å, with the other distances from C(4) being 1.669 to B(1), 1.735 to B(5) and 1.724 Å to B(9). The molecule is fluxional with respect to exchange of character between the inner-sphere bridging and the *endo*-terminal hydrogen atoms associated with the B(6)B(7)B(8) "notch" site on the open face, so the molecule on time-average appears as if it has a mirror plane in solution, exhibiting a 2 : 2 : 2 : 1 : 1 relative-intensity pattern in the ^{11}B NMR spectrum

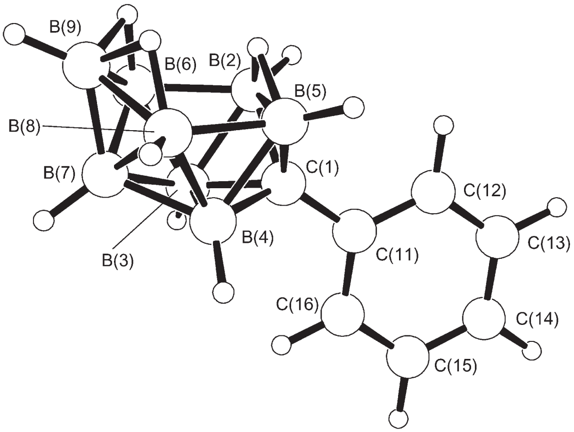


FIG. 6
Molecular structure of neutral [1-Ph-*nido*-1-CB_8H_{11}] (compound **8**) as derived from DFT calculations at the B3LYP/6-31G* level. The C(1)–C(phenyl) distance is 1.450 Å, with the other distances from C(1) being 1.605 to B(2), 1.611 to B(3), 1.611 to B(4) and 1.605 Å to B(5)

in the skeletal geometries in Figs 5 and 6, and within Scheme 4. The *arachno* nine-vertex compound **7** is also precursor to the *C*-phenylated eight- and seven-vertex monocarbaborane species as summarised in the next section.

4. EIGHT-VERTEX AND SEVEN-VERTEX *closo* SPECIES

Cluster dismantling by the loss of either one or two boron vertices can be induced by the action of the nucleophilic base NEt_3 upon either of the neutral species [4-Ph-*arachno*-4-CB_8H_{13}] (compound **7**) or [1-Ph-*nido*-1-CB_8H_{11}] (compound **8**)[6]. In refluxing toluene, NEt_3 and the *nido* species **8** give predominantly the eight-vertex anion [1-Ph-*closo*-1-CB_7H_7]$^-$ (species **9**) which may be precipitated out of the product mixture in 72% yield as its $[NEt_4]^+$ salt. This precipitation and subsequent recrystallisation clears it from residual quantities of the seven-vertex congener anion [2-Ph-*closo*-2-CB_6H_6]$^-$ (species **10**) which is present to the extent of about 5% in the reaction mixture. The eight-vertex species **9** has been characterised by single-crystal X-ray diffraction analysis (Fig. 7). As with the unsubstituted parent $[CB_7H_8]^-$

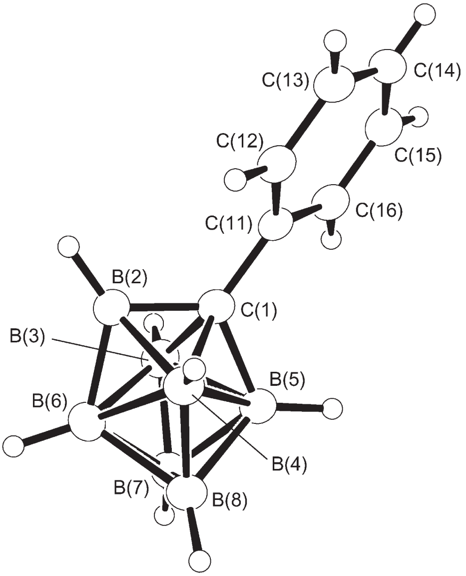
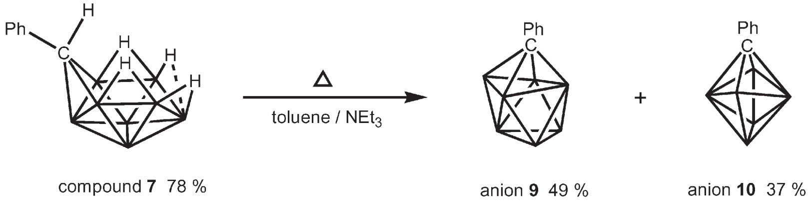


FIG. 7
Crystallographically determined molecular structure of the [1-Ph-*closo*-1-CB_7H_7]$^-$ anion **9** as its $[NEt_4]^+$ salt [CCDC 172016]. The C(1)–C(phenyl) distance is 1.484(2) Å, with the other distances from C(1) being 1.528(2) to B(2), 1.723(2) to B(3), 1.716(2) to B(4) and 1.622(2) Å to B(5)

anion, and in accord with general observations in carbaborane chemistry, the carbon atom occupies a position of low cluster-connectivity four. In contrast to the $[PhCB_9H_9]^-$ system above (species **3a** and **3b** (Section 2 above)), there is no evidence for an alternative isomer in which the carbon atom occupies a position of cluster-connectivity five, but the isolation of such a species is unlikely in an unconstrained system in view of the well-recognised fluxionality of the eight-vertex *closo* cluster[15–18].

Use of the *arachno* species **7**, rather than the *nido* species **8**, in the toluene thermolysis with NEt_3 gives an enhanced proportion of the seven-vertex *closo* anion [2-Ph-*closo*-2-CB_6H_6]$^-$ (species **10**; 37%) at the expense of the eight-vertex [1-Ph-*closo*-1-CB_7H_7]$^-$ congener **9** (49%)[9]. The skeletal geometries of **7**, **9** and **10** are represented in Scheme 5.



SCHEME 5

Salts of anion **10** have not been sufficiently separated from those of anion **9** to give a pure bulk sample of a salt of anion **10**, but a clean mixture of the two is evident from NMR spectroscopy. The NMR experiments clearly identify the $[PhCB_6H_6]^-$ anion **10** as its 2-isomer, with the structure being substantiated by DFT calculations from which the predicted ^{11}B NMR nuclear shieldings match those observed experimentally[11a]. There are also clear parallels with Štíbr's recently reported unsubstituted parent *closo* $[HCB_6H_6]^-$ anion[19]. The calculated structure is shown in Fig. 8, although here it may be noted that, since the original preparation of this manuscript, the molecular structure of anion **10** has been determined crystallographically[11b]. That both the eight- and seven-vertex anions **9** and **10** are obtained from these reactions with NEt_3 in toluene suggests that appropriate modifications of base and reaction conditions may further enhance either the formation of the anion **9** *versus* anion **10**, or *vice versa*, but this type of developmental work has not yet been carried out in this *C*-phenylated system.

5. ELEVEN-VERTEX *nido* AND *closo* SPECIES

As mentioned above (Section 2), the eleven-vertex *nido* anion [7-Ph-7-$CB_{10}H_{12}]^-$ (species **5**) results from the solid-state thermolysis of the $[NEt_4]^+$ salt of the [6-Ph-*nido*-6-$CB_9H_{11}]^-$ anion **1**, and may be isolated in 22% yield from that process[5,10]. A more designed synthesis results from the Aufbau reaction of $[BH_3(thf)]$ with anion **1** (Eq. (*4*), where L is tetrahydrofuran)[10].

$$[nido\text{-}PhCB_9H_{11}]^- \ (\mathbf{1}) + [BH_3L] \rightarrow [nido\text{-}PhCB_{10}H_{12}]^- \ (\mathbf{5}) + H_2 + L \qquad (4)$$

$$[nido\text{-}PhCB_{10}H_{12}]^- \ (\mathbf{5}) + [BH_3L] \rightarrow [closo\text{-}PhCB_{11}H_{11}]^- \ (\mathbf{6}) + 2\ H_2 + L \qquad (5)$$

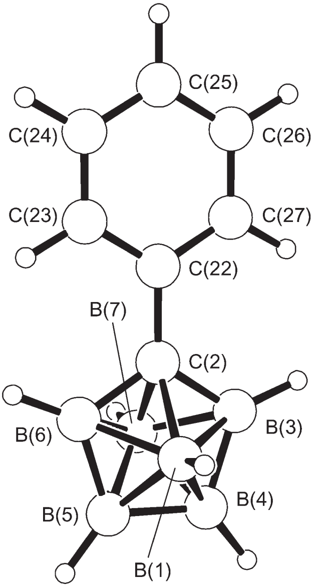
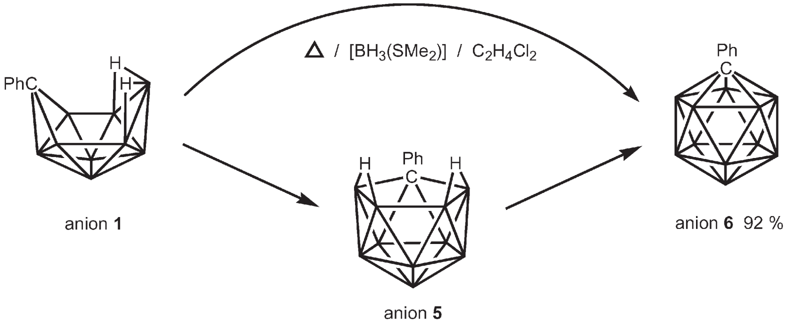


FIG. 8

Molecular structure of the [2-Ph-*closo*-2-$CB_6H_6]^-$ anion **10** as derived from DFT calculations at the B3LYP/6-31G* level. Selected dimensions in Å are as follows: C(2)–C(phenyl) 1.518, C(2)–B(1) 1.753, C(2)–B(3) 1.538, C(2)–B(6) 1.538 and C(2)–B(7) 1.753, with interboron distances 1.611 to 1.798 Å. Since the original submission of this manuscript, the structure of this anion has now been determined crystallographically in its $[NEt_4]^+$ salt [CCDC 184222][11b], with C(2)–C(phenyl) 1.492(2), C(2)–B(1) 1.744(2), C(2)–B(3) 1.559(2), C(2)–B(6) 1.555(2) and C(2)–B(7) 1.736(2), with interboron distances 1.645(3) to 1.825(3) Å

However, this is an intermediate step in a two-step quasi-cascade process that ultimately results in the formation of the twelve-vertex [1-Ph-*closo*-1-$CB_{11}H_{11}$]$^-$ anion **6** (Eq. (*5*), where L is thf; see also Scheme 6), and conditions must be chosen to minimise the presence of **6** in the product mixture; the presence of the starting *nido* anion **1** in the product mixture is not so critical as this can be removed by conversion to neutral [1-Ph-*arachno*-1-CB_8H_{13}] (compound **7**) by treatment with aqueous acidic $FeCl_3$ (Section 3 above) followed by extraction into a non-polar organic solvent.

