POLYHEDRAL MONOCARBABORANE CHEMISTRY. FUNCTIONALITY AND ISOMERISM: REACTIONS OF THE [6-Ph-*nido*-6-CB_9H_{11}]$^-$ ANION WITH AMINOPYRIDINES $NC_5H_4NH_2$ TO YIELD NEUTRAL *arachno* AND *closo* TEN-VERTEX MONOCARBABORANE DERIVATIVES

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Reaction of NC_5H_4-2-NH_2 with the [6-Ph-*nido*-6-CB_9H_{11}]$^-$ anion (**1**) in the presence of hydrated $FeCl_3$ gives [6-Ph-9-(NC_5H_4-2-NH_2)-*arachno*-6-CB_9H_{12}] (**4**) and thence [1-Ph-2-(NC_5H_4-2-NH_2)-*closo*-1-CB_9H_8] (**5**), in which the pyridine substituent is on a boron atom α to the cluster carbon atom. This behaviour contrasts to the reactions of organyl-substituted pyridines NC_5H_4R to yield neutral 9-pyridine *arachno* species [6-Ph-9-(NC_5H_4R)-*arachno*-6-CB_9H_{12}] and thence neutral 6-pyridine *closo* species [1-Ph-6-(NC_5H_4R)-*closo*-1-CB_9H_8], in which the pyridine substituent is on a boron atom β to the cluster carbon atom. The chlorinated analogue [1-Ph-2-(NC_5H_4-2-NH_2)-4-Cl-*closo*-1-CB_9H_7] (**7**) is also identified as a minor by-product from the reaction system. Reaction of anion **1** with NC_5H_4-4-NH_2 does not proceed further than [6-Ph-9-(NC_5H_4-4-NH_2)-*arachno*-6-CB_9H_{12}] (**8**). The 2-NH_2 compounds **4**, **5** and **7** exhibit intramolecular BH–HN dihydrogen bonding, whereas the 4-NH_2 compound **8** exhibits an intermolecular BH–HN dihydrogen-bonded network that involves inversion-related pairs of dihydrogen-bonded chains.

Keywords: Boranes; Monocarbaboranes; Carboranes; Amine-functionalised carbaboranes; Pyridine adducts; Crystal and molecular structure; X-ray diffraction; NMR spectroscopy; Dihydrogen bonding.

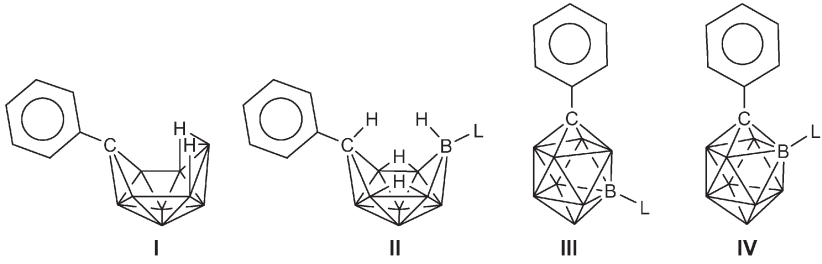
The chemistry of the monocarbaboranes – boron hydride cluster compounds that contain one carbon atom in the cluster – is relatively unexplored in comparison to the flanking fields of binary boranes – boron hydride cluster compounds that contain only boron atoms in the cluster – and dicarbaboranes – boron hydride cluster compounds that contain two carbon atoms in the cluster. In the past this was often due to the lack of convenient syntheses for monocarbaboranes[1]. The relatively recent discovery

