ELSEVIER

Journal of Organometallic Chemistry 657 (2002) 180–186

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Polyhedral monocarbaborane chemistry The *closo*-$[PhCB_7H_7]^-$ and *closo*-$[PhCB_{10}H_{10}]^-$ anions: the two missing species in the *closo*-$[PhCB_nH_n]^-$ sequence[1]

Andreas Franken, Colin A. Kilner, Mark Thornton-Pett, John D. Kennedy *

The School of Chemistry, University of Leeds, Leeds LS2 9JT, UK

Received 15 October 2001; accepted 20 April 2002

Abstract

Reaction of the ten-vertex *nido*-$[PhCB_9H_{11}]^-$ anion with $FeCl_3$ in aqueous acid results in cluster dismantling to give nine-vertex *arachno*-$[PhCB_8H_{13}]$, which gives the eight-vertex *closo*-$[PhCB_7H_7]^-$ anion on treatment with NEt_3. Reaction of the *nido*-$[PhCB_9H_{11}]^-$ anion with $[BH_3(THF)]$ results in cluster Aufbau to give the eleven-vertex *nido*-$[PhCB_{10}H_{12}]^-$ anion, which, on treatment with I_2 in aqueous alkali solution, gives the eleven-vertex *closo*-$[PhCB_{10}H_{10}]^-$ anion. Both of the new *closo* anions, $[PhCB_7H_7]^-$ and $[PhCB_{10}H_{10}]^-$, are characterised by NMR spectroscopy and by single-crystal X-ray diffraction analyses of their $[NEt_4]^+$ salts. The sequence of *closo*-$[PhCB_nH_n]^-$ anions, where $n = 7$–11, is thereby completed.

Keywords: *Closo* monocarbaborane series; C-phenylated carbaboranes; C-substituted carbaboranes; X-ray structures

1. Introduction

There is current high interest in the *closo* monocarbaborane series of anions $[HCB_nH_n]^-$ because their very low Lewis and Brønsted basicities engender interesting chemistries [1–3]. These chemistries can in principle be finely tuned by the variation of the substituent chemistry of these anions, and consequently there is interest and activity in their substituent chemistry. In this context, C-phenylation has been an elusive target that has only very recently been achieved by the synthesis and characterisation of the short C-phenylated series consisting of the *closo*-$[PhCB_8H_8]^-$, *closo*-$[PhCB_9H_9]^-$ and *closo*-$[PhCB_{11}H_{11}]^-$ anions [3,4]. There is merit in the extension of this series, and here we report the completion and extension of this potentially interesting sequence by the synthesis, isolation, and characterisation of the missing *closo*-$[PhCB_7H_7]^-$ and *closo*-$[PhCB_{10}H_{10}]^-$ anions. As an additional intermediate within these syntheses, we describe the neutral [4-Ph-*arachno*-4-CB_8H_{13}] species also. As with *closo*-$[PhCB_8H_8]^-$ and *closo*-$[PhCB_9H_9]$, and with one of the routes to *closo*-$[PhCB_{11}H_{11}]^-$, the syntheses rely on the initial reaction of PhCHO with $B_{10}H_{14}$ to give the [6-Ph-*nido*-6-$CB_9H_{11}]^-$ anion [3,5]. This approach has the advantage of commencing with a pre-phenylated carbon atom, thus eliminating the need for subsequent extensive experimental protocol for substitution on the carbaborane C-atom.

2. Results and discussion

The complete series of [*closo*-$PhCB_xH_x]^-$ anions, where x can be 7, 8, 9, 10 or 11 (compounds **1**–**5**, respectively), can all be derived from the [6-Ph-*nido*-6-$CB_9H_{11}]^-$ anion **6**. This last anion is obtainable from

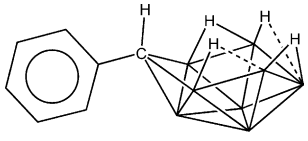
* Corresponding author

E-mail address: johnk@chem.leeds.ac.uk (J.D. Kennedy).

[1] Systematic IUPC nomenclature: The 1-phenyl-*closo*-1-carbaoctaborate(1−) and 2-phenyl-*closo*-2-carbaundecaborate(1−) anions, characterised crystallographically as their tetraethylammonium salts. This article was freely submitted for publication without royalty. By acceptance of this paper, the publisher and/or recipient acknowledges the right of the authors to retain non-exclusive, royalty-free license in and to any copyright covering this paper, along with the right to reproduce all or part of the copyrighted paper.

0022-328X/02/$ - see front matter
PII: S0022-328X(02)01544-9

the 'Brellochs Reaction' of PhCHO with the common higher borane starting substrate $B_{10}H_{14}$ [5]. Initially reported yields were as high as 94% [3], although for this present work we have not been able to achieve greater than 64%. The eight- and nine-vertex members of the series, the [1-Ph-*closo*-1-CB_7H_7]$^-$ anion **1** and the [4-Ph-*closo*-4-CB_8H_8]$^-$ anion **2**, can be formed from [6-Ph-*nido*-6-CB_9H_{11}]$^-$ by cluster-dismantling reactions. As previously described [3], the nine-vertex [4-Ph-*closo*-4-CB_8H_8]$^-$ anion **2** is formed in 68% yield by the solid-state thermolysis of the $[NEt_4]^+$ salt of the ten-vertex [6-Ph-*nido*-6-CB_9H_{11}]$^-$ anion **6** at 200 °C for 4 h. We have now found that, in the presence of hydrochloric acid and $FeCl_3$ as oxidant, an alternative cluster dismantling of the [6-Ph-*nido*-6-CB_9H_{11}]$^-$ anion **6** occurs, now to give the nine-vertex neutral [4-Ph-*arachno*-4-CB_8H_{13}] (**7**) in 78% yield, rather than the [4-Ph-*closo*-4-CB_8H_8]$^-$ anion **2**. A stoichiometry may be written down as in Eq. (1). As far as we are aware, this neutral C-phenylated species **7** is previously unreported, although the unsubstituted neutral 'parent' species [*arachno*-1-CB_8H_{14}] has been synthesised by Štíbr and co-workers [6–8]. Its structure is represented in schematic diagram **I**, in which unlettered vertices represent BH(*exo*) units. Treatment of [4-Ph-*arachno*-4-CB_8H_{13}] (**7**) with NEt_3 in refluxing toluene thence results in the formation of the eight-vertex [1-Ph-*closo*-1-CB_7H_7]$^-$ anion **1**, isolatable in 72% yield as its $[NEt_4]^+$ salt. A stoichiometry may be written down as in Eq. (2). This C-phenyl *closo* species **1** is also new, although, again, the unsubstituted parent [*closo*-1-CB_7H_8]$^-$ anion **8** is recognised. This latter anion **8** has not been structurally characterised, but the molecular structures of two B-iodo derivatives have been reported [9].