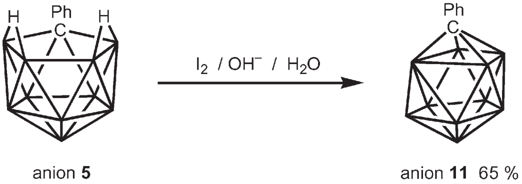


SCHEME 6

The best conditions so far obtained for reaction (*4*) are a heating at reflux temperature in $C_2H_4Cl_2$ solution for 48 hours, followed by the $FeCl_3$ treatment. This yields neutral compound **7** (22%), which is removed as just described, and the target anion **5** may thence be isolated in 40% yield as its $[NEt_4]^+$ salt, albeit contaminated with *ca* 10 mole % of anion **6** [10]. It is difficult to free anion **5** from anion **6**, as the two anions are quasi-isomorphous. In this regard the $[NEt_4]^+$ salts are in fact isomorphous crystallographically. Both have space group $P\ 2_1/c$, $Z = 4$, and their unit cell dimensions are essentially identical. The converse problem can arise in the preparation of [1-Ph-*closo*-1-$CB_{11}H_{11}$]$^-$ (anion **6**) by the route of Eq. (*5*), in which it is difficult to clear contamination from anion **5** (Section 6 below); in this case, however, it is feasible to drive the reaction to completion. The quasi-isomorphology of the {$PhCB_{10}H_{12}$}-based and {$PhCB_{11}H_{11}$}-based skeletons is also apparent in the SMe_2-ligated systems in Section 11 below (Fig. 32).

The crystallographically determined molecular structure of the [7-Ph-*nido*-7-$CB_{10}H_{12}$]$^-$ anion **5** (Fig. 9) clearly shows the *nido* eleven-vertex cluster geometry with two interboron bridging hydrogen atoms on the open face. In principle, deprotonation at one of these sites should yield the corresponding {$PhCB_{10}H_{11}$}$^{2-}$ dianion, which, *via* differential solubility *versus* the twelve-vertex monoanion **6**, would provide a means of mutual decontamination of the *nido* eleven-vertex and *closo* twelve-vertex systems. In common with its all-boron [*nido*-$B_{11}H_{13}$]$^{2-}$ equivalent, however, the [$PhCB_{10}H_{12}$]$^{-}$ unit **5** is resistant to deprotonation in aqueous solution[10].

Anion **5** is, however, amenable to oxidation, and reaction with elemental I_2 in aqueous alkaline solution results in cluster closure to give the eleven-vertex *closo* congener [2-Ph-*closo*-2-$CB_{10}H_{10}$]$^{-}$ (anion **11**; 65%)[6]. The gross structural aspects of the reaction are represented in Scheme 7.



SCHEME 7

The non-phenylated analogue [*closo*-2-$CB_{10}H_{11}$]$^{-}$ has long been known, and results from the reaction of the sodium salt of a proposed [$CB_{10}H_{11}$]$^{3-}$ anion in thf, also with elemental iodine[15]. The crystallographically determined molecular structure of anion **11** (Fig. 10) shows that the carbon atom adopts the 2-position of lowest cluster-connectivity four. As also in the "parent" anion [*closo*-$CB_{10}H_{11}$]$^{-}$, and the all-boron analogue, the

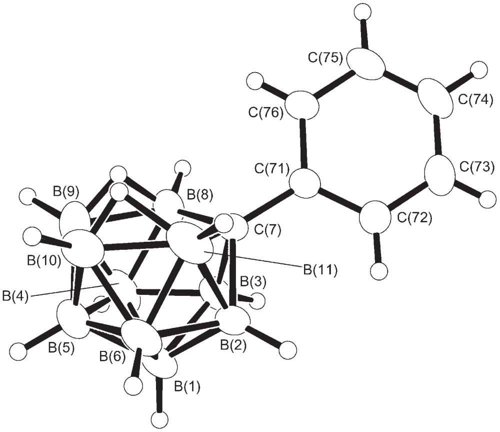


FIG. 9
Crystallographically determined molecular structure of the [7-Ph-*nido*-7-$CB_{10}H_{12}$]$^{-}$ anion **5** as its [NEt_4]$^{+}$ salt [CCDC 184222]. The C(7)–C(phenyl) distance is 1.506(2) Å, with the other distances from C(7) being 1.686(3) to B(2), 1.693(3) to B(3), 1.680(3) to B(8) and 1.656(3) Å to B(11)

[*closo*-$B_{11}H_{11}$]$^{2-}$ anion[18,20,21], the eleven-vertex *closo* cluster of anion **11** is fluxional in solution with respect to interchange of all the boron sites. As with the [$PhCB_7H_7$]$^-$ system (anion **9**; Section 3 above), therefore, but in contrast to the [$PhCB_9H_9$]$^-$ system (anions **3a** and **3b**; Section 2 above), isolation of other *C*-positional isomers is unlikely in an unconstrained system.

6. THE *closo* TWELVE-VERTEX SYSTEM

This system is of particular contemporary interest. Because of the "least-coordinating anion" nature of {CB_{11}} monoanionic moieties, the twelve-vertex [*closo*-$CB_{11}H_{12}$]$^-$ anion **14** and its substituted derivatives have received a relatively higher attention than other polyhedral monocarbaboranes over the last pentadecade or so[22–24]. However, *C*-aryl substitution has until recently been elusive. The *C*-phenylated derivative [1-Ph-*closo*-1-$CB_{11}H_{11}$]$^-$ (anion **6**; Fig. 11) can be prepared by two basic routes: Firstly by Aufbau on the ten-vertex [6-Ph-*nido*-6-CB_9H_{11}]$^-$ anion **1**, using [$BH_3(NEt_3)$] or [$BH_3(SMe_2)$] essentially according to Eqs (*4*) and (*5*) (see also Scheme 6 above)[5,10], or, secondly by phenylcarbene insertion into the eleven-vertex [*nido*-$B_{11}H_{14}$]$^-$ anion by treatment with NaH in thf solution followed by addition of a mixture of $PhCHCl_2$ and EtOH [25]. A third route, well established for dicarbaboranes, *via* *C*-metallation of the parent unsubstituted [$CB_{11}H_{12}$]$^-$

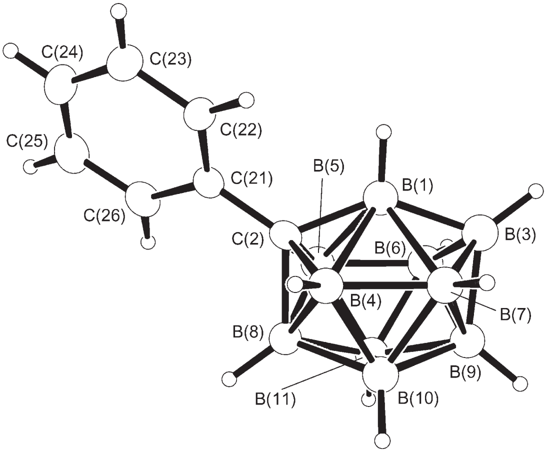


FIG. 10

Crystallographically determined molecular structure of the [2-Ph-*closo*-2-$CB_{10}H_{10}$]$^-$ anion **11** as its [NEt_4]$^+$ salt [CCDC 172017]. The C(2)–C(phenyl) distance is 1.492(3) Å, with the other distances to C(2) being 1.643(3) to B(1), 1.584(3) to B(4), 1.593(2) to B(5) and 1.676(3) Å to B(8) anion followed by aryl coupling, might offer possibilities, but this has not yet been reported.

The reaction between the ten-vertex *nido* anion **1** and [$BH_3(NEt_3)$] in the absence of solvent to yield the *closo* twelve-vertex anion **6** (*ca* 50%) is mentioned above (Section 2). However, these reaction conditions also engender a competing cluster closure to give the ten-vertex [1-Ph-*closo*-1-CB_9H_9]$^-$ anion **3a** (*e.g.* Scheme 3 above)^5. A fractional crystallisation of the Cs^+ salts of anions **3a** and **6** is thence required to separate the two products. A cleaner conversion (92%) is afforded by the use of [$BH_3(SMe_2)$] in $C_2H_4Cl_2$ as solvent (Eqs (*4*) and (*5*) above, where L is SMe_2; see also Scheme 6 above)^{10}. The route has also been used to generate the *para*-brominated [1-(*p*-BrC_6H_4)-*closo*-1-$CB_{11}H_{11}$]$^-$ anion **12** (Fig. 12) *via* the [6-(*p*-BrC_6H_4)-*nido*-6-CB_9H_{11}]$^-$ anion **2** (Section 9), and is in principle extendable to an extensive *C*-substituent chemistry *via* choices of appropriate aldehydes in the initial Brellochs Reaction with $B_{10}H_{14}$ ^{9}. This consideration also of course applies to *C*-substituent chemistry in all the monocarbaborane systems above and below.

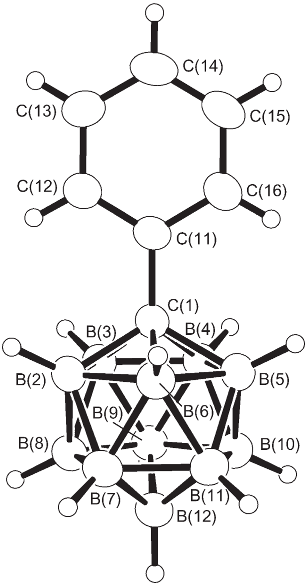


FIG. 11

Crystallographically determined molecular structure of the [1-Ph-*closo*-1-$CB_{11}H_{11}$]$^-$ anion **6** as its [NEt_4]$^+$ salt [CCDC 164850]. The C(1)–C(phenyl) distance is 1.512(3) Å, with the distances from C(1) to its five adjacent boron atoms ranging from 1.715(3) to 1.730(4) Å

7. HALOGENO DERIVATIVES OF THE TEN-VERTEX *closo*-SYSTEM

As mentioned above, because of their globular nature and their even surface-charge distributions, the ten-vertex and twelve-vertex *closo* anions $[CB_9H_{10}]^-$ and $[CB_{11}H_{12}]^-$ (anions **13** and **14**, respectively) have attracted much attention because of their properties as "least coordinating anions" and thence their abilities to act as counter-anions in highly acidic systems[22–24]. Within this interest, halogenation and poly-halogenation have been relatively well examined as a means of tuning these anionic properties, though, in systems reported so far, much more so for the twelve-vertex system than for the ten-vertex system. In the ten-vertex case[23], electrophilic halogenation occurs initially at the 6-position of the $[1\text{-}CB_9H_{10}]^-$ anion, "*meta*" to the carbon site; di-halogenation gives predominantly the "*di-meta*" $[1\text{-}CB_9H_8\text{-}6,8\text{-}X_2]^-$ anions, although the 6,7 "*di-meta*" isomers are also formed along with smaller amounts of the "*meta para*" 6,10 species. Penta-halogenation with chlorine and bromine gives $[1\text{-}CB_9H_5\text{-}$

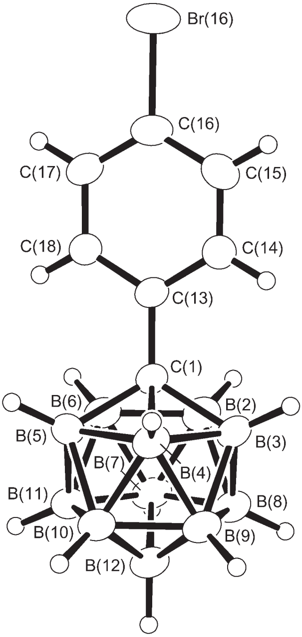
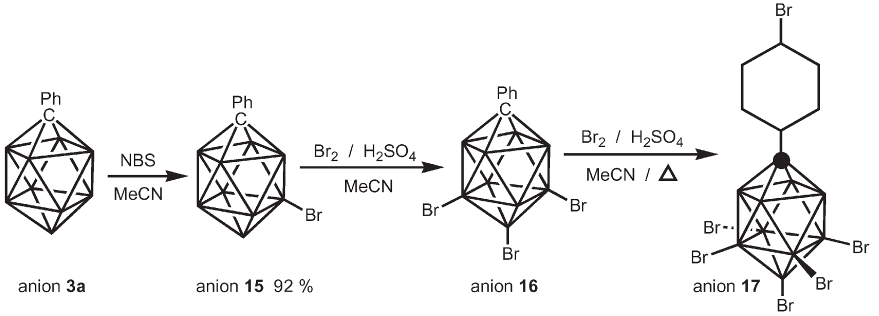


FIG. 12

Crystallographically determined molecular structure of the $[1\text{-}(p\text{-}BrC_6H_4)\text{-}closo\text{-}1\text{-}CB_{11}H_{11}]^-$ anion **12** as its $[NEt_4]^+$ salt [CCDC 184223]. The C(1)–C(aryl) distance is 1.506(4) Å, with the distances from C(1) to its five adjacent boron atoms ranging from 1.716(5) to 1.721(4) Å. The bromine–C(phenyl) distance is 1.895(3) Å

6,7,8,9,10-$X_5]^-$ with the "*meta*" belt and the *para* site completely halogenated[21]. Estimation of relative electrophilic susceptibilities *via* relative rates of D^+/H^+ exchange[23] suggests that tri-halogenation may favour the "*para di-meta*" [1-CB_9H_7-6,8,10-$X_3]^-$ isomer, although it seems likely that the isomer specificity would be lower. Tetra-halogenation would then yield predominantly [1-CB_9H_6-6,7,8,10-$X_4]^-$. These findings seem to be mirrored in the bromination and iodination of the 1-*C*-phenylated [1-Ph-*closo*-1-$CB_9H_9]^-$ anion **3a** (Scheme 8), although there is a perception that the BH sites of **3a** may be somewhat deactivated towards (presumably electrophilic) halogenation compared to the non *C*-phenylated parent anion **13** [9].