of the Brellochs reaction[2], between *nido*-$B_{10}H_{14}$ and aldehydes RCHO in alkaline solution, for the generation of {RCB_9} cluster species, now offers a convenient one-step entry into monocarbaborane chemistry. Choice of aldehyde makes a variety of C-substituted monocarbaboranes available[3–10]. Potentially very useful among these for further chemistry are anionic derivatives that have amine or carboxyl groups either directly or indirectly bound to the carbon atom of the monocarbaborane cluster[11–14]. Recently reported carboxyl derivatives include the [*nido*-6-CB_9H_{11}-6-(C_6H_4-4-COOH)]$^-$, [*closo*-2-CB_9H_9-2-(C_6H_4-4-COOH)]$^-$, [*closo*-1-CB_9H_9-1-(C_6H_4-4-COOH)]$^-$, [*arachno*-6-CB_9H_{13}-6-(COOH)]$^-$, [*closo*-2-CB_9H_9-2-(COOH)]$^-$, [*closo*-1-CB_9H_9-1-(COOH)]$^-$, [*closo*-1-CB_9H_9-1-(C_6H_4-4-CHO)]– and [*closo*-1-CB_9H_9-1-(CHO)]$^-$ anions, and recently reported amine derivatives include the [*closo*-1-CB_9H_9-1-(C_6H_4-*para*-NH_2)]$^-$, [*closo*-2-CB_9H_9-2-(C_6H_4-*para*-NH_2)]$^-$ and [1-{4-(4-H_2N-C_6H_4-N=N)-C_6H_4}-*closo*-1-CB_9H_9]$^-$ anions. The latter anions that include {-NH_2} groupings are of interest because previous isolations of amine derivatives of monocarbaborane anions typically give protonated {-NH_3}$^+$ residues and thence compounds with some zwitterionic character[1]. The overall anionic nature of these {-NH_2) monocarbaborane compounds may, however, be disadvantageous in some systems and, consequently, there is some merit in the establishment of equivalent neutral monocarbaborane species that retain the {-NH_2} grouping.

The product of the Brellochs reaction[2] between *nido*-$B_{10}H_{14}$ and PhCHO (refs[3–5]) is an anionic species, the [6-Ph-*nido*-6-CB_9H_{11}]$^-$ anion **1** (schematic cluster structure **I**). In terms of conversion to a neutral system, we have previously reported the reaction of **1** with pyridine and some organyl-substituted pyridines NC_5H_4R in the presence of iron(III) chloride hexahydrate, {$FeCl_3(OH_2)_6$}*, to give neutral monocarbaborane derivatives [6-Ph-9-(NC_5H_4R)-*arachno*-6-CB_9H_{12}] (schematic cluster structure **II**) as initial products, and thence cluster closure was observed to give neutral species [1-Ph-6-(NC_5H_4R)-*closo*-1-CB_9H_8] (schematic cluster structure **III**) as ultimate products[15]. In order to derive new amine-functionalised neutral monocarbaboranes, as opposed to anionic monocarbaboranes, we now extend this work by the investigation of reactions between aminopyridines and anion **1**, again in the presence of {$FeCl_3(OH_2)_6$}. Thence we have found that compounds of the general *arachno* configuration **II** are again the initial

* We use {$FeCl_3(OH_2)_6$} conveniently to describe iron(III) chloride hexahydrate, rather than the more exact, but more cumbersome, solid-state formulation [$FeCl_2(OH_2)_4$]Cl($OH_2)_2$].

products, but now, in the subsequent cluster-closure reaction, compounds of a new [1-Ph-2-L-*closo*-1-CB_9H_8] configuration **IV** are formed. Note that, in schematics **I**–**IV**, and also below in **V**–**VIII** and in Scheme 1, unlabelled vertices represent {BH(*exo*)} units.



RESULTS AND DISCUSSION

The [6-Ph-*nido*-6-CB_9H_{11}]$^-$ anion **1** was prepared via the Brellochs reaction from *nido*-$B_{10}H_{14}$ and benzaldehyde according to literature methods[4,5]. It has been previously reported that, in the presence of {$FeCl_3(OH_2)_6$}, anion **1** reacts with two-electron donor species such as SMe_2 and $PhNH_2$ to form neutral compounds such as [6-Ph-9-(SMe_2)-*arachno*-6-CB_9H_{12}] and [6-Ph-9-(NH_2Ph)-*arachno*-6-CB_9H_{12}] of schematic cluster structure II. When the two-electron donor species is pyridine, however, a subsequent reaction occurs. Although the initial product is the analogous neutral [6-Ph-9-(NC_5H_5)-*arachno*-6-CB_9H_{12}] species **2**, this initial product then very readily undergoes oxidative cage-closure under the reaction conditions to give its neutral *closo* congener [1-Ph-6-(NC_5H_5)-*closo*-1-CB_9H_8] (**3**) (schematic configuration **III**). This very ready further reaction precludes the isolation of the *arachno* species **2** in high yield and good purity. However, when organyl substituents are included on the pyridine ring, for example in the cases of NC_5H_4-4-CH_2Ph and NC_5H_4-4-Ph, this second reaction that gives cluster closure is slower, and the *arachno* intermediate products are much more easily isolated and purified before oxidation to the corresponding *closo* products occurs[15]. In an extension of this work, we now report results from the study of the reaction of the [6-Ph-*nido*-6-CB_9H_{11}]$^-$ anion **1** with 2-aminopyridine and 4-aminopyridine, again in the presence of {$FeCl_3(OH_2)_6$}, now to yield new neutral amine-functionalised monocarbaborane derivatives.