I

$$nido\text{-}[PhCB_9H_{11}]^- \ (\mathbf{6}) + 2Fe^{3+} + 3H_2O \rightarrow arachno\text{-}[PhCB_8H_{13}] \ (\mathbf{7}) + [B(OH)_3] + 2Fe^{2+} + H^+ \quad (1)$$

$$arachno\text{-}[PhCB_8H_{13}] \ (\mathbf{7}) + 2NEt_3 \rightarrow [NHEt_3]^+ + closo\text{-}[PhCB_7H_7]^- \ (\mathbf{1}) + [BH_3(NEt_3)] + H_2 \quad (2)$$

Previously from our laboratories we reported that the next compound in the sequence, the ten-vertex [1-Ph-*closo*-1-CB_9H_9]$^-$ anion **3**, could be prepared in ca. 25% yield when the $[NEt_4]^+$ salt of the [6-Ph-*nido*-6-CB_9H_{11}]$^-$ anion **6** was suspended in [$BH_3(NEt_3)$], and the mixture heated under nitrogen in an oil bath at 210 °C for 6 h [3]. This reaction, however, gave the twelve-vertex congener anion [1-Ph-*closo*-1-$CB_{11}H_{11}$]$^-$ (**5**) as the major product (ca. 50%), and chromatography or fractional crystallisation was required for the separation of these two product anions. It is therefore pertinent to mention a new preliminary result here that indicates an improved preparation of the ten-vertex *closo* species **3**, eliminating the need for chromatography or fractional crystallisation. Thus, in an initial experiment, when the [6-Ph-*nido*-6-CB_9H_{11}]$^-$ anion **6** was heated at reflux in THF solution in the presence of elemental sodium for 48 h, the [1-Ph-*closo*-1-CB_9H_9]$^-$ anion **3** was formed by a cage closure in 90% yield. It is interesting that the sodium does not appear in a reasonable stoichiometry that can be written down (Eq. (3)), even though the closure appears not occur without it. We would hope to be able report further on this and related reactions in the future.

$$nido\text{-}[PhCB_9H_{11}]^- \ (6) \rightarrow closo\text{-}[PhCB_9H_9]^- \ (\mathbf{3}) + H_2 \quad (3)$$

The higher eleven- and twelve-vertex anions [2-Ph-*closo*-2-$CB_{10}H_{10}$]$^-$ anion **4** and [1-Ph-*closo*-1-$CB_{11}H_{11}$]$^-$ anion **5** can both be obtained in cluster *Aufbau* processes by the insertion of {BH_3} moieties into the [6-Ph-*nido*-6-CB_9H_{11}]$^-$ anion **6** with concomitant loss of hydrogen. In the previous preliminary report from our laboratories [3], we had found that, when the [6-Ph-*nido*-6-CB_9H_{11}]$^-$ anion **6** was heated with [$BH_3(SMe_2)$] in 1,2-$Cl_2C_2H_4$ as solvent, then a mixture of the [1-Ph-*closo*-1-$CB_{11}H_{11}$]$^-$ anion **5** and the [7-Ph-*nido*-7-$CB_{10}H_{12}$]$^-$ anion **9** was formed [3]. It thence seemed reasonable that the reaction to form the twelve-vertex *closo* anion **5** proceeds via the eleven-vertex *nido* species **9** as intermediate. This idea is supported by the observation that a more prolonged heating with [$BH_3(SMe_2)$] converts species **9** more completely to the [1-Ph-*closo*-1-$CB_{11}H_{11}$]$^-$ anion **5**. We now find that, under slightly milder conditions, the reaction can indeed be stayed at the intermediate stage to give the [7-Ph-*nido*-7-$CB_{10}H_{12}$]$^-$ anion **9** in reasonable isolatable yield, with little of the [1-Ph-*closo*-1-$CB_{11}H_{11}$]$^-$ anion **5** present. Thus, the [1-Ph-*nido*-1-CB_9H_{11}]$^-$ anion **6** reacts with [BH_3(THF)] in refluxing THF solution to give the intermediate [7-Ph-*nido*-7-$CB_{10}H_{12}$]$^-$ anion **9** in 40% yield (Eq. (4)). Under conditions that we have been able to establish so far there is still unreacted anion **6** present (ca. 22%), and, because of the cascade nature of the reaction sequence (Eqs. (4) and (5)), it has not yet been possible to generate a product mixture in which neither **5** nor **6** contaminate species **9**. However, the anionic species **6** can conveniently be converted in situ to the neutral [4-Ph-*arachno*-4-CB_8H_{13}] species **7** by adding hydrochloric acid and the oxidant $FeCl_3$ (Eq. (1) above). For purification of the desired [7-Ph-*nido*-7-$CB_{10}H_{12}$]$^-$ anion **9**, therefore, the neutral [4-Ph-*arachno*-4-CB_8H_{13}] species **7** can thence be removed by extraction into *n*-

hexane. Although, after crystallisation, a salt of the eleven-vertex [7-Ph-*nido*-7-$CB_{10}H_{12}$]$^-$ anion **9** is still contaminated with small amounts of the twelve-vertex [1-Ph-*closo*-1-$CB_{11}H_{11}$]$^-$ anion **5** that is formed in the reaction, species **9** is generally sufficiently pure enough for many aspects of further chemistry to be established, and, furthermore, anion **5** is relatively inert. A more complete formation of the latter [1-Ph-*closo*-1-$CB_{11}H_{11}$]$^-$ anion **5** slowly occurs under prolonged heating of the intermediate [7-Ph-*nido*-7-$CB_{10}H_{12}$]$^-$ anion **9** in the presence of excess [BH_3(THF)] (Eq. (5)).