SCHEME 8

Thus, bromination of the anion **3a** using a stoichiometric quantity of *N*-bromosuccinimide in CH_3CN at room temperature gives the [1-Ph-*closo*-1-CB_9H_8-6-Br$]^-$ anion **15**, isolatable as its $[NEt_4]^+$ salt in 92% yield (Fig. 13). More forcing conditions involving elemental bromine and H_2SO_4 in CH_3CN as solvent result in a mixture of mono-, di- and tri-brominated species, from which a sample of the tri-brominated isomer [1-Ph-*closo*-1-CB_9H_6-6,8,10-$Br_3]^-$ (anion **16**) has been isolated by crystallisation as its $[NEt_4]^+$ salt (Fig. 14)[9a].

A large excess of elemental bromine with anion **3a** under the same conditions results in the hexa-brominated anion [1-(*p*-BrC_6H_4)-*closo*-1-CB_9H_4-6,7,8,9,10-$Br_5]^-$ (species **17**; Fig. 15), isolatable in 77% yield as its $[NEt_4]^+$ salt as a white solid[9]. As with the non *C*-phenylated [*closo*-1-CB_9H_5-6,7,8,9,10-$X_5]^-$ analogue anions, where X_5 = Cl_5 or Br_5, mentioned above, there is a clean halogenation of the "*para*" 10-position together with the four "*meta*" 6, 7, 8 and 9 positions, with no significant halogenation of the four-boron belt adjacent to the cluster carbon atom in the 1-position. Interestingly, however, these conditions also brominate the *para*-positioned carbon atom of the *C*-phenyl unit of anion **3a**. It seems likely that, with appropriate choice of stoichiometry and conditions, the di- and tetra-brominated members of the [1-Ph-*closo*-1-$CB_9H_{9-n}Br_n]^-$ family will also be isolatable.

Poly-iodination with elemental I_2 under the same conditions is not so effective, but use of an excess of ICl generates the penta-iodo derivative [1-Ph-*closo*-1-CB_9H_4-6,7,8,9,10-$I_5]^-$ (anion **18**; Fig. 16). In contrast to the bromination referred to in the previous paragraph, no significant iodination of the aromatic unit is observed[9,26]. Anion **18** is a useful intermediate for the polyarylation of the *C*-phenylated ten-vertex *closo*-1-carbadecaborane cluster as summarised below (Section 7).

The preference for initial halogenation at the "*meta*" 6-position of the [1-Ph-*closo*-1-$CB_9H_9]^-$ parent anion **3a** at present precludes the synthesis directly from **3a** of the antipodal "*para*" 10-halogenated [1-Ph-*closo*-1-CB_9H_8-10-X]$^-$ anions which would be synthetically more useful and interesting in terms of currently popular initiatives. These 10-halogenated species can, however, be obtained *via* the isomerisation of the 7-halogenated derivatives of the [2-Ph-*closo*-2-$CB_9H_9]^-$ anion **3b** (*e.g.* Scheme 9)[9,10].

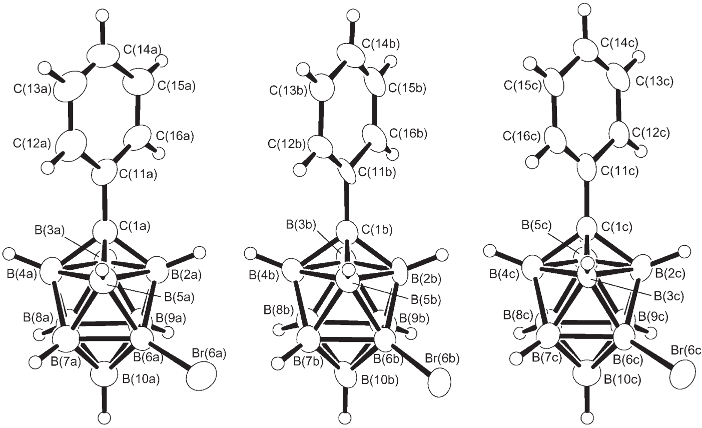
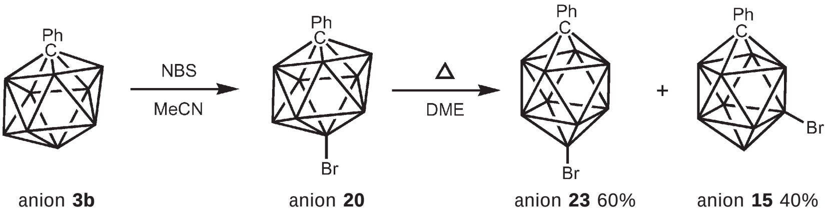


FIG. 13

Crystallographically determined molecular structure of the [1-Ph-*closo*-1-CB_9H_8-6-Br]$^-$ anion **15**, as determined in its $[NEt_4]^+$ salt [CCDC 184224]. There are three crystallographically independent anions in the unit cell. The C(1a)–C(phenyl) distance is 1.464(11) Å, with the other distances from C(1a) being 1.588(11) to B(2a), 1.604(12) to B(3a), 1.625(11) to B(4a) and 1.605(10) Å to B(5a). The C(1b)–C(phenyl) distance is 1.504(11) Å, with the other distances from C(1b) being 1.618(11) to B(2b), 1.603(11) to B(3b), 1.622(10) to B(4b) and 1.608(12) Å to B(5b). The C(1c)–C(phenyl) distance is 1.480(11) Å, with the other distances from C(1c) being 1.634(10) to B(2c), 1.596(10) to B(3c), 1.625(10) to B(4c) and 1.621(11) Å to B(5c)



SCHEME 9

These 7-halogenated species [2-Ph-*closo*-2-CB_9H_8-7-Cl]$^-$ (anion **19**), [2-Ph-*closo*-2-CB_9H_8-7-Br]$^-$ (anion **20**) and [2-Ph-*closo*-2-CB_9H_8-7-I]$^-$ (anion **21**) are obtained *via* the halogenation of the parent anion **3b** using stoichiometric amounts of the relevant *N*-halogenosuccinimide in CH_3CN at room temperature, and may be isolated as their $[NEt_4]^+$ salts in yields of 85% (anion **19**), 89% (anion **20**) and 90% (anion **21**). Small quantities of the 10-halogen-

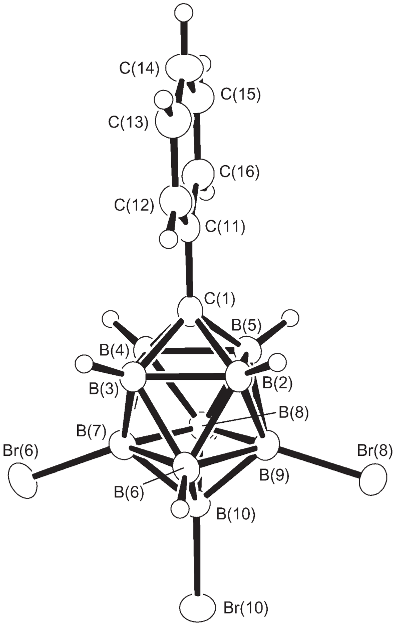


FIG. 14

Crystallographically determined molecular structure of the [1-Ph-*closo*-1-CB_9H_6-6,8,10-Br_3]$^-$ anion **16**, as determined in its $[NEt_4]^+$ salt [CCDC 184225]. The C(1)–C(phenyl) distance is 1.494(5) Å, with the other distances from C(1) being 1.606(5) to B(2), 1.622(5) to B(3), 1.615(5) to B(4) and 1.612(5) Å to B(5). The B(7) distance to Br(6) is 1.973(4), the B(9) distance to Br(8) is 1.986(4) and the B(10) distance to Br(10) is 1.946(4) Å ated species [2-Ph-*closo*-2-CB_9H_8-10-X]$^-$ are also present in the crude product mixtures, but, at the time of writing, these have not yet been reported in a pure state. The 7-bromo compound **20** has been characterised crystallographically (Fig. 17). It is interesting that the directional activation at the "lower" four-boron belt, resulting in 7-substitution, mimics that of the 1-carbaborane **3a** discussed above. That it is the distal β-positioned B(7) site of **3b** that is activated, rather than the adjacent α-site, may imply that this could be a β-activation phenomenon rather than a general lower-belt activation, both for the 1-carbaborane **3a** and the 2-carbaborane **3b**.