With a relatively low concentration of {$FeCl_3(OH_2)_6$}, of the order of ca. 1.2 molar equivalents relative to anion **1**, the reaction of the [NEt_4]$^+$ salt of **1** with NC_5H_4-2-NH_2 in chloroform at reflux temperature yields [6-Ph-9-

(NC_5H_4-2-NH_2)-*arachno*-6-CB_9H_{12}] (**4**), isolatable in 62% yield. The crystal and molecular structure of compound **4** have been determined crystallographically. From the crystallographically determined molecular structure (Fig. 1) it can be seen that molecules of compound **4** exhibit the expected ten-vertex *arachno* monocarbaborane structural framework, i.e. that based on the parent binary borane model, the [*arachno*-$B_{10}H_{14}]^{2-}$ dianion. This is analogous to the previously reported neutral species [6-Ph-9-(NC_5H_5)-*arachno*-6-CB_9H_{12}] (ref.[15]), with the phenyl and pyridine groups bound *exo* to the cluster in the C(6) and B(9) positions respectively (schematic configuration **II**). It is obviously apparent that the pyridine nitrogen atom preferentially binds to the cluster rather than the amine nitrogen atom. An interesting feature of the overall crystal structure is that the compound crystallises in the non-centrosymmetric space group *Cc*, so that crystals are polar. Characterisation of **4** was further substantiated by ^{11}B and ^{1}H NMR spectroscopy. There are six resonances (all doublets) in the ^{11}B spectrum, corresponding to the six chemically inequivalent sets of boron atoms B(1,3),

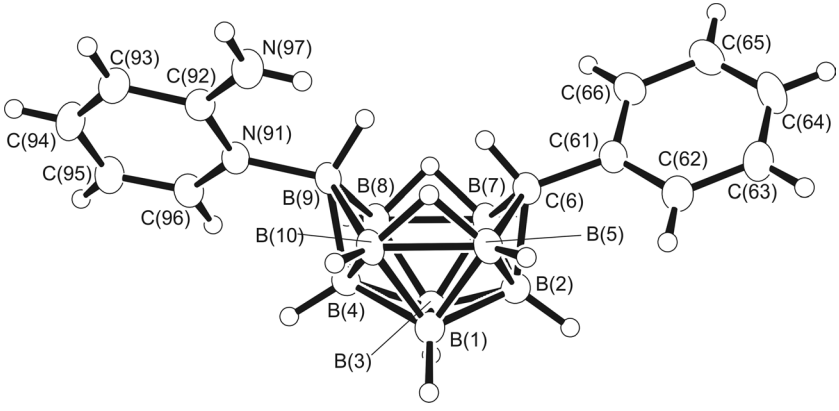
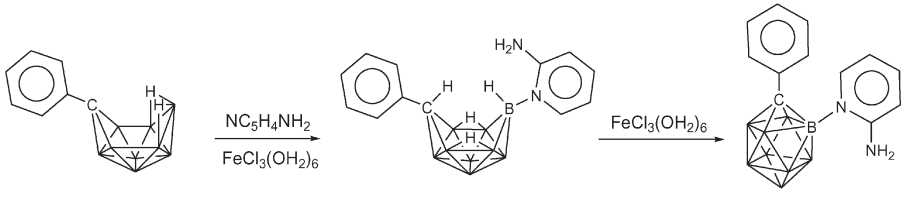


FIG. 1

ORTEP-3 diagram[44] illustrating the crystallographically determined molecular structure of [6-Ph-9-(NC_5H_4-2-NH_2)-*arachno*-6-CB_9H_{12}] (**4**). Anisotropic displacement parameters are shown at the 50% probability level. Selected interatomic distances (in Å) are as follows: B(5)–C(6) 1.734(3), C(6)–B(7) 1.745(3), B(7)–B(8) 1.869(4), B(8)–B(9) 1.887(4), B(9)–B(10) 1.903(3), B(10)–B(5) 1.877(4), C(6)–C(61) 1.508(3) and B(9)–N(91) 1.559(3). Intramolecular BH–HB dihydrogen-bonding interaction is evident from the NH(97a)–HB(9) 'short' interhydrogen distance of 2.04 Å, associated with angles BHH and NHH of 96.0 and 122.6° respectively (see also schematic **V** in the text). For BH–HB dihydrogen bonding the following ranges can be quoted as typical[18]: NH–HB distances 1.7–2.2 Å; mean NHH angle 149(17)°, range 117–171°; mean HHB angle 120(26)°, range 90–171°