$$\textit{nido}\text{-}[PhCB_9H_{11}]^- \ (\mathbf{6}) + [BH_3(THF)] \rightarrow \textit{nido}\text{-}[PhCB_{10}H_{12}]^- \ (\mathbf{9}) + THF + H_2 \quad (4)$$

$$\textit{nido}\text{-}[PhCB_{10}H_{12}]^- \ (\mathbf{9}) + [BH_3(THF)] \rightarrow \textit{closo}\text{-}[PhCB_{11}H_{11}]^- \ (\mathbf{5}) + THF + H_2 \quad (5)$$

We have found that the [7-Ph-*nido*-7-$CB_{10}H_{12}$]$^-$ anion **9** is thence amenable to oxidative closure with elemental iodine in the presence of base, just like its related unsubstituted parent trianion [*nido*-7-$CB_{10}H_{11}$]$^{3-}$, which, as the $Na_3[CB_{10}H_{11}][THF]$ salt complex, also reacts with elemental iodine to form its corresponding [*closo*-2-$CB_{10}H_{11}$]$^-$ anion [10]. Thus, a dissolution extraction of the effective Cs^+ salt of anion **9** into an aqueous alkaline solution (see Section 4), followed by treatment with elemental iodine, results in the formation of the target [2-Ph-*closo*-2-$CB_{10}H_{10}$]$^-$ anion **4**, isolated in 65% yield as its $[NEt_4]^+$ salt. A simple stoichiometry for this oxidation may be written down as in Eq. (6).

$$\textit{nido}\text{-}[PhCB_{10}H_{12}]^- \ (\mathbf{9}) + I_2 + 2OH^- \rightarrow \textit{closo}\text{-}[PhCB_{10}H_{10}]^- \ (\mathbf{4}) + 2I^- + 2H_2O \quad (6)$$

Each of the new *closo* anions **1** and **4** has been characterised by a single-crystal X-ray diffraction analysis of its $[NEt_4]^+$ salt (Figs. 1 and 2, respectively). The basic structural type for the eight-vertex anion **1** has previously been established for its B-iodinated [*closo*-1-CB_7H_7-7-I]$^-$ and [*closo*-1-CB_7H_6-7,8-I_2]$^-$ analogues **10** and **11** [9], with the {CB_7} unit having the classical closed eight-vertex dodecahedral architecture [11,12], as crystallographically established some 30 years ago for the all-boron [*closo*-B_8H_8]$^{2-}$ pattern-maker in its $[Zn(NH_3)_4]^{2+}$ salt [13]. Of the two types of cluster position in principle available, five- and four-connectivity, the carbon atom takes up a position of the lower cluster connectivity, in accord with the well-recognised carbon-siting behaviour for carbaborane clusters [11,12,14]. Within the carbaborane cluster unit, the dimensions are very similar to those of the C-unsubstituted anions **10** and **11**, which themselves are mutually similar in this regard. The exceptions to this generalisation are the distances from C(1) to the

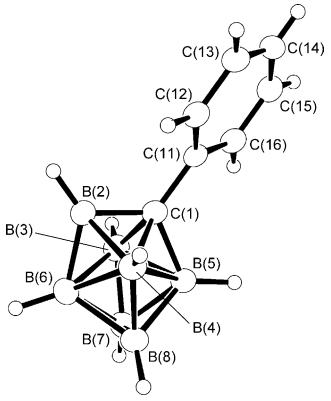


Fig. 1. Drawing of the molecular structure of the [1-Ph-*closo*-1-CB_7H_7]$^-$ anion **1**, as determined crystallographically in its $[NEt_4]^+$ salt. Selected intermolecular distances in Å are as follows: C(1) to C(11) is 1.484(2), and C(1) to B(2), B(3), B(4) and B(6) are 1.528(2), 1.723(2), 1.716(2) and 1.622(2), respectively; B(2) to B(3), B(4) and B(6) are 1.820(3), 1.820(4) and 1.707(3), respectively, B(8) to B(4), B(5), B(6) and B(7) are 1.700(2), 1.801(3), 1.818(3) and 1.622(3), respectively, and B(7) to B(3), B(5) and B(6) are 1.700(3), 1.811(3) and 1.821(3), respectively; B(3) to B(5) and B(3) to B(6) are 1.890(3) and 1.937(3), respectively, with B(4) to B(5) and B(4) to B(6) being 1.904(3) and 1.902(3), respectively.

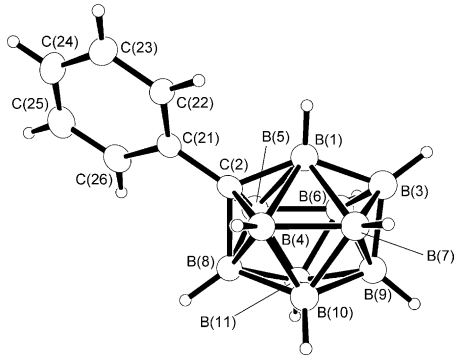


Fig. 2. Drawing of the molecular structure of the [2-Ph-*closo*-2-$CB_{10}H_{10}$]$^-$ anion **4**, as determined crystallographically in its $[NEt_4]^+$ salt. Selected intermolecular dimensions in Å are as follows: C(2) to C(21) is 1.492(3), with distances from C(2) to the adjacent boron sites B(1), B(4), B(5) and B(8) being 1.643(3), 1.584(3), 1.593(3) and 1.676(3) Å, respectively, corresponding distances from B(3) to B(1), B(6), B(7), and B(9) being 1.711(4), 1.638(4) 1.667(4) and 1.748(4), respectively. Distances from B(1) to B(4), B(5), B(6), and B(7) are 2.057(4), 2.043(4), 2.023(4) and 2.015(4), respectively, from B(10) to B(4), B(7), B(8), B(9) and B(11) are 1.789(4), 1.816(4), 1.781(4), 1.776(4) and 1.817(4), respectively, and from B(11) to B(5), B(6), B(8) and B(9) are 1.775(4), 1.792(4), 1.783(3) and 1.789(4), respectively; B(5) to B(6) is 1.826(4) and B(4) to B(7) is 1.849(4).