Empirical structural observations in carbaborane chemistry have always involved a perception that configurations in which the carbon atoms adopt the position of lower cluster connectivity are more stable[14]. In accord with

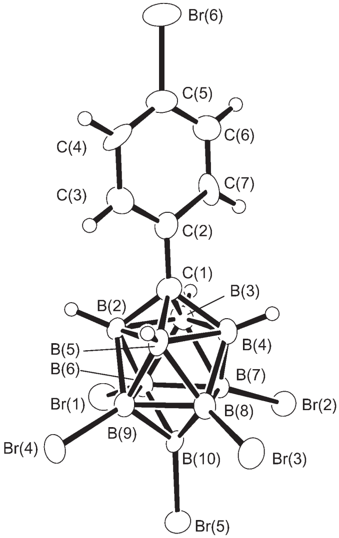


FIG. 15

Crystallographically determined molecular structure of the [1-(*p*-BrC_6H_4)-*closo*-1-CB_9H_4-6,7,8,9,10-Br_5]$^-$ species **17**, as determined in its $[NEt_4]^+$ salt [CCDC 184226]. There are two crystallographically independent anions in the unit cell. The C(1a)–C(phenyl) distance is 1.448(12) Å, with the other distances from C(1a) being 1.620(15) to B(2a), 1.611(16) to B(3a), 1.569(15) to B(4a) and 1.717(5) Å to B(5a). Distances to bromine are as follows: from B(6a) 1.953(12), from B(7a) 1.954(11), from B(8a) 1.947(12), from B(9a) 1.954(11), from B(10a) 1.915(11) and from C(5a) 1.908(7) Å. The C(1b)–C(phenyl) distance is 1.711(18) Å, with the other distances to C(1b) being 1.566(19) to B(2b), 1.540(20) to B(3b), 1.610(20) to B(4b) and 1.600(20) Å to B(5b). Distances to bromine are as follows: from B(6b) 1.964(14), from B(7b) 1.974(15), from B(8b) 1.962(16), from B(9b) 1.952(13), from B(10b) 1.928(18) and from C(5b) 1.723(10) Å this, heating of the non-substituted [2-Ph-*closo*-2-CB_9H_9]$^-$ isomer **3b** generates [1-Ph-*closo*-1-CB_9H_9]$^-$ (isomer **3a**) *via* a probable DDSD mechanism as mentioned above (Section 2)[9]. Concomitantly, the 7-halogenated *closo*-2-carbadecaborane species give *closo*-1-carbadecaboranes upon heating under reflux in 1,2-dimethoxyethane (DME) overnight[9,10]. The chlorides, bromides and iodides (compounds **19**, **20** and **21**) have been examined, and two products are formed in each case: the 10-halogenated species [1-Ph-*closo*-1-CB_9H_8-10-X]$^-$, where X = Cl, Br or I (compounds **22**, **23**, and **24**, respectively) together with the 6-halogenated species [1-Ph-*closo*-1-CB_9H_8-6-X]$^-$, where X = Cl, Br or I (compounds **25**, **15** and **26**, respectively, as described above). The 10-halogenated species arise (see Scheme 10) when the DDSD process involves the halogenated boron atom (schematics **I**) in which two initial diamonds are defined by {B(1)C(2)B(3)B(6)} and {B(3)B(6)B(7)B(10)} (bold lines in schematic **IA**). The 6-substituted spe-

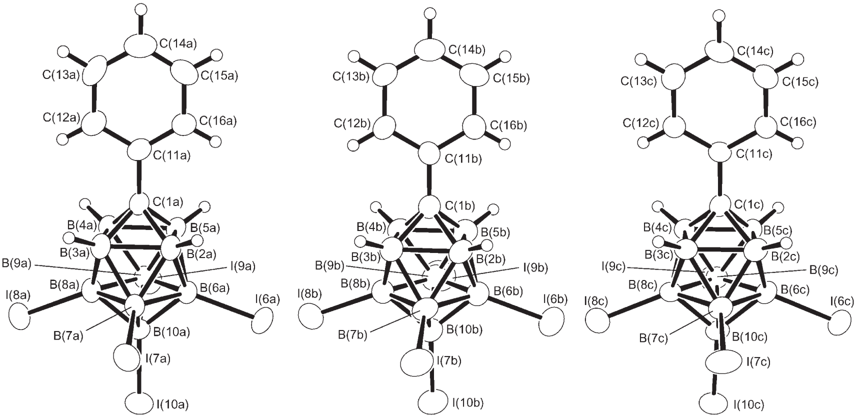
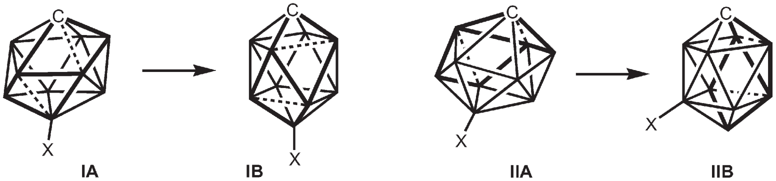


FIG. 16

Crystallographically determined molecular structure of the [1-Ph-*closo*-1-CB_9H_4-6,7,8,9,10-I_5]$^-$ anion **18**, as determined in its $[NEt_4]^+$ salt [CCDC 184227]. There are three crystallographically independent anions in the unit cell. The C(1a)–C(phenyl) distance is 1.492(11) Å, with the other distances from C(1a) being 1.610(10) to B(2a), 1.618(10) to B(3a), 1.603(10) to B(4a) and 1.601(10) Å to B(5a). Distances to iodine are as follows: from B(6a) 2.171(7), from B(7a) 2.172(7), from B(8a) 2.161(8), from B(9a) 2.177(8) and from B(10a) 2.135(4) Å. The C(1b)–C(phenyl) distance is 1.481(11) Å, with the other distances from C(1b) being 1.621(12) to B(2b), 1.608(12) to B(3b), 1.602(13) to B(4b) and 1.599(12) Å to B(5b). Distances to iodine are as follows: from B(6b) 2.167(9), from B(7b) 2.164(9), from B(8b) 2.166(9), from B(9b) 2.176(10) and from B(10b) 2.142(9) Å. The C(1c)–C(phenyl) distance is 1.482(9) Å, with the other distances from C(1c) being 1.611(10) to B(2c), 1.608(10) to B(3c), 1.603(9) to B(4c) and 1.613(9) Å to B(5c). Distances to iodine are as follows: from B(6c) 2.184(7), from B(7c) 2.169(7), from B(8c) 2.134(8), from B(9c) 2.169(7) and from B(10c) 2.126(8) Å cies arises from the otherwise equivalent process in which all the boron sites in the DDSD process are non-halogenated (schematics **II**), *i.e.* the two initial diamonds are defined by {B(1)C(2)B(5)B(9)} and {B(5)B(9)B(8)B(10)} (bold lines in schematic **IIA**).



SCHEME 10

Since only one of these DDSD arrangements involves the *B*-halogenated vertex, differential activation energies are to be expected, so that the relative proportions of the two product isomers are not necessarily equal and should also in principle vary as the halogen changes among Cl, Br and I. In accord with this, the ratio of 6-substituted to 10-substituted isomers for the chloride, bromide and iodide are approximately 70 : 30, 60 : 40 and 50 : 50, respectively. Since the 10-substituted isomers are not available by direct halogenation of the [1-Ph-*closo*-1-CB_9H_9]$^-$ anion **3a**, this at present constitutes the only route to these species, though in the general case separation

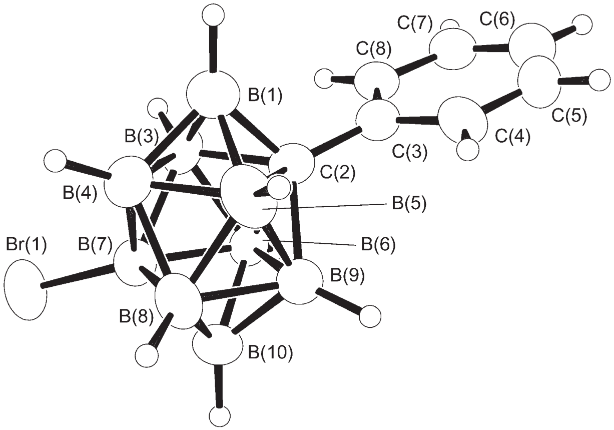


FIG. 17
Crystallographically determined molecular structure of the [2-Ph-*closo*-2-CB_9H_8-7-Br]$^-$ anion **20**, as determined in its [NEt_4]$^+$ salt [CCDC 184228]. The C(2)–C(phenyl) distance is 1.494(10) Å, with the other distances from C(2) being 1.657(11) to B(1), 1.7443(10) to B(3), 1.791(11) to B(5), 1.741(10) to B(6) and 1.748(10) Å to B(9). The B(7)–Br(1) distance is 1.975(8) Å

of the two isomers may be difficult. Fractional crystallisation from the iodinated system consisting of the $[NEt_4]^+$ salts of the 6-substituted and 10-substituted isomers **26** and **24** has, however, resulted in the isolation of $[1\text{-Ph-}closo\text{-}1\text{-}CB_9H_8\text{-}10\text{-}I]^-$ (anion **24**) in 44% yield (Fig. 18). Such a "*para*" iodinated species constitutes a potentially useful synthon for the generation of extended chain and rod-like molecular architectures in which there is current interest[27–30].

An additional 6-substituted 1-phenyl-*closo*-1-carbadecaborane that is convienent to deal with in this Section is the 6-hydroxy-substitued species $[1\text{-Ph-}closo\text{-}1\text{-}CB_9H_8\text{-}6\text{-}OH]^-$ (anion **28**)[9]. This species was formed by oxidation of $[1\text{-Ph-}closo\text{-}1\text{-}CB_9H_9]^-$ (anion **3a**) with $KMnO_4$ in 10% H_2SO_4 in an unsuccessful attempt oxidatively to fuse two *closo* $[PhCB_9H_9]^-$ clusters together in an analogous manner to the reported oxidative fusion of two binary borane $[B_{10}H_{10}]^{2-}$ anions to give the binuclear $[B_{20}H_{18}]^{4-}$ species[31]. It was isolated in 42% yield as its $[NEt_4]^+$ salt. Its crystallographically determ-

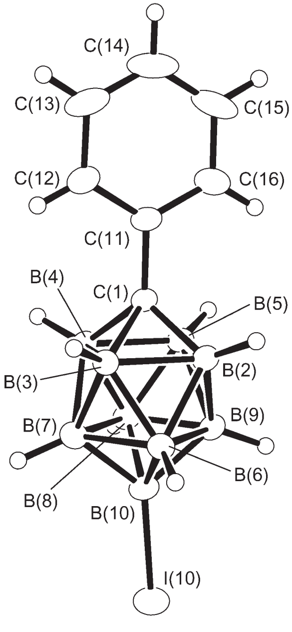


FIG. 18
Crystallographically determined molecular structure of the $[1\text{-Ph-}closo\text{-}1\text{-}CB_9H_8\text{-}10\text{-}I]^-$ anion **24**, as determined in its $[NEt_4]^+$ salt [CCDC 184229]. The C(1)–C(phenyl) distance is 1.486(7) Å, with the other distances from C(1) being 1.611(7) to B(2), 1.614(7) to B(3), 1.615(7) to B(4) and 1.614(7) Å to B(5). The B(10)–I(10) distance is 1.163(6) Å

ined structure (Fig. 19) clearly demonstrates that the {CB_9} cage is substituted in the 6-position by the hydroxy group.

8. HALOGENO DERIVATIVES OF THE TWELVE-VERTEX *closo*-SYSTEM

Halogenation and thence further substituent chemistry of the *C*-unsubstituted twelve-vertex [*closo*-$CB_{11}H_{12}$]$^-$ anion is much more extensively investigated than that of the corresponding *C*-unsubstituted ten-vertex [*closo*-CB_9H_{10}]$^-$ species[24,32–34]. Conversely, of the corresponding *C*-phenylated systems reviewed here, the twelve-vertex system based on [1-Ph-*closo*-1-$CB_{11}H_{11}$]$^-$ (anion **6**) is not at present as extensively examined as the ten-vertex systems involving anions **3a** and **3b** summarised above in Section 7.