B(2), B(4), B(5,7), B(8,10) and B(9). The chemical shifts are in good agreement with those previously reported for similar species such as [6-Ph-9-(NC_5H_5)-*arachno*-6-CB_9H_{12}] (ref.[15]). Full assignments for both ^{11}B and ^{1}H NMR spectra are in the Experimental.

If the {$FeCl_3(OH_2)_6$} is present in a greater excess, the *arachno* species **4** is oxidised to a *closo* congener **5**. However, the product that we initially expected, [1-Ph-6-(NC_5H_4-2-NH_2)-*closo*-1-CB_9H_8] (**6**) (schematic configuration **III**), has only been observed in trace quantities in the ^{11}B NMR spectra of reaction mixtures, and has not proved to be isolatable in our hands so far. Instead, the B(2)-substituted isomer [1-Ph-2-(NC_5H_4-2-NH_2)-*closo*-1-CB_9H_8] (**5**) (schematic configuration **IV**) is obtained as the major reaction product, isolatable in 66% yield. The reaction can be envisaged as a four-electron oxidation of the *arachno* compound **4** by {$FeCl_3(OH_2)_6$} to yield *closo* **5** (see Scheme 1). The crystallographically determined molecular structure of **5** is shown in Fig. 2. Compound **5** was also characterised by ^{11}B and ^{1}H NMR spectroscopy. The ^{11}B NMR spectrum shows five resonance centres. One resonance, that corresponding to B(2), appears as a singlet with relative intensity 1×B, as is expected for the position of substitution. The ^{11}B signals corresponding to the B(3,5) and B(4) positions were accidentally coincident (total relative intensity 3×B), and the remaining resonances arising from B(10), B(6,9) and B(7,8) are doublets with relative intensities 1×B : 2×B : 2×B. It is noteworthy that the chemical shift of the B(10) position antipodal to the cluster carbon atom is shifted by ca. 5 ppm to lower shielding relative to values observed for [1-Ph-6-(NC_5H_5)-*closo*-1-CB_9H_8] (**4**) and related derivatives[15]. Full assignments for both ^{11}B and ^{1}H NMR spectra are in the Experimental.



1
anionic
[6-Ph-*nido*-6-CB_9H_{11}]

4
neutral
[6-Ph-9-(NC_5H_4-2-NH_2)-*arachno*-6-CB_9H_{12}]

5
neutral
[1-Ph-2-(NC_5H_4-2-NH_2)-*closo*-1-CB_9H_8]

SCHEME 1
Schematic diagram exemplifying the formation of *arachno* and *closo* monocarbaborane products **4** and **5** from the reaction of the [6-Ph-*nido*-6-CB_9H_{11}]$^-$ anion **1** with NC_5H_4-2-NH_2

Stoichiometries as in Eqs (*1*) and (*2*) can be respectively written for the reaction of anion **1** with aminopyridines and for the subsequent oxidation of the intermediate *arachno* species **4** to the *closo* product **5**.

$$[6\text{-Ph-}\textit{nido}\text{-6-}CB_9H_{11}]^- \textbf{(1)} + H_2O + NC_5H_4\text{-2-}NH_2 \rightarrow$$

$$[6\text{-Ph-9-}(NC_5H_4\text{-2-}NH_2)\text{-}\textit{arachno}\text{-6-}CB_9H_{12}] \textbf{(4)} + OH^- \quad (1)$$

Although the stoichiometry of Eq. (*1*) does not involve an iron(III) species, the reaction nevertheless does not proceed in the absence of $\{FeCl_3(OH_2)_6\}$, as was also observed previously for the generic reaction of anion **1** with 4-organyl substituted pyridines in the presence of $\{FeCl_3(OH_2)_6\}$. The role of the $\{FeCl_3(OH_2)_6\}$ in the initial pyridine addition to the cluster therefore remains unclear[15], although a redox stoichiometry as in Eq. (*2*) can be readily written down to account for the subsequent oxidative cluster-closure process.