adjacent boron atoms B(2), B(3), B(4) and B(5), which, at 1.528(2), 1.723(2), 1.716(2), and 1.622(2) Å, respectively in C-phenylated **1**, are perhaps marginally longer than the values of 1.517(4), 1.701(4), 1.699(4) and 1.596(4) Å, respectively in the monoiodo compound **10** and the values of 1.517(5), 1.705(5), 1.706(5) and 1.591(4) Å, respectively in the dioido compound **11** (in this comparison it may be noted that diffraction data for

11 were collected at a crystal temperature of 200 K whereas for both **1** and **10** the data were collected at 150 K, and that the two iodinated species **10** and **11** were measured as their $[PPh_4]^+$ salts). Among the whole series of $[PhCB_xH_x]^-$ *closo* monocarbaborane anions ranging from eight-vertex **1** to twelve-vertex **5**, the cluster-to-phenyl carbon–carbon linkage is perhaps the most significant common feature for a structural comparison. This takes the crystallographically determined values of 1.484(2), 1.490(2), 1.503(4), 1.492(3), and 1.512(3) in compounds **1**–**5**, respectively. It is not clear how significant this apparent increase with increasing cluster size may be, as the differences are close to the experimental uncertainties; any real increase would obviously be linked to the cluster electronics. The cluster electronics have been examined via calculational theory for the unsubstituted $[CB_xH_{(x+1)}]^-$ sequence [15], but any extent of C-phenyl involvement with the cluster in the new *closo* C-phenyl monocarbaboranes has not yet been assessed by such calculations.

The crystallographically determined structure of the eleven-vertex [2-Ph-*closo*-2-$CB_{10}H_{10}]^-$ anion **4** is in Fig. 2. Although the basic structural type for the *closo* eleven-vertex cluster type was established some 35 years ago for the neutral [2,3-Me_2-*closo*-2,3-$C_2B_9H_9$] dicarbaborane species **12** [16], that of the borons-only parent [*closo*-$B_{11}H_{11}]^{2-}$ itself had been particularly elusive until the recent report of a crystallographic analysis of its of $[Li(tph)_3]^+$ salt [17]. In the meantime several substituted derivatives, such as the $[B_{11}H_{10}(SMe_2)]^-$ monoanion [18] and the interesting $[B_{11}H_9Se_3]^{2-}$ dianion [19], have been established, as well as several neutral eleven-vertex *closo*-structured metallacarbaboranes [20,21] and metallaheteroboranes [22,23]. The basic crystallographic confirmation of the *closo* $\{CB_{10}\}$ skeleton has not been reported, however, even though the parent [*closo*-2-$CB_{10}H_{11}]^-$ anion **13** itself was synthesised many years ago [24], and its structure reasonably proposed from calculations shortly after [25]. From Fig. 2 it is seen that the C-phenylated anion **4** adopts the closed octadecahedral skeleton that is based on the ideally C_{2v} configuration of [*closo*-$B_{11}H_{11}]^{2-}$, with the cluster carbon atom occupying one of the four-connectivity vertices rather than a vertex of five- or six-connectivity, all in accord with the classical Williams–Wade formalisms [11,12,14]. The smaller carbon atom C(2), versus the larger boron atom at the other four-connectivity position B(3), distorts the cluster from idealised C_{2v} towards a C_s appearance, distances from C(2) to the adjacent boron sites B(1), B(4), B(5) and B(8) being 1.643(3), 1.584(3), 1.593(3) and 1.676(3) Å, respectively, shorter than the equivalent distances from B(3) at the other end of the cluster to B(1), B(6), B(7) and B(9) of 1.711(4), 1.638(4), 1.667(4) and 1.748(4) Å, respectively. The distances from C(2) in anion **4** are comparable to the values of 1.67, 1.59, 1.60, and 1.70 Å, respectively reported for the dicarbaborane species [2,3-Me_2-*closo*-2,3-$C_2B_9H_9$] (**12**) mentioned above [16].