The twelve-vertex anion **6** appears to be less reactive towards electrophilic halogenation than its unsubstituted [$CB_{11}H_{12}$]$^-$ parent, but hexahalogenation occurs upon treatment with excess bromine in acetic acid at 110 °C for 3 days, to give the [1-Ph-*closo*-1-$CB_{11}H_5$-7,8,9,10,11,12-Br_6]$^-$

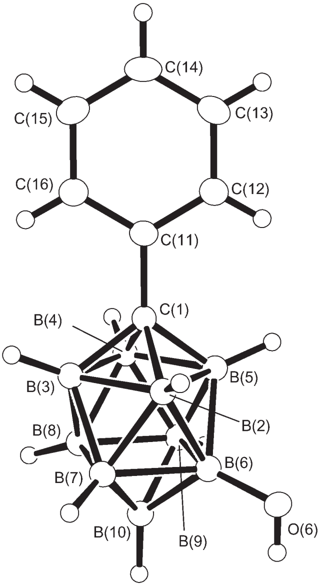
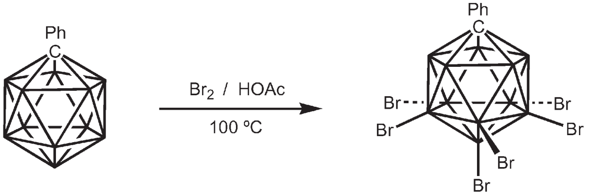


FIG. 19
Crystallographically determined molecular structure of the [1-Ph-*closo*-1-CB_9H_8-6-(OH)]$^-$ anion **28**, as determined in its [NEt_4]$^+$ salt [CCDC 184230]. The C(1)–C(phenyl) distance is 1.4948(17) Å, with the other distances from C(1) being 1.6121(19) to B(2), 1.6126(19) to B(3), 1.6199(19) to B(4) and 1.6116(18) Å to B(5). The B(6)–O(6) distance is 1.4226(7) Å

anion (species **29**), isolatable in 75% yield as its $[NEt_4]^+$ salt (Scheme 11)[9]. In contrast to the poly-bromination of ten-vertex **3a** under similar conditions, to give *para*-halogenation of the phenyl unit as well as cluster bromination, in the formation of [1-(*p*-BrC_6H_4)-*closo*-1-CB_9H_4-6,7,8,9,10-$Br_5]^-$ (anion **17**; Fig. 15 above), no aromatic bromination of the phenyl group of the twelve-vertex species has been observed.



anion **6** anion **29** 86 %

SCHEME 11

This difference in behaviour may imply differential activation of the aromatic ring by the $\{CB_9\}$ *versus* $\{CB_{11}\}$ units. In this regard there may be differential cluster-to-phenyl bonding characteristics: for example there appears to be a small but significant trend of the diminution of the C(cluster)–C(phenyl) distance across the series of anions $[PhCB_nH_n]^-$ as n decreases, with the crystallographically determined distances being 1.512(3), 1.492(3), 1.503(4), 1.498(2), 1.490(2) and 1.484(2) for n = 11 (anion **6**), 10 (anion **11**), 9 (anions **3a** and **3b**), 8 (anion **4**) and 7 (anion **9**), respectively[11a].

In the twelve-vertex system, bromination occurs at the 12-position antipodal to the carbon atom, and at the five adjacent "lower belt" boron sites, positions 7–11. There is no indication of bromination at the "upper belt" adjacent to the carbon atom under these conditions. The halogenation occurs initially at the antipodal 12-position, as confirmed in the mono-iodination under milder conditions of [1-(*p*-BrC_6H_4)-*closo*-1-$CB_{11}H_{11}]^-$ (anion **12**). Thus, treatment of anion **12** with an excess of iodine in acetic acid at 110 °C for 48 hours, gives the [1-(*p*-BrC_6H_4)-*closo*-1-$CB_{11}H_{10}$-12-I$]^-$ anion **30**, isolatable in 78% as its $[NEt_4]^+$ salt. Anion **30** has been used in further substituent chemistry *via* bromine and iodine replacement, for example in the formation of the rod-like anion [1-(*p*-Tol-C_6H_4)-*closo*-1-$CB_{11}H_{10}$-12-(*p*-Tol)$]^-$ (species **31**) mentioned below (Section 10)[9,35].

The sequence of halogenation, initially at the 12-position, and then at the five adjacent sites in the "lower belt" distant from the carbon atom, is in accord with observations made on the halogenation of the non-phenylated $[CB_{11}H_{12}]^-$ anion[32]. Extended halogenation under more forcing conditions thence gives the undeca-halogenated $[HCB_{11}X_{11}]^-$ species[36], but higher than a hexa-halogenation of the cluster has not been yet achieved for the *C*-phenylated system reviewed here. Under conditions of shorter reaction times for the poly-bromination of anion **6**, a penta-brominated derivative [1-Ph-*closo*-1-$CB_{11}H_6$-7,8,9,10,12-$Br_5]^-$ (anion **32**) has been isolated and characterised crystallographically as its $[NEt_4]^+$ salt (Fig. 20)[9]. In this species the initial halogenation at the antipodal 12-position has occured, but halogenation of only four out of the five boron atoms of the adjacent belt has taken place. The relatively high yield of 86% suggests a higher activation energy for the halogenation of the final site in the lower 7,8,9,10,11 belt.

Similar results to the poly-bromination occur in the poly-iodination of anion **6** under very closely related conditions[9]. Thus, reaction with ICl in CH_3COOH solution at 110 °C for 3 days resulted in the formation of the hexa-iodinated species [1-Ph-*closo*-1-$CB_{11}H_5$-7,8,9,10,11,12-$I_6]^-$ (anion **33**),

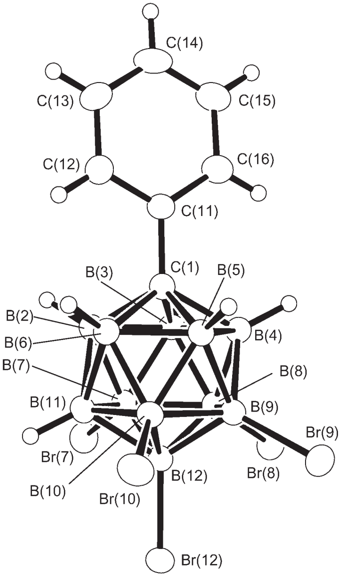


FIG. 20

Crystallographically determined molecular structure of the [1-Ph-*closo*-1-$CB_{11}H_6$-7,8,9,10,12-$Br_5]^-$ anion **32**, as determined in its $[NEt_4]^+$ salt [CCDC 184231]. The C(1)–C(phenyl) distance is 1.515(5) Å, with the other distances from C(1) being 1.721(5) to B(2), 1.719(5) to B(3), 1.724(5) to B(4), 1.717(5) to B(5) and 1.729(5) Å to B(6). Distances to bromine are as follows: from B(8) 1.961(4), from B(9) 1.951(4), from B(10) 1.950(4), from B(7) 1.961(4) and from B(12) 1.947(4) Å isolated in 78% yield as its $[NEt_4]^+$ salt (Fig. 21). As with the hexa-bromide, the antipodal 12-position and all atoms in the adjacent “lower belt” were iodinated, with no evidence for upper-belt halogenation. All of the five lower-belt halogen atoms, but not the antipodal one, can be replaced by aryl substituents, as reviewed below in Section 9 (*e.g.* Fig. 28).

Also in parallel with the bromination, the penta-iodo analogue of the penta-bromo anion **32**, *viz.* the [1-Ph-*closo*-1-$CB_{11}H_6$-7,8,9,10,12-$I_5]^-$ anion **34**, may be isolated after shorter reaction times[9]. Thus a 48-hours heating of anion **6** in CH_3COOH with excess ICl resulted the formation of anion **34**, isolatable as its $[NEt_4]^+$ salt in 87% yield (Fig. 22); the structural similarity with the penta-bromo analogue (Fig. 20) is apparent.

Another parallel with the bromo system is that, under milder conditions, the mono-iodoinated species [1-Ph-*closo*-1-$CB_{11}H_{10}$-12-$I]^-$ (anion **35**) can be synthesised. Treatment of anion **6** with elemental I_2, rather than ICl, in CH_3COOH at 110 °C for 18 h gave this mono-iodinated anion **35**, isolatable

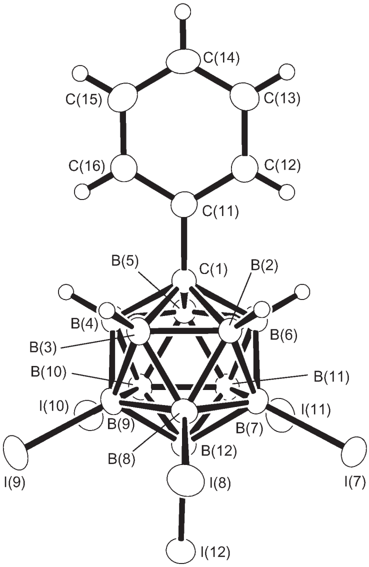


FIG. 21
Crystallographically determined molecular structure of the [1-Ph-*closo*-1-$CB_{11}H_5$-7,8,9,10,11,12-$I_6]^-$ anion **33**, as determined in its $[NEt_4]^+$ salt [CCDC 184232]. The C(1)–C(phenyl) distance is 1.513(6) Å, with the other distances from C(1) being 1.711(7) to B(2), 1.715(7) to B(3), 1.719(7) to B(4), 1.726(7) to B(5) and 1.724(7) Å to B(6). Distances to iodine are as follows: from B(7) 2.163(5), from B(8) 2.153(6), from B(9) 2.170(5), from B(10) 2.171(5), from B(11) 2.164(5) and from B(12) 2.153(5) Å

as its Cs^+ salt in 78% yield (Scheme 14, Section 10 below). Anion **35** is useful for further substituent chemistry *via* iodine replacement reactions (again, see Section 10 below)[7].

9. *B*-ARYLATED DERIVATIVES OF THE *closo* TEN-VERTEX SYSTEM

The mono-halogenated and poly-halogenated anions derived from the [1-Ph-*closo*-1-$CB_9H_9]^-$ anion **3a** and its 2-isomer **3b** (Section 7 above) in principle provide routes into extensive substituent chemistries *via* halogen replacement reactions. However, this potentiality has been explored in only one system so far. This is the reaction between the penta-iodinated species [1-Ph-*closo*-1-CB_9H_4-6,7,8,9,10-$I_5]^-$ (anion **18**; Fig. 16 above) and a large excess of the *para*-tolyl Grignard reagent *p*-TolMgBr in the presence of $[PdCl_2(PPh_3)_2]$. This results in tetra-arylation to give the [1-Ph-*closo*-

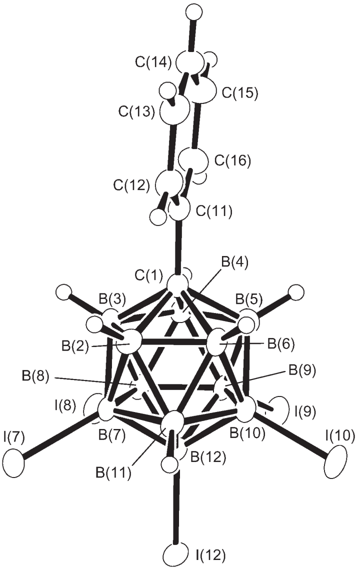
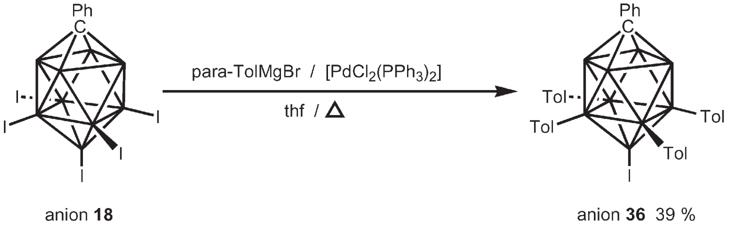


FIG. 22
Crystallographically determined molecular structure of the [1-Ph-*closo*-1-$CB_{11}H_6$-7,8,9,10,12-$I_5]^-$ anion **34**, as determined in its $[NEt_4]^+$ salt [CCDC 184233]. The C(1)–C(phenyl) distance is 1.507(8) Å, with the other distances from C(1) being 1.713(9) to B(2), 1.639(8) to B(3), 1.730(8) to B(4), 1.642(8) to B(5) and 1.668(8) Å to B(6). The other boron–iodine distances are: from B(7) 2.084(6), from B(8) 2.087(6), from B(9) 2.124(6), from B(10) 2.025(6) and from B(12) 2.159(6) Å

1-CB_9H_4-10-I-6,7,8,9-(*p*-Tol)$_4$]$^-$ anion **36** (Fig. 23)^{26}. Complete arylation occurs around the "lower belt" at the 6, 7, 8 and 9 positions, but the antipodal 10-iodinated site remains unsubstituted (Scheme 12).