$$[6\text{-Ph-9-}(NC_5H_4\text{-2-}NH_2)\text{-}\textit{arachno}\text{-6-}CB_9H_{12}] \textbf{(4)} + 4\ Fe^{3+} \rightarrow$$

$$[1\text{-Ph-2-}(NC_5H_4\text{-2-}NH_2)\text{-}\textit{closo}\text{-6-}CB_9H_8] \textbf{(5)} + 4\ Fe^{2+} + 4\ H^+ \quad (2)$$

As implied above, the formation of $[1\text{-Ph-2-}(NC_5H_4\text{-2-}NH_2)\text{-}\textit{closo}\text{-1-}CB_9H_8]$ (**5**) is interesting, because instances of 1,2-disubstituted {*closo*-1-CB_9} units are rare. Substitution on the 'lower' tropical four-atom belt of boron atoms, i.e. those more distal from the C(1) cluster-carbon centre, is much more usual, for example in the formation of $[1\text{-Ph-6-}(NC_5H_5)\text{-}\textit{closo}\text{-1-}CB_9H_8]$ (**3**) in work precursive to that presented here[15], as noted above. Additional examples include that previous studies of halogen substitution reactions of ten-vertex monocarbaboranes, such as in reactions of the parent $[\textit{closo}\text{-1-}CB_9H_{10}]^-$ and $[1\text{-Ph-}\textit{closo}\text{-1-}CB_9H_9]^-$ anions, observe that halogenation of these anions occurs initially at the 6-position[3,16,17]. It may also be noted that it is possible to obtain an antipodally substituted (i.e. B(10)-substituted) {*closo*-CB_9} anion, but such a synthesis is not direct[3]: it proceeds via halogenation of a $[2\text{-Ph-}\textit{closo}\text{-2-}CB_9H_9]^-$ anion, yielding a $[2\text{-Ph-7-X-}\textit{closo}\text{-2-}CB_9H_8]^-$ anion, from which a subsequent thermal isomerisation yields a $[1\text{-Ph-10-X-}\textit{closo}\text{-1-}CB_9H_8]^-$ anion.

An additional product that has been isolated, albeit only in the low yield of 2%, from the reaction of the $[6\text{-Ph-}\textit{nido}\text{-6-}CB_9H_{11}]^-$ anion **1** and NC_5H_4-2-NH_2 with an excess of $\{FeCl_3(OH_2)_6\}$ is the chlorinated derivative of **5**, viz. $[1\text{-Ph-2-}(NC_5H_4\text{-2-}NH_2)\text{-4-Cl-}\textit{closo}\text{-1-}CB_9H_7]$ (**7**). This species was also characterised by a single-crystal X-ray diffraction analysis and by

multinuclear NMR spectroscopy. The crystallographically determined molecular structure is shown in Fig. 3. It is thought that the chlorine substituent originates in the $\{FeCl_3(OH_2)_6\}$ reagent, although definitive mechanistic studies have not been undertaken. Again it is of interest that the substituent, now chlorine, is positioned on the 'upper' tropical four-boron belt that is adjacent to, rather than distal from, the carbon vertex.

In addition to the reactions with NC_5H_4-2-NH_2 detailed above, we have also investigated for analogous behaviour with NC_5H_4-4-NH_2. We have thence found that the reaction of the [6-Ph-*nido*-6-CB_9H_{11}]$^-$ anion **1** with NC_5H_4-4-NH_2 and $\{FeCl_3(OH_2)_6\}$ is much slower than the NC_5H_4-2-NH_2 reaction above, and, whereas an initial *arachno* product [6-Ph-9-