NMR spectroscopy shows that both the new anions [1-Ph-*closo*-1-$CB_7H_7]^-$ (**1**) and [2-Ph-*closo*-2-$CB_{10}H_{10}]^-$ (**4**) are fluxional in solution. They therefore give ^{11}B and ^1H spectra that are simpler than would be expected on the basis of their static structures in Figs. 1 and 2. This fluxional behaviour parallels that of the parent unsubstituted [*closo*-1-$CB_7H_8]^-$ and [*closo*-2-$CB_{10}H_{11}]^-$ anions **8** and **13**. The fluxionality of the unsubstituted parent eight-vertex [*closo*-1-$CB_7H_8]^-$ anion **8** has long been recognised [10,13], and is reasonably believed to proceed through a diamond–square–diamond cluster rearrangement of very low activation energy, resulting in the observation of a 3:4 relative intensity pattern in the ^{11}B-NMR spectrum, rather than the 2:2:1:1:1 pattern that would be expected on the basis of a static structure. The mechanism has been adequately discussed in the literature [9,10,13,26], both for the carbaborane **8**, and for the all-boron analogue, the [*closo*-$B_8H_8]^{2-}$ dianion **14**, which also exhibits an analogous fluxionality [27,28], and there is no merit in rehearsing this discussion in this present communication. Similar considerations apply to the eleven-vertex species **4**, for which a static structure would imply the observation of a 2:2:2:1:1:1:1 relative intensity pattern in the ^{11}B-NMR spectrum. As with the eight-vertex species, the fluxionality of the unsubstituted parent [*closo*-2-$CB_{10}H_{11}]^-$ anion **13**, as well as the all-boron analogue, the [*closo*-$B_{11}H_{11}]^{2-}$ dianion **15**, has been well-examined and discussed in the literature [24,29,30], so does not warrant another detailed description here. A diamond–square–diamond rearrangement mechanism is again reasonably invoked for this cluster type also, and in this case an asymmetric substitution on the cluster can result in the stabilisation of the square-faced intermediate, as in neutral [2,3-Me_2-*closo*-2,3-$C_2B_9H_6$-4,7-$(OH)_2$-10-Br] that has been examined by single-crystal work [31]. The fluxionality results in the observation of a simpler 1:5:4 relative-intensity pattern in the ^{11}B-NMR spectrum for the rapidly rearranging molecule, as also observed for the parent unsubstituted anion **13**. In order to investigate the possibility that the C-phenyl substituents in anions **1** and **4** may induce higher activation energies for the cluster rearrangements than observed for the parents **8** and **13**, and therefore perhaps permit the observation of quasi-static structures at low temperatures, we examined the ^1H- and ^{11}B-NMR spectra of both of the new species **1** and **4** in CD_2Cl_2 solution at lower temperatures. However, although there were signs of broadening at 273 K, this could equally have arisen from relaxation effects arising from the gelling of the supercooled solvent as well as a slowing down of the rate of rearrangement, and there was no indication of any incipient de-coalescence of the

resonances to give the greater multiplicities of chemical shifts expected for static structures. This would put an upper limit of ca. 30 kJ mol^{-1} on the activation energies, and so, as with the unsubstituted parent anions **8** and **13**, the fluxionality occurs very readily indeed.

3. Conclusions

Although carbaborane chemistry is a very extensively investigated area, the literature is dominated by two-carbons-in-the-cluster dicarbaborane chemistry, with monocarbaborane chemistry being relatively very unexplored [32]. The syntheses of these two new anions that are reported in this present communication completes a systematic fundamental sequence of the C-phenylated monocarbaborane anions, *closo*-$[PhCB_7H_7]^-$, *closo*-$[PhCB_8H_8]^-$, *closo*-$[PhCB_9H_9]^-$, *closo*-$[PhCB_{10}H_{10}]^-$ and *closo*-$[PhCB_{11}H_{11}]^-$, and thereby nicely augments the variety of monocarbaboranes available for further chemistry. The reaction chemistry leading to this complete sequence, based on the reaction of PhCHO with the common higher-borane starting material $B_{10}H_{14}$ to give the *nido*-$[PhCB_9H_{11}]^-$ anion, from which the five *closo* species are thence readily made by dismantling, closure, and *Aufbau* reactions, is in principle readily adaptable to other aromatic residues for which aldehydes are available, and presages an extensive derivative chemistry.

4. Experimental

4.1. Preparation of neutral [4-Ph-arachno-4-CB_8H_{13}] (7) from the [6-Ph-nido-6-CB_9H_{11}]$^-$ anion 6

The $[NEt_4]^+$ salt of the [6-Ph-*nido*-6-CB_9H_{11}]$^-$ anion **6** was prepared as in Ref. [3], and 1.0 g (3.1 mmol) was added to a solution of CsCl (1.0 g, 5.9 mmol) in aq. HCl (10%, 50 ml). The aq. layer was extracted several times with Et_2O, the extracts combined and the Et_2O removed in vacuo. The residual colourless oil was stirred in a mixture of aq. HCl (10%, 50 ml), *n*-C_6H_{14} (50 ml) and $[FeCl_3(OH_2)_6]$ (6.0 g, 22 mmol) for 3 h at room temperature (r.t.). The *n*-C_6H_{14} layer was then separated, and the organic volatile components were removed from it in vacuo to give neutral [4-Ph-*arachno*-4-CB_8H_{13}] (compound **7**, 0.45 g, 78%) as a white solid with m.p. 74 °C. NMR data for [4-Ph-*arachno*-4-CB_8H_{13}] (**7**), in $CDCl_3$ at 294–299 K, ordered as assignment $\delta(^{11}B)$/ppm [$\delta(^1H)$/ppm], are as follows: BH(7) +18.7 [+4.29], BH(1) −1.5 [+3.53], BH(5,9) −3.2 [+3.01], BH(6,8) −32.6 [+1.70] and BH(2,3) −40.9 [−0.60], with $\delta(^1H)$ for μH(5,6)/μH(8,9) at −2.53 ppm, for μH(6,7)/μH(7,8) at +0.28 ppm and for CH(4)(*endo*) at +0.67 ppm; additionally $\delta(^1H)$(Ph) centred at ca. +7.29 (5H, compact overlapping multiplet), and $\delta(^{13}C)$(Ph) +126.7 (1C), +128.4 (2C), +128.8 (2C) and +145.8 (1C), with $\delta(^{13}C)$(cluster) +13.4 ppm.

4.2. Preparation of the $[NEt_4]^+$ salt of the [1-Ph-closo-1-CB_7H_7]$^-$ anion 1 from the reaction of [4-Ph-arachno-4-CB_8H_{13}] (7) with NEt_3