SCHEME 12

A similar phenomenon is observed in the formation of the twelve-vertex {CB_{11}} congener [1-Ph-*closo*-1-$CB_{11}H_5$-12-I-7,8,9,10,11-(*p*-Tol)$_5$]$^-$ (anion **37**) dealt with in Section 10 below. This non-participation by the antipodal sites could be due to a different cluster activation behaviour for this reaction to that observed in the simpler electrophilic halogenations reviewed in Sections 7 and 8 above, and could also involve a sterical inaccessibility of

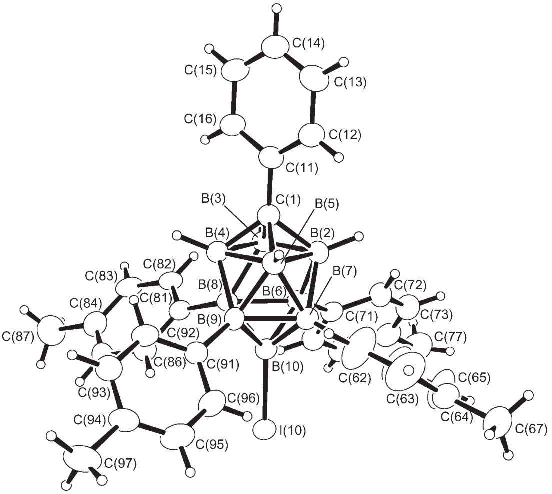


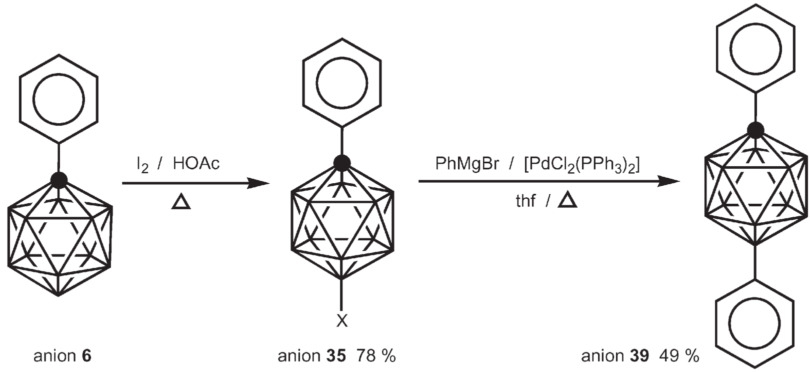
FIG. 23

Crystallographically determined molecular structure of the [1-Ph-*closo*-1-CB_9H_4-10-I-6,7,8,9-(*p*-Tol)$_4$]$^-$ anion **36**, as determined in a salt with the [Pd_2I_2{P(*p*-Tol)$_3$}$_4$]$^{2+}$ dication **38** [CCDC 184234]. The C(1)–C(aryl) distance is 1.492(7) Å, with the other distances from C(1) being 1.617(7) to B(2), 1.596(7) to B(3), 1.600(7) to B(4) and 1.616(7) Å to B(5). The other boron–carbon distances are: B(6) to C(61) 1.583(7), B(7) to C(71) 1.583(7), B(8) to B(81) 1.587(7) and B(9) to C(91) 1.589(7) Å. The boron–iodine distance B(10) to I(10) is 2.179(6) Å the antipodal iodinated site as it becomes progressively more shielded as its adjacent "lower belt" boron atoms are successively arylated. The large stereochemical bulk of the iodine atoms themselves may also inhibit access at the antipodal site of anion **18**.

An interesting co-product of this reaction is the halogen-bridged binuclear $[Pd_2I_2\{P(p\text{-Tol})_3\}_4]^{2+}$ dication (species **38**) resulting from (i) the replacement of chloride in the starting $[PdCl_2(PPh_3)_2]$ by iodide, and, more interestingly, from (ii) the replacement of all the phenyl groupings on the phosphines by *para*-tolyl groupings originating from the excess *para*-tolyl Grignard reagent. Anion **36** is isolatable from the reaction mixture as its salt with cation **38** in 39% yield. In the solid state there is an interesting interionic association in which cation **38** is intimately sandwiched between two anions **36** [26]. An association may persist in solution, as the [**36**]$_2$[**38**] salt is chromatographically quite mobile. A corresponding sandwiching phenomenon also occurs between cation **38** and the twelve-vertex $\{CB_{11}\}$-based anion **37** mentioned in the following section.

10. *B*-ARYLATED DERIVATIVES OF THE *closo* TWELVE-VERTEX SYSTEM

Compared to the nine-vertex system, there has been relatively much more interest in the substitution chemistry of the twelve-vertex $\{closo\text{-}CB_{11}\}$ system, principally derived from an interest in fine-tuning the "least coordinating" anionic properties that this system possesses[22–24,33,34]. Within this context, however, *B*-arylation of $\{closo\text{-}CB_{11}\}$ clusters, other than recent reports on the *C*-arylated systems reviewed here, has received scant attention. The various *B*-halogenated species summarised in Section 8 above, however, now permit *B*-arylation *via* halogen displacement using organometallic reagents, and results are now emerging from this approach.



SCHEME 13

Treatment of the antipodally mono-halogenated *closo* twelve-vertex anion [1-Ph-*closo*-1-$CB_{11}H_{10}$-12-I]$^-$ (anion **35**; Section 8 above) with phenyl Grignard reagent in the presence of [$PdCl_2(PPh_3)_2$] in refluxing thf solution gives the 12-phenylated [1-Ph-*closo*-1-$CB_{11}H_{10}$-12-Ph]$^-$ anion (species **39**), isolatable as its Cs^+ salt in 49% yield (Scheme 13)^7. The overall structure has been examined by a single-crystal X-ray diffraction analysis of its [NEt_4]$^+$ salt (Fig. 24), but the extreme similarities of the *C*-phenyl and *B*-phenyl ends of the molecule engender a crystallographic disorder such that the two phenylated ends of the anion are crystallographically indistinguishable.

No such crystallographic disorder should be observed in the mixed aryl species [1-Ph-*closo*-1-$CB_{11}H_{10}$-12-(*p*-Tol)]$^-$ (anion **40**), which may be prepared in 44% yield by the treatment of the iodinated anion **35** with *para*-tolyl Grignard reagent instead of phenyl. However, a crystallographic investigation of anion **40** has not yet been reported, although its constitution

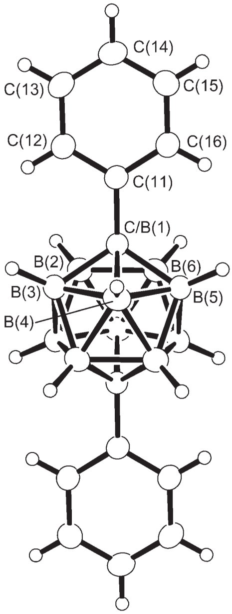
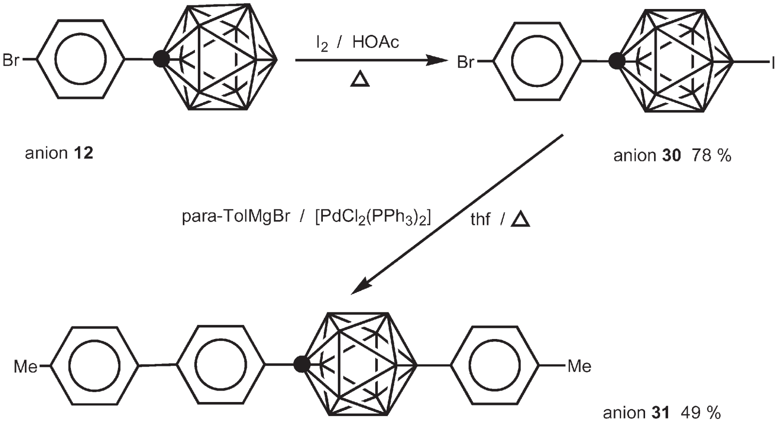


FIG. 24
Crystallographically determined molecular structure of the [1-Ph-*closo*-1-$CB_{11}H_{10}$-12-Ph]$^-$ anion **39**, as determined in its [NEt_4]$^+$ salt [CCDC 172018/184235]. Because of the similarities of the *C*-phenyl and *B*-phenyl ends of the molecule, they are not distinguished crystallographically. The disordered C(1)/B(1)–C(phenyl) distance is 1.5525(15) Å, with the other distances from C(1)/B(1) being 1.7499(17) to B(2), 1.7515(17) to B(3), 1.7601(18) to B(4), 1.7550(17) to B(5) and 1.7555(17) Å to B(6)

confirms the sequence of addition and verifies an absence of any aryl group scrambling between C(1) and B(12) sites during the reaction process.

An alternative synthetic route to the [1-Ph-*closo*-1-$CB_{11}H_{10}$-12-Ph]$^-$ anion **39**, more directly from the non-halogenated precursor [*closo*-1-$CB_{11}H_{11}$-12-Ph]$^-$ anion **14a**, is to treat anion **14a** firstly with BuLi, followed secondly by $ZnCl_2$, and thence followed thirdly by PhI in the presence of palladium(0) or palladium(II) in an "inverse-Negishi" coupling[37]. No information on yield is yet available. The exploitation of these and other related coupling reactions, *e.g.* for the preparation of compounds **36** and **37** as summarised above, together with **31** and **43a** as summarised below, promise much new interesting molecular architecture.

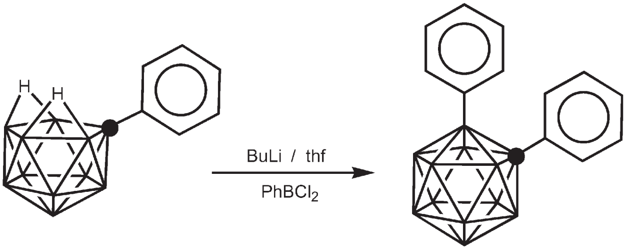


SCHEME 14

There is interest in rod-shaped molecules that incorporate carbaborane and borane cluster units[27–30,35]. The rod-shaped aspect of the monocarbaborane chemistry demonstrated by anions **39** and **40** is extended in the *para*-arylated species [1-(*p*-Tol-C_6H_4)-*closo*-1-$CB_{11}H_{10}$-12-(*p*-Tol)]$^-$ (anion **31**). This is prepared by the reaction in tetrahydrofuran of the *para*-tolyl Grignard reagent *p*-TolMgBr with the *C*-bromo, *B*-iodo species [1-(*p*-Br-C_6H_4)-*closo*-1-$CB_{11}H_{10}$-12-I]$^-$ (anion **30**) mentioned above in Section 8. The reaction is carried out in the presence of [$PdCl_2(PPh_3)_2$] (Scheme 14), and anion **31** may be isolated as its [NEt_4]$^+$ salt in 43% yield from this system. The rod-shaped molecule measures 20.1 Å between the methyl hydrogen-atom centres of the extreme *para*-tolyl groups, implying an overall van der Waals length of some 22.7 Å from tip to tip (Fig. 25).