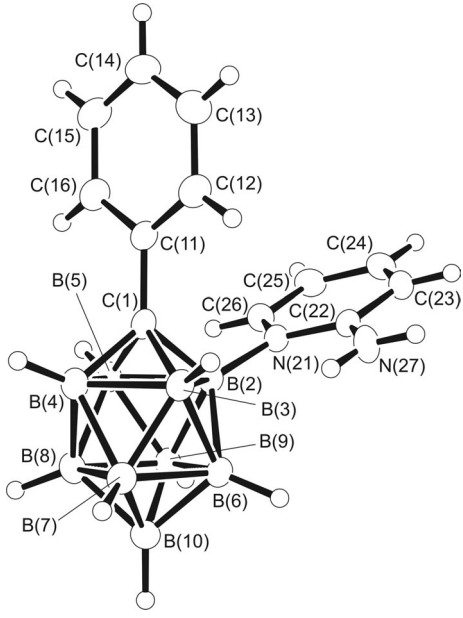


FIG. 2

ORTEP-3 diagram[44] illustrating the crystallographically determined molecular structure of [1-Ph-2-(NC_5H_4-2-NH_2)-*closo*-1-CB_9H_8] (**5**). Anisotropic displacement parameters are shown at the 50% probability level. Selected interatomic distances (in Å) are as follows: C(1)–C(11) 1.492(2), B(2)–N(21) 1.536(2), C(1)–B(2) 1.624(2), B(2)–B(3) 1.825(2), B(2)–B(5) 1.840(2), B(2)–B(6) 1.794(2) and B(2)–B(9) 1.804(2). There are two independent molecules in the crystallographic asymmetric unit. As both have similar intramolecular dimensions, only one diagram and one set of bond distances is given. Weak intramolecular dihydrogen-bonding interactions (see also schematic **VI** in the text) are evident from the NH(27a)–HB(3) and NH(27a)–HB(6) interhydrogen distances of 2.27 and 2.40 Å respectively, BHH angles being 87.9 and 89.9° respectively, with NHH angles 151.6 and 125.0° respectively (compare caption for Fig. 1)

(NC_5H_4-4-NH_2)-*arachno*-6-CB_9H_{12}] (**8**) is formed, and can isolated in a reasonable yield of 43%, we have not yet observed the *closo* congener in reaction mixtures on the basis of inspection using ^{11}B NMR spectroscopy, even after prolonged reaction times. The ^{11}B NMR spectrum of **8** is similar to that of the NC_5H_4-2-NH_2 analogue **4**, and its molecular structure was substantiated by a single-crystal X-ray diffraction analysis, as illustrated in Fig. 4. Compound **8** crystallises in the triclinic space group $P\bar{1}$, with four molecules in the asymmetric unit, arranged about a pseudo-inversion centre. Both ^{11}B and ^{1}H NMR spectra are fully assigned as summarised in the Experimental.

It is of interest to note that all four new compounds **4**, **5**, **7** and **8** that have been characterised by single-crystal X-ray work show evidence for NH–HB dihydrogen bonding in the solid state. This arises from the inherent polarities of the {(δ–)N–H(δ+)} and {(δ+)B–H(δ–)} units that result from

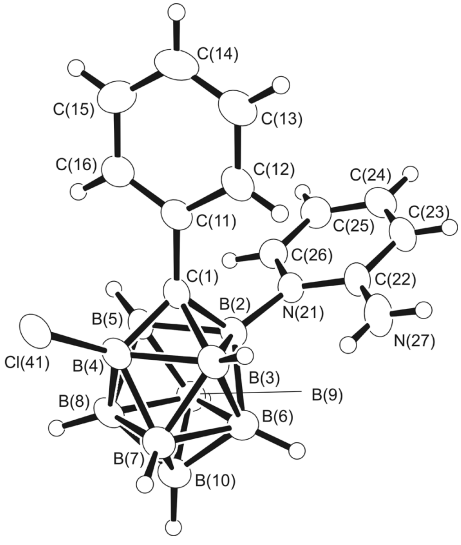
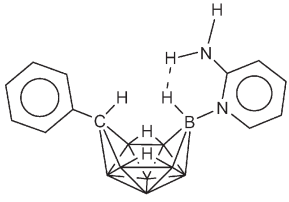


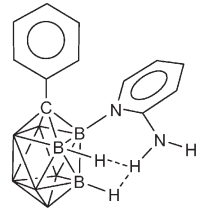
FIG. 3

ORTEP-3 diagram[44] illustrating the crystallographically-determined molecular structure of [1-Ph-2-(NC_5H_4-2-NH_2)-4-Cl-*closo*-1-CB_9H_7] (**7**). Anisotropic displacement parameters are shown at the 50% probability level. Selected interatomic distances (in Å) are as follows: C(1)–C(11) 1.493(4), B(2)–N(21) 1.522(4), C(1)–B(2) 1.608(4), B(2)–B(3) 1.844(4), B(2)–B(5) 1.819(4), B(2)–B(6) 1.811(4), B(2)–B(9) 1.802(4), B(4)–Cl(41) 1.823(3), C(1)–B(4) 1.606(4), B(3)–B(4) 1.829(4), B(4)–B(5) 1.830(4), B(4)–B(7) 1.809(5) and B(4)–B(8) 1.814(4). Weak intramolecular dihydrogen-bonding interactions (see also schematic **VI** in the text) are evident from the NH(27a)–HB(3) and NH(27a)–HB(6) interhydrogen distances of 2.30 and 2.35 Å respectively