A solution of [4-Ph-*arachno*-4-CB_8H_{13}] (compound **7**, prepared as above, 1.0 g, 5.4 mmol) in $C_6H_5CH_3$ (20 ml) and NEt_3 (10 ml) was heated under reflux for 18 h. The reaction mixture was allowed to cool down to r.t. and the volatile organic solvents were removed in vacuo. After adding H_2O (50 ml) and CsCl (1.0 g, 5.9 mmol), the aq. layer was extracted several times with Et_2O (ca. 30 ml aliquots). The combined Et_2O extracts were evaporated in vacuo. The monitoring by ^{11}B-NMR spectroscopy of the residue at this stage showed predominantly the eight-vertex anionic product **1**, but with smaller quantities (ca. 5 mol%) of a species tentatively identified as the [2-Ph-*closo*-2-CB_6H_6]$^-$ anion **16**, with $\delta(^{11}B)$/ppm: +6.4 (2BH), +0.4 (2BH), and −19.5 (2BH), these $\delta(^{11}B)$ values being close to those reported by Štíbr and co-workers for the parent [*closo*-CB_6H_7]$^-$ species [8], and also close to the values of ca. +3, −2 and −20 ppm arising from preliminary calculations at the B3LYP/6-31G* level for anion **16** in the gas-phase [33]. The residue was dissolved in H_2O (50 ml), and a solution of $[NEt_4]^+$ Cl^- (1.0 g, 6.0 mmol) in H_2O (30 ml) was added to this aq. solution. The resulting pale yellow precipitate was filtered off and dried in vacuo, to yield the $[NEt_4]^+$ salt of the [1-Ph-*closo*-1-CB_7H_7]$^-$ anion **1** (1.17 g, 3.90 mmol, 72%); crystals suitable for a single-crystal X-ray diffraction analysis were obtained from a concentrated solution in $(CH_3)_2CO$ that was overlayered with a ca. fivefold excess of Et_2O. NMR data for $[NEt_4]^+$[1-Ph-*closo*-1-CB_7H_7]$^-$ anion **1**, in $(CD_3)_2CO$ at 294–299 K, ordered as assignment $\delta(^{11}B)$/ppm [$\delta(^1H)$/ppm], are as follows: BH(6,7,8) +3.7 [+3.18], BH(2,3,4,5) −1.3 [+2.61]; additionally $\delta(^1H)$(Ph) ca. +7.76–+6.93 (5H, compact overlapping multiplet), and $\delta(^1H)$(Et) at +3.49 (8H, quartet), +1.33 (12H, triplet), also $\delta(^{13}C)$(Ph) +124.35 (1C), +127.24 (2C), +127.68 (2C) and +141.46 (1C), with $\delta(^{13}C)$(cluster) +47.41 and $\delta(^{13}C)$(Et) +7.07 and +52.47 ppm.

4.3. Preparation of the [7-Ph-nido-7-$CB_{10}H_{12}$]$^-$ anion 9 from the [6-Ph-nido-6-CB_9H_{11}]$^-$ anion 6

A sample of the $[NEt_4]^+$ salt of the [6-Ph-*nido*-6-CB_9H_{11}]$^-$ anion **6** (6.0 g, 18.3 mmol) was dissolved in THF (40 ml), a solution of $[BH_3(THF)]$ in THF (1.0 M, 75 ml, corresponding to 75 mmol of $\{BH_3\}$) was added, and the mixture heated under reflux for 48 h. After cooling down to 0 °C, H_2O (100 ml) was added slowly,

and then aq. HCl (10%, 20 ml). Following removal of the THF under reduced pressure, the resulting aq. solution was extracted with Et_2O (3 × 60 ml), and the combined ether layers were evaporated in vacuo to give a colourless oil. A mixture of $[FeCl_3(OH_2)_6]$ (18 g, 67 mmol), aq. HCl (10%, 120 ml) and *n*-C_6H_{14} (100 ml) was then added to the residual oil, the resulting two-phase system was stirred for 3 h, the *n*-C_6H_{14} layer was separated off, and the aq. layer then extracted with *n*-C_6H_{14} (3 × 40 ml). The combined *n*-C_6H_{14} layers were evaporated in vacuo to yield a colourless solid, [4-Ph-*arachno*-4-CB_8H_{13}] (compound **7**, 750 mg, 4.0 mmol, 22%). The remaining aq. layer was extracted with Et_2O (3 × 60 ml), and the combined ethereal extracts were evaporated in vacuo, to yield a colourless oil. This oily residue was then dissolved in H_2O (50 ml) and, after addition of $[NEt_4]^+Cl^-$ (2.0 g, 12 mmol), a colourless precipitate developed. This white precipitate was filtered off, and dried in vacuo, to yield a colourless mixture of the $[NEt_4]^+$ salts of the eleven-vertex [7-Ph-*nido*-7-$CB_{10}H_{12}]^-$ anion **9** and the twelve-vertex [1-Ph-*closo*-1-$CB_{11}H_{11}]^-$ anion **5** (3.14 g), molar ratio ca. 9:1 by integrated ^{11}B-NMR spectroscopy, corresponding to ca. 7.3 mmol (40%) of **9** and ca. 0.8 mmol (ca. 5%) of **5**.

4.4. Preparation of the $[NEt_4]^+$ salt of the [2-Ph-closo-2-$CB_{10}H_{10}]^-$ anion 4 from the reaction of the [7-Ph-nido-7-$CB_{10}H_{12}]^-$ anion 9 with iodine