In principle 1,2-isomers and 1,7-isomers of these 1,12-diarylated anions are possible, but only "*ortho*" 1,2-diarylated species have been synthesised at the time of writing. These require a different preparative protocol than for the "*para*" 1,12 species. Thus, rather than *B*-substitution on the preformed twelve-vertex $\{CB_{11}\}$ skeleton, a pre-arylated boron atom is inserted into the *nido* eleven-vertex $\{CB_{10}\}$ cage of [7-Ph-*nido*-7-$CB_{10}H_{12}]^-$ (anion **5**; Section 2 above, Fig. 9) or [7-(*p*-Tol)-*nido*-7-$CB_{10}H_{12}]^-$ (anion **5a**).

Thus, reaction of anion **5** in tetrahydrofuran solution with BuLi, followed by addition of $PhBCl_2$, formed the [1-Ph-*closo*-1-$CB_{11}H_{10}$-2-Ph$]^-$ anion (species **41**), which has been isolated in 78% yield as its $[NEt_4]^+$ salt (Scheme 15). Because of the geometric similarities of the B-phenylated and *C*-phenylated sites, the X-ray diffraction analysis of anion **41** (Fig. 26) is subject to a similar disorder problem to that encountered for its 1,12 isomer **39** (Fig. 24 above)[9].



anion **5**

anion **41** 78 %

SCHEME 15

As, in principle, with the 1,12-substituted system, this disorder problem is in this case removed by the formation of the mixed diarylated species [1-(*p*-Tol)-*closo*-1-$CB_{11}H_{10}$-2-Ph$]^-$ (anion **42**; Fig. 27 below). This is synthe-

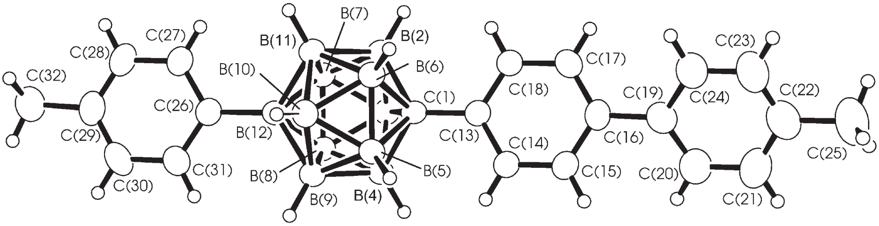


FIG. 25

Crystallographically determined molecular structure of the [1-(*p*-$TolC_6H_4$)-*closo*-1-$CB_{11}H_{10}$-12-(*p*-Tol)$]^-$ anion **31**, as determined in its $[NEt_4]^+$ salt [CCDC 184236]. The C(1)–C(biaryl) distance is 1.511(4) Å, with the other distances from C(1) being 1.725(4) to B(2), 1.729(4) to B(3), 1.725(4) to B(4), 1.728(4) to B(5) and 1.723(4) Å to B(6). The boron–aryl distance B(12) to C(26) is 1.591(4) Å. The rod-shaped molecule measures 20.1 Å between the methyl hydrogen-atom centres of the extreme *para*-tolyl groups, implying an overall van der Waals length of some 22.7 Å from tip to tip

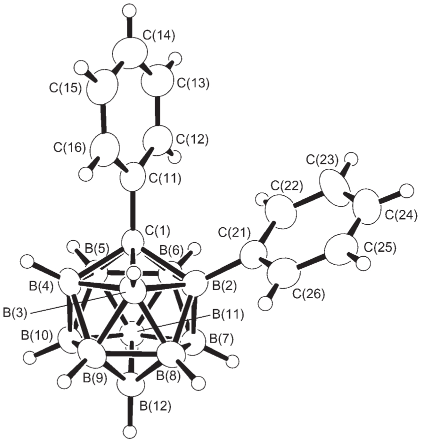


FIG. 26
Crystallographically determined molecular structure of the [1-Ph-*closo*-1-$CB_{11}H_{10}$-2-Ph]$^-$ anion **41**, as determined in its $[NEt_4]^+$ salt [CCDC 184237]. The C(1)–C(phenyl) distance is 1.524(3) Å, with the other distances from C(1) being 1.730(3) to B(2), 1.727(3) to B(3), 1.734(3) to B(4), 1.743(3) to B(5) and 1.757(3) Å to B(6). The B(2)–C(phenyl) distance is 1.558(3) Å

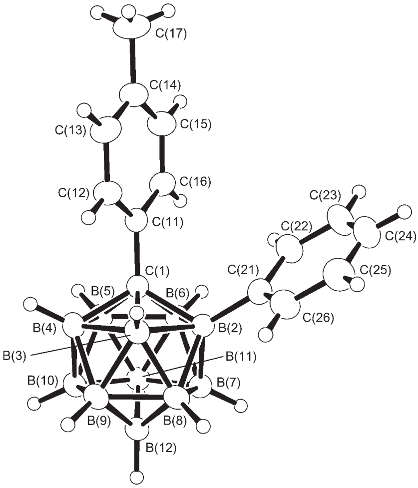


FIG. 27
Crystallographically determined molecular structure of the [1-*p*-Tol-*closo*-1-$CB_{11}H_{10}$-2-Ph]$^-$ anion **42**, as determined in its $[NEt_4]^+$ salt [CCDC 184238]. The C(1)–C(11) distance is 1.510(3) Å, with the other distances from C(1) being 1.754(3) to B(2), 1.714(3) to B(3), 1.724(3) to B(4), 1.722(3) to B(5) and 1.730(3) Å to B(6). The B(2)–C(21) distance is 1.575(3) Å

sised by the use of the $[7\text{-}(p\text{-Tol})\text{-}nido\text{-}7\text{-}CB_{10}H_{12}]^-$ anion **5a** instead of its *C*-phenyl analogue **5** in the reaction with BuLi followed by addition of $PhBCl_2$. Its $[NEt_4]^+$ salt may be isolated in 73% yield and its crystallographic characterisation confirms the absence of aryl group scrambling between *C*- and B-substituted sites during the course of its formation, as is observed also for its 1,12 isomer **40** mentioned above[9].

As with the poly-halogenated anions derived from the ten-vertex $[1\text{-Ph-}closo\text{-}1\text{-}CB_9H_9]^-$ anion **3a** and its 2-isomer **3b** (Section 9 above)[26], the poly-halogenated derivatives of the twelve-vertex $[1\text{-Ph-}closo\text{-}1\text{-}CB_{11}H_{11}]^-$ anion **6** also in principle provide routes into extensive poly-substituent chemistries *via* halogen-replacement reactions. However, this potentiality has been explored in only one system so far. In a parallel with the ten-vertex reaction, the reaction between the hexa-iodinated species $[1\text{-Ph-}closo\text{-}1\text{-}CB_{11}H_5\text{-}7,8,9,10,11,12\text{-}I_6]^-$ (anion **33**; Fig. 21 above) and a large excess of the *para*-tolyl Grignard reagent *p*-TolMgBr in the presence of $[PdCl_2(PPh_3)_2]$ results in penta-arylation to give the $[1\text{-Ph-}closo\text{-}1\text{-}CB_{11}H_5\text{-}12\text{-}I\text{-}7,8,9,10,11\text{-}(p\text{-Tol})_5]^-$ anion **37** (Fig. 28). As with the ten-vertex $\{CB_9\}$

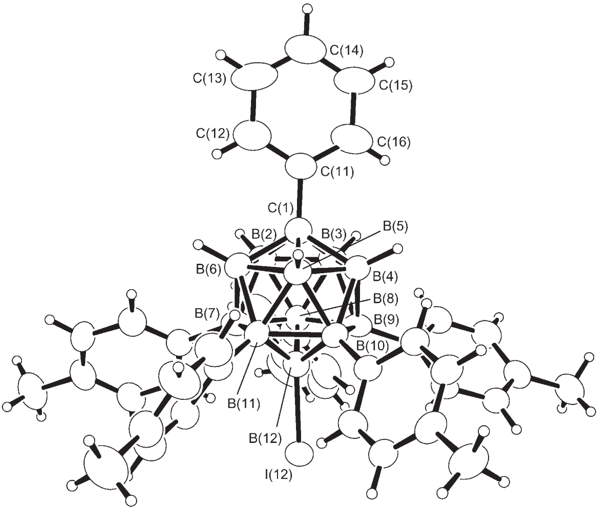


FIG. 28

Crystallographically determined molecular structure of the $[1\text{-Ph-}closo\text{-}1\text{-}CB_{11}H_5\text{-}12\text{-}I\text{-}7,8,9,10,11\text{-}(p\text{-Tol})_5]^-$ anion **37**, as determined in a salt with the $[Pd_2I_2\{P(p\text{-Tol})_3\}_4]^{2+}$ (dication **38**) [CCDC 184239]. The C(1)–C(phenyl) distance is 1.517(9) Å, with the other distances from C(1) being 1.704(11) to B(2), 1.716(11) to B(3), 1.719(10) to B(4), 1.724(10) to B(5) and 1.707(10) Å to B(6). The other boron–carbon distances are: B(7) to C(71) 1.644(11), B(8) to C(81) 1.607(11), B(9) to C(91) 1.569(11), B(10) to C(101) 1.614(10) and B(11) to C(111) 1.612(10) Å. The boron–iodine distance B(12) to I(12) is 2.213(8) Å system dealt with in Section 9 above (species **36**; Fig. 23, see also Scheme 12), complete arylation occurs around the "lower belt", at the 7, 8, 9, 10 and 11 positions, but the antipodal 12-iodinated site remains unsubstituted. Also in parallel with the $\{CB_9\}$ system, the twelve-vertex anion is isolated as a salt of the cationic halogen-bridged binuclear $[Pd_2I_2\{P(p\text{-Tol})_3\}_4]^{2+}$ co-product (species **38**), this salt being obtained in 36% yield. In another parallel with anion **36**[26], there is an interesting interionic association the solid state in which cation **38** is intimately sandwiched between two **37** anions[9].

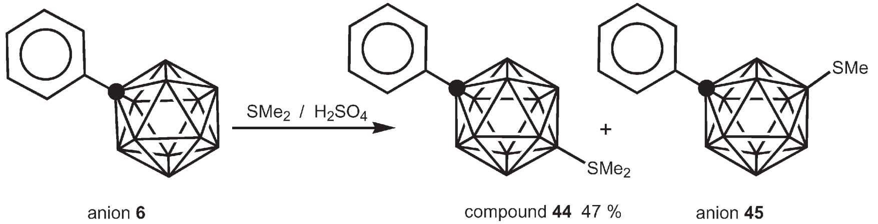
11. ADDITIONAL *C*-ARYL MONOCARBABORANE SUBSTITUENT CHEMISTRY

Sections 7–10 above summarise the *B*-halogenation and *B*-arylation chemistry of the *C*-arylated monocarbaboranes, which at the time of writing is limited to examples from the *closo* ten-vertex and *closo* twelve-vertex systems. Except for the *B*-hydroxy species (anion **28**; Fig. 19, Section 7 above), any additional substituent chemistry is principally limited to the twelve-vertex *closo* system.