the differential electronegativities of boron and nitrogen versus hydrogen[18,19]. There are a number of recent reports on this type of phenomenon in boron hydride chemistry[20–28]. In this present work, it can be seen that the 2-NH_2 group in a molecule of the *arachno* species **4** shows a close intramolecular interaction at 2.04 Å with the BH(9) position (see caption to Fig. 1), forming a six-membered {–CNH–HBN–} ring (schematic **V**). This separation of 2.04 Å may be compared to literature values for NH–HB dihydrogen bonding that typically fall within the range 1.7–2.2 Å (ref.[18]). The two 2-NH_2 *closo* species **5** and **7** also show intramolecular NH–HB hydrogen–hydrogen close approaches, of 2.27–2.40 Å. Individually these are obviously weaker than the 2.04 Å interaction in **4**, but in each of **5** and **7** the NH dihydrogen-bonding interaction is divided between two {BH} units, BH(3) and BH(6), rather than just the one as in **4**. Fused seven-membered {–CNH–HBBN–} rings result (see schematic **VI** and captions to Figs 2 and 3).

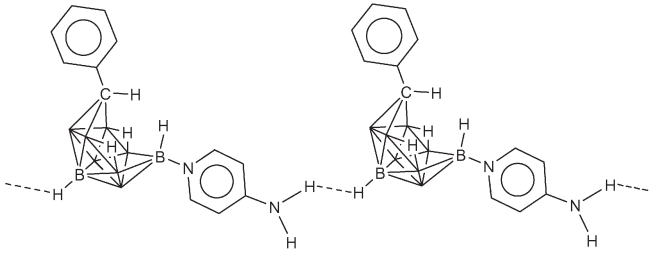


V



VI

By contrast, the 4-NH_2 *arachno* species **8**, with its more exposed amine functionality, shows an extended intermolecular BH–HN dihydrogen-bonded network in the solid state, based essentially on intermolecular interactions between the {NH_2} units and BH(1) or BH(3) positions on adjacent molecules. These associative interactions generate chain assemblies as represented schematically in diagram **VII**.



VII

There are four independent molecules in the unit cell of crystalline **8**. These may be designated as types **A**, **B**, **C** and **D**. Individual molecules of types **A** and **B** are very similar, differing only very subtly in C–C_6H_5 and B–$NC_5H_4NH_2$ rotamer angles. At first sight the asymmetric unit appears to contain non-lattice 'pseudo-inversion' symmetry that relates these two very similar types **A** and **B** (Fig. 5, upper diagram). However this pseudo-symmetry is not a lattice symmetry element in that it is not consistent with the remainder of the contents of the asymmetric unit: most specifically, molecules of types **C** and **D** (see below and Fig. 5, lower) are quite different from each other and are not related by inversion or pseudoinversion. Molecules of types **A** and **B** form double chains propagating in the direction of the unit-cell *ac* diagonal. Each chain consists of alternating independent molecules **A** and **B** linked by BH–HN dihydrogen interactions. In one chain the interaction occurs to the formal BH(1) position, and in the other to the formal BH(3) position, with BH–HN interhydrogen distances of 2.041 Å (between NH in molecules **A** and BH(1) in molecules **B**) and 2.048 Å (between NH in molecules **B** and BH(3) in molecules **A**). The BHH and HHN angles are 123.5 and 158.2° respectively in the first case, and 124.3 and 161.0° respectively in the second, close to the typical mean values of 120 and 149°