A sample of the $[NEt_4]^+$ salts of the mixture of the [7-Ph-*nido*-7-$CB_{10}H_{12}]^-$ anion **9** and the [1-Ph-*closo*-1-$CB_{11}H_{11}]^-$ anion **5** (prepared as above, 0.68 g) was added to a solution of CsCl (2.0 g, 12 mmol) in aq. HCl (10%, 40 ml). The mixture was extracted with Et_2O (3 × 30 ml), and the combined ethereal layers were evaporated in vacuo. The residual pale yellow oil was dissolved in aq. KOH (5%, 50 ml), elemental I_2 (1.0 g, 3.9 mmol) was added, and then the reaction mixture was stirred for 1 h at r.t. Aqueous HCl (10%, 30 ml) and $Na_2[SO_3]$ (0.38 g, 3.0 mmol) were added, the reaction mixture filtered, and a solution of $[NEt_4]^+Cl^-$ (0.50 g, 3.0 mmol) in H_2O (50 ml) was added to the filtrate. The resulting white precipitate was filtered off, and dried in vacuo to yield the $[NEt_4]^+$ the salts of the [2-Ph-*closo*-2-$CB_{10}H_{10}]^-$ anion **4** and the [1-Ph-*closo*-1-$CB_{11}H_{11}]^-$ anion **5**. The white solid was crystallised from hot H_2O–MeOH (proportions ca. 1:1) to yield the $[NEt_4]^+$ salt of the [2-Ph-*closo*-2-$CB_{10}H_{10}]^-$ anion **4** as a white crystalline solid (0.44 g, 1.3 mmol, 65%). Crystals suitable for single-crystal X-ray diffraction analysis were obtained from a concd. solution in $(CH_3)_2CO$ that was overlayered with a ca. fivefold excess of Et_2O. NMR data for $[NEt_4]^+$[*closo*-$PhCB_{10}H_{10}]^-$, in $(CD_3)_2CO$ at 294–299 K, ordered as assignment $\delta(^{11}B)$/ppm [$\delta(^1H)$/ppm] are as follows: BH(9) −4.5 [+1.59], BH(3,6,7,10,11) −10.4 [+2.10], BH(1,4,5,8) −12.3 [+1.88]; additionally $\delta(^1H)$(Ph) ca. +7.77–+6.93 (5H, compact overlapping multiplet), and $\delta(^1H)$(Et) at +3.49 (8H, quartet), +1.40 (12H, triplet), also $\delta(^{13}C)$(Ph) +124.25 (1C), +126.19 (2C), +126.96 (2C) and +145.95 (1C) with $\delta(^{13}C)$(clus-cluster) +50.90 and $\delta(^{13}C)$(Et) +7.05 and +52.45 ppm.

4.5. Nuclear magnetic resonance spectroscopy

NMR spectroscopy was performed at 294–299 K and 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 [34–40]. Chemical shifts δ are given in ppm relative to $\Xi = 100$ MHz for $\delta(^1H)$ (±0.05 ppm) (nominally Me_4Si), $\Xi = 32.083972$ MHz for $\delta(^{11}B)$ (± 0.5 ppm) (nominally $Et_2O{\cdot}BF_3$ in $CDCl_3$) [34] and Ξ = 25.145004 MHz for $\delta(^{13}C)$ (±0.5 ppm) (nominally Me_4Si). Ξ is as defined by McFarlane [41].

4.6. X-ray crystallography

Crystal data for the $[NEt_4]^+$ salt of the [1-Ph-*closo*-1-$CB_7H_7]^-$ anion **1**, $C_{15}H_{32}B_7N$: $M = 302.09$, monoclinic (from C_3H_6O–Et_2O), 0.41 × 0.28 × 0.23 mm, space group $P2_1/n$, $a = 9.5758(2)$, $b = 16.5323(4)$, $c = 12.2821(3)$ Å, $\beta = 98.0110(10)^\circ$, $U = 1925.40(8)$ Å^3, $D_{calc} = 1.042$ Mg m^{-3}, $Z = 4$, Mo–K_α, $\lambda = 0.71073$ Å, $\mu = 0.054$ mm^{-1}, $T = 150(2)$ K, $R1 = 0.0588$ for 3410 reflections with $I > 2\sigma(I)$, and $wR_2 = 0.152$ for all 3772 independent reflections; CCDC reference number 172016. Crystal data for the $[NEt_4]^+$ salt of the [2-Ph-*closo*-2-$CB_{10}H_{10}]^-$ anion **4**, $C_{15}H_{35}B_{10}N$: $M = 337.54$, monoclinic (from C_3H_6O–Et_2O), 0.48 × 0.40 × 0.36 mm, space group $C2/c$, $a = 17.4206(4)$, $b = 13.939(4)$, $c = 19.5909(5)$ Å, $\beta = 113.5340(15)^\circ$, $U = 4359.9(2)$ Å^3, $D_{calc} = 1.028$ Mg m^{-3}, $Z = 8$, Mo–K_α, $\lambda = 0.71073$ Å, $\mu = 0.051$ mm^{-1}, $T = 150(2)$ K, $R_1 = 0.0726$ for 3179 reflections with $I > 2\sigma(I)$, and $wR_2 = 0.2019$ for all 4216 independent reflections; CCDC reference number 172017. Methods and programs were standard [42,43].

5. Supplementary material

Crystallographic data for the $[NEt_4]^+$ salts of the [1-Ph-*closo*-1-$CB_7H_7]^-$ anion **1** and [2-Ph-*closo*-2-$CB_{10}H_{10}]^-$ anion **4**, are deposited at the Cambridge Crystallographic Data Centre, CCDC nos. 172016 and 172017 respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank the UK DTI and the UK EPSRC (grants nos. J56929, L49505 and M83360) for support. We also express our appreciation to Bob Štíbr and Tom Jelínek for helpful discussions and advice.