The Grignard coupling reaction of the $[1\text{-Ph-}closo\text{-}1\text{-}CB_{11}H_{10}\text{-}12\text{-I}]^-$ anion **35** with PhMgI in the presence of $[PdCl_2(PPh_3)_2]$ to give the *B*-phenylated anion **39** (Section 10 above, near Scheme 13) can also be extended to other Grignard reagents. Use of $CH_2{=}CHCH_2MgCl$ in the presence of $[PdCl_2(PPh_3)_2]$ gives the anion $[1\text{-Ph-}closo\text{-}1\text{-}CB_{11}H_{10}\text{-}12\text{-}(trans\text{-}CH{=}CHCH_3)]^-$ (species **43a**), isolatable in 42% yield as its $[NEt_4]^+$ salt (Fig. 29)[9]. NMR evidence has been taken to suggest the initial formation of its terminal alkene isomer $[1\text{-Ph-}closo\text{-}1\text{-}CB_{11}H_{10}\text{-}12\text{-}(CH_2CH{=}CH_2)]^-$ (species **43b**), which readily rearranges in acidic aqueous solution to give the final product **43a**. It is apparent that extension of Grignard and other metal-mediated couplings on the basic halogenated building blocks of Sections 7 and 8 above should lead to much fascinating anion architecture chemistry, as presaged by anions **31**, **36** and **37** mentioned above, as well as by anion **43a** mentioned here.

To complement the potential of this anionic chemistry, an extensive neutral-molecule chemistry also is perhaps presaged, for example, by the reaction of the non-boron-substituted parent $[1\text{-Ph-}closo\text{-}1\text{-}CB_{11}H_{11}]^-$ anion **6** with the two-electron ligand SMe_2 in the presence of H_2SO_4 as effective oxidising agent (Scheme 16).

This reaction gives the 12-$\{SMe_2\}$-substituted neutral species $[1\text{-Ph-}closo\text{-}1\text{-}CB_{11}H_{10}\text{-}12\text{-}(SMe_2)]$ (compound **44**) in 47% yield (Fig. 30)[9]. The reaction is related to that of Me_2SO with the non-*C*-phenylated parent [*closo*-1-$CB_{11}H_{12}$]$^-$ anion **14** to give neutral [*closo*-1-$CB_{11}H_{11}$-12-(SMe_2)]^{32}.



SCHEME 16

The reaction is not so site-specific as the electrophilic halogenations reviewed in Section 8 above, because the anionic 7-{SMe}-substituted relative of neutral **44**, *viz*. the [1-Ph-*closo*-1-$CB_{11}H_{10}$-7-SMe]$^-$ anion **45**, is also

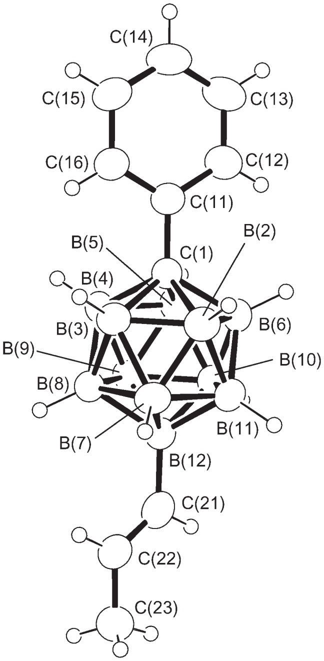


FIG. 29

Crystallographically determined molecular structure of the [1-Ph-*closo*-1-$CB_{11}H_{10}$-12-(*trans*-CH=$CHCH_3$)]$^-$ anion **43a**, as determined in its [NEt_4]$^+$ salt [CCDC 184240]. The C(1)–C(phenyl) distance is 1.507(3) Å, with the other distances from C(1) being 1.731(3) to B(2), 1.724(3) to B(3), 1.720(3) to B(4), 1.722(3) to B(5) and 1.727(3) Å to B(6). The other distances are: B(12) to C(21) 1.587(3), C(21) to C(22) 1.293(3) and C(22) to C(23) 1.482(3) Å isolatable as a product from this system in 27% yield. Here, the quasi-isosteric nature of the eleven-vertex {*nido*-$PhCB_{10}H_{12}$}-based and the twelve-vertex {*closo*-$PhCB_{11}H_{11}$}-based skeletal systems, mentioned above in Section 5 with reference to anions **5** and **6**, is also manifest in these {SMe}-substituted species. In this regard, contamination of *closo* twelve-vertex **6** with *nido* eleven-vertex **5** has been observed to follow through to the isolation of anion **45** just mentioned, in that single-crystal X-ray diffraction data for **45** are thereby often interpretable in terms not only of molecules of **45** alone, but also of a proportion of molecules of the quasi-isosteric *nido* eleven-vertex species [7-Ph-*nido*-7-$CB_{10}H_{11}$-4-SMe]$^-$ (anion **46**)[9]. The crystallographically derived molecular structures for these two species **45** and **46** are in Fig. 31.

Further chemistry derived from the neutral SMe_2 compound **45** results from its reaction with tetrahydrofuran. Heating of compound **44** at reflux temperature in tetrahydrofuran solution for 18 h engenders the formation

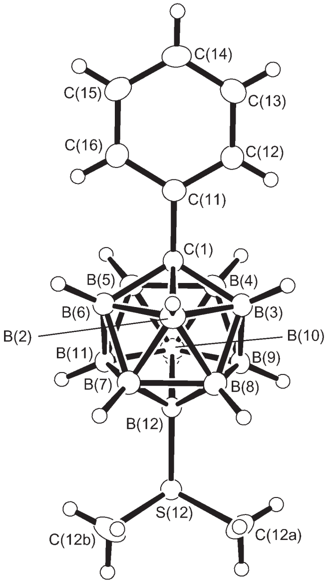


FIG. 30

Crystallographically determined molecular structure of the neutral [1-Ph-*closo*-1-$CB_{11}H_{10}$-12-(SMe_2)] compound **44** [CCDC 184241]. The C(1)–C(phenyl) distance is 1.515(2) Å, with the other distances from C(1) being 1.728(3) to B(2), 1.722(3) to B(3), 1.721(3) to B(4), 1.723(3) to B(5) and 1.725(3) Å to B(6). The other distances are: B(12) to S(12) 1.790(2), S(12) to C(12a) 1.790(2) and S(12) to C(12b) 1.790(2) Å of neutral [1-Ph-*closo*-1-$CB_{11}H_{10}$-12-{$SMe(CH_2)_4OH$}] (compound **47**; Fig. 32)[9]. This has involved an assimilation and ring-opening of tetrahydrofuran, presumably *via* nucleophilic attack at the α-position of an initially electrophilic thf residue; related nucleophilic attacks involving thf have long been recognised in polyhedral boron-containing cluster chemistry[39], and are, for example, of contemporary interest in twelve-vertex non-carbaborane chemistry involving the {*closo*-B_{12}} residue[40].

12. CONCLUSION

The discovery by Brellochs[3], that aldehydes react in alkaline solution with $B_{10}H_{14}$ to give good yields of {CB_9} open-cluster species, which in turn are amenable to good-yield cluster-Aufbau and cluster-dismantling reactions to generate other monocarbaborane skeletons, now permits a more rapid development of new horizons in monocarbaborane chemistry. One intention of this presentation is that the chemistries of the *C*-arylated systems

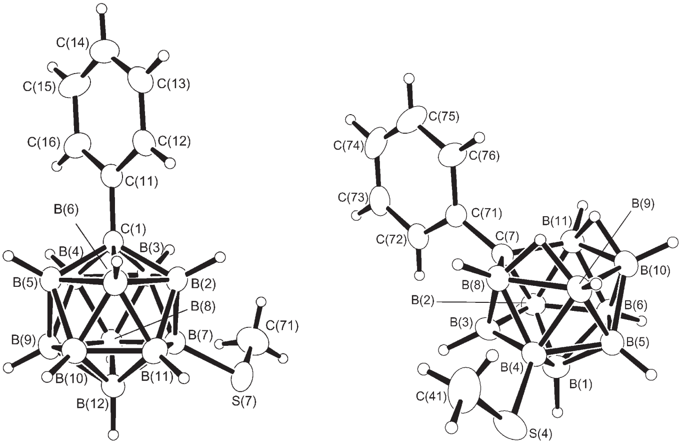


Fig. 31

Crystallographically determined molecular structure of (left) the [1-Ph-*closo*-1-$CB_{11}H_{10}$-7-SMe]$^-$ anion **45**, and (right) the quasi-isosteric [7-Ph-*nido*-7-$CB_{10}H_{11}$-4-SMe]$^-$ anion **46**. Both are present in the same crystal [CCDC 184242]. For compound **45** the C(1)–C(phenyl) distance is 1.500(4) Å, with the other distances from C(1) being 1.703(4) to B(2), 1.692(4) to B(3), 1.713(6) to B(4), 1.690(4) to B(5) and 1.711(4) Å to B(6). Other distances are: B(7) to S(7) 1.874(3) and S(7) to C(71) 1.820(6) Å. For compound **46** the C(7)–C(phenyl) distance is 1.500(4) Å, with the other distances from C(7) being 1.713(6) to B(2), 1.703(4) to B(3), 1.692(4) to B(8) and 1.690(4) Å to B(11). Other distances are: B(4) to S(4) 1.874(3) and S(4) to C(41) 1.820(6) Å that are summarised will exemplify aspects of how this potential may start to be realised, not only with *C*-arylated monocarbaboranes, but also with *C*-alkylated monocarbaboranes and other related systems. It is to be hoped that this presentation will therefore stimulate and engender chemical novelty and consequent applications[41]. These may include further developments in "least coordinating anion" chemistry[22–24,33], including the incorporation of least-coordinating anions into polymeric substrates, anionic polymers based on the carbaborane cores themselves, rigid zwitterions of high dipolarities[42] and hyperpolarisabilities[43], liquid-crystal chemistry[27] and other rheological applications, building blocks for "molecular meccano" or "molecular tinkertoy" chemistries[25,30,44,45], the tailoring of compounds for host-guest "molecular recognition" and supramolecular assembly[26,46,47], the introduction of pharmacophore synthonic groups for

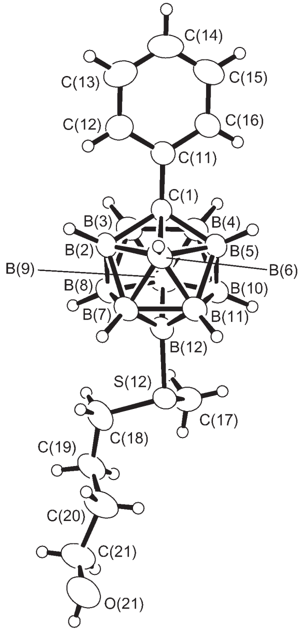


FIG. 32
Crystallographically determined molecular structure of neutral [1-Ph-*closo*-1-$CB_{11}H_{10}$-12-{$SMe(CH_2)_4OH$}] (compound **47**) [CCDC 184243]. There are two independent molecules in the unit cell; only one is pictured here; dimensions for the other are a similar. The C(1)–C(phenyl) distance is 1.514(3) Å, with the other distances to C(1) being 1.721(3) to B(2), 1.717(4) to B(3), 1.713(4) to B(4), 1.722(4) to B(5) and 1.724(4) Å to B(6). Other distances are: B(12) to S(12) 1.895(3), S(12) to C(17) 1.803(3), S(12) to C(18) 1.804(4), C(18) to C(19) 1.526(5), C(19) to C(20) 1.467(5), C(20) to C(21) 1.584(6) and C(21) to O(21) 1.407(8) Å

applications in medical therapies[48,49], and so on. The *B*-halogenated and *C*-halogenoarylated species in particular should constitute particularly useful building-blocks for most of these types of currently developing chemistry.

For convenience, CCDC deposition numbers for all crystallographically determined structures in the Figures are provided in the appropriate figure captions. 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). The DFT-calculated coordinates for the anions in Figs 5, 6 and 8 are available from the authors on request.

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