References

[1] S.H. Strauss, Chem. Rev. 93 (1993) 927.
[2] C.A. Reed, Acc. Chem. Res. 31 (1998) 133.
[3] T. Jelínek, C.A. Kilner, M. Thornton-Pett, J.D. Kennedy, Chem. Commun. (2001) 1790.
[4] Z. Janoušek, P.R. Craig, C.L. Hilton, J. Michl, Abstracts Second European Symposium on Boron Chemistry, EUROBORON 2, Dinard, France, 2–7 September 2001, Abstract no. P 18.
[5] B. Brellochs, in: M.G. Davidson, A.K. Hughes, T.B. Marder, K. Wade (Eds.), Contemporary Boron Chemistry, Royal Society of Chemistry, Cambridge, England, 2000, pp. 212–214.
[6] K. Baše, B. Štíbr, J. Dolanský, J. Duben, Collect. Czech. Chem. Commun. 46 (1981) 2345.
[7] T. Jelínek, B. Štíbr, J. Holub, M. Bakardjiev, D. Hnyk, D.L. Ormsby, C.A. Kilner, M. Thornton-Pett, H.-J. Schanz, B. Wrackmeyer, J.D. Kennedy, Chem. Commun. (2001) 1756.
[8] (a) B. Štíbr, B. Wrackmeyer, Abstracts Second European Symposium on Boron Chemistry, EUROBORON 2, Dinard, France, 2–7 September 2001, Abstract no. L 5;
(b) T. Jelínek, B. Štíbr, J. Holub, M. Bakardjiev, M. Thornton-Pett, J.D. Kennedy, O.L. Tok, W. Milius, B. Wrackmeyer, Abstracts Second European Symposium on Boron Chemistry, EUROBORON 2, Dinard, France, 2–7 September 2001, Abstract no. P 19.
[9] T. Jelínek, B. Štíbr, J. Plešek, J.D. Kennedy, M. Thornton-Pett, J. Chem. Soc. Dalton Trans. (1995) 431.
[10] D.E. Hyatt, F.R. Scholer, L.J. Todd, J.L. Warner, Inorg. Chem. 6 (1967) 2229.
[11] (a) R.E. Williams, Inorg. Chem. 10 (1971) 210;
(b) R.E. Williams, Adv. Inorg. Chem. Radiochem. 18 (1976) 67;
(c) R.E. Williams, Adv. Organomet. Chem. 36 (1994) 1.
[12] (a) K. Wade, Chem. Commun. (1971) 792;
(b) K. Wade, Adv. Inorg. Chem. Radiochem. 18 (1976) 1.
[13] L.J. Guggenberger, Inorg. Chem. 8 (1969) 2771.
[14] See, for example: T. Onak, in: E.L. Muetterties (Ed.), Boron Hydride Chemistry, Academic, New York, 1973, pp. 349–382.
[15] P.v.R. Schleyer, K. Najafian, Inorg. Chem. 37 (1998) 3454.
[16] C. Tsai, W.E. Streib, J. Am. Chem. Soc. 88 (1966) 4513.
[17] O. Volkov, K. Radacki, P. Paetzold, X. Zheng, Z. Anorg. Allg. Chem. 627 (2001) 1185.
[18] E.H. Wong, L. Prasad, E.J. Gabe, M.G. Gatter, Inorg. Chem. 22 (1983) 1143.
[19] G.D. Friesen, J.L. Little, J.C. Huffman, L.J. Todd, Inorg. Chem. 18 (1979) 755.
[20] See for example: J.D. Kennedy, B. Štíbr, T. Jelínek, X.L.R. Fontaine, M. Thornton-Pett, Collect. Czech. Chem. Commun. 58 (1993) 2090 (and references therein).
[21] See, for example: M. Bown, B. Štíbr, X.L.R. Fontaine, T. Jelínek, J. Holub, J.D. Kennedy, M. Thornton-Pett, J. Organomet. Chem. 614–615 (2000) 269 (and references cited therein).
[22] K. Nestor, J.D. Kennedy, M. Thornton-Pett, J. Holub, B. Štíbr, Inorg. Chem. 31 (1992) 3339.
[23] S. Coughlan, T.R. Spalding, G. Ferguson, J.F. Gallagher, A.J. Lough, B. Štíbr, X.L.R. Fontaine, J.D. Kennedy, J. Chem. Soc. Dalton Trans. (1992) 2865.
[24] R.J. Wiersema, M.F. Hawthorne, Inorg. Chem. 12 (1973) 785.
[25] D.A. Kleier, D.A. Dixon, W.N. Lipscomb, Inorg. Chem. 17 (1978) 166.
[26] J.W. Bausch, G.K. Surya Prakash, R.E. Williams, Inorg. Chem. 31 (1992) 3763 (and references therein).
[27] F. Klanberg, D.R. Eaton, L.J. Guggenberger, E.L. Muetterties, Inorg. Chem. 6 (1967) 1271.
[28] B.M. Gimarc, J.J. Ott, J. Am. Chem. Soc. 109 (1987) 1388.
[29] E.L. Muetterties, R.J. Wiersema, M.F. Hawthorne, J. Am. Chem. Soc. 95 (1973) 7521.
[30] E.I. Tolpin, W.N. Lipscomb, J. Am. Chem. Soc. 95 (1973) 2384.
[31] M.E. Leonowicz, F.R. Scholer, Inorg. Chem. 19 (1980) 122.
[32] B. Štíbr, Chem. Rev. 92 (1992) 225.
[33] A. Franken, D.L. Ormsby, C.A. Kilner, W. Clegg, M. Thornton-Pett, J.D. Kennedy, J. Chem. Soc., Dalton Trans. (2002) in press, paper no. B205016C.
[34] See, for example: J.D. Kennedy, Boron, in: J. Mason (Ed.), Multinuclear NMR (Chapter 8, and references therein), Plenum, New York and London, 1987, pp. 221–254.
[35] X.L.R. Fontaine, J.D. Kennedy, J. Chem. Soc. Chem. Commun. (1986) 779.
[36] J.D. Kennedy, J. Staves, Z. Naturforsch. Teil B 34 (1989) 808.
[37] X.L.R. Fontaine, J.D. Kennedy, J. Chem. Soc. Dalton Trans. (1987) 1573.
[38] See, for example M.A. Beckett, M. Bown, X.L.R. Fontaine, N.N. Greenwood, J.D. Kennedy, M. Thornton-Pett, J. Chem. Soc. Dalton Trans. (1988) 1969 (and references therein).
[39] See, for example, G. Ferguson, J.D. Kennedy, X.L.R. Fontaine, Faridoon, T.R. Spalding, J. Chem. Soc. Dalton Trans. (1988) 2555, and references therein.
[40] See, for example: D. Reed, Chem. Soc. Rev. 22 (1993) 109 (and references therein).
[41] W. McFarlane, Proc. R. Soc. (Lond.) Ser. A 306 (1968) 185.
[42] Z. Otwinowski, W. Minor, DENZO-SMN, Processing of x-ray diffraction data collected in oscillation mode, in: C.W. Carter, R.M. Sweet (Eds.), Methods Enzymology, vol. 276, Academic Press, New York, 1997, p. 307.
[43] COLLECT, Data Collection Strategy Program, Nonius, 1999.