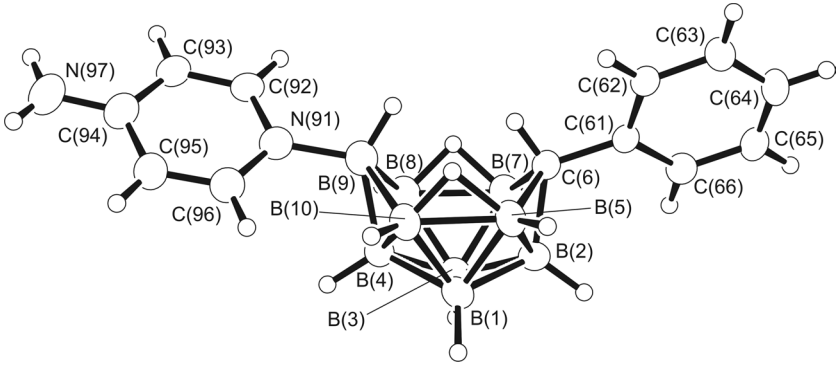


FIG. 4

ORTEP-3 diagram[44] illustrating the crystallographically-determined molecular structure of [6-Ph-9-(NC_5H_4-4-NH_2)-*arachno*-6-CB_9H_{12}] (**8**). Anisotropic displacement parameters are shown at the 50% probability level. Selected interatomic distances (in Å) are as follows: B(5)–C(6) 1.737(3), C(6)–B(7) 1.764(3), B(7)–B(8) 1.872(4), B(8)–B(9) 1.914(4), B(9)–B(10) 1.872(4), B(10)–B(5) 1.861(4), C(6)–C(61) 1.503(3) and B(9)–N(91) 1.562(3). There are four independent molecules, designated as types **A**, **B**, **C** and **D**, in the crystallographic asymmetric unit (see Fig. 5), differing principally in their C–C_6H_5 and B–$NC_5H_4NH_2$ rotamer angles. As all have similar intramolecular interatomic distances, and so only one diagram and one set of intramolecular dimensions is presented here. There is intermolecular dihydrogen bonding interaction in the solid state (schematic **VII** and Fig. 5)

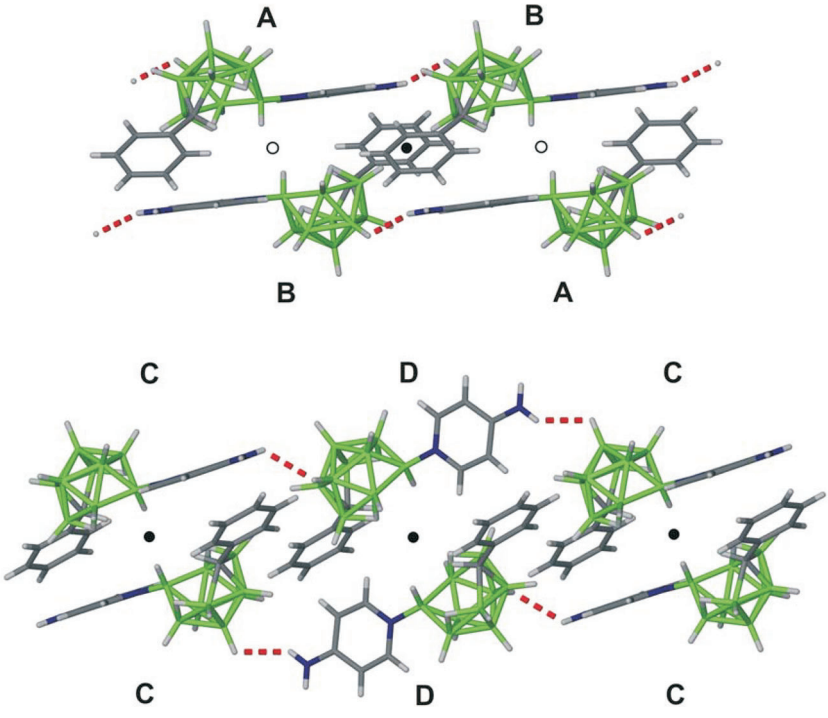


FIG. 5
Xseed diagrams[45] illustrating elements of the extended crystal structure of [6-Ph-9-(NC_5H_4-4-NH_2)-*arachno*-6-CB_9H_{12}] (**8**). See also schematic **VII** in the text. The upper diagram shows the double chain consisting of alternating independent molecules of types **A** and **B**. The rotamer configurations of **A** and **B** are very similar, and individual pairs of molecules of **A** and **B** in adjacent chains can be said to be related by a non-crystallographic pseudo-inversion centre. Each chain can be described as a sequence of molecules bound by BH–HN dihydrogen interactions between amine-group hydrogen atoms and the BH vertex in position B(1) in one chain and B(3) in the other. The BH–HN interhydrogen distances are short at 2.041 and 2.048 Å. The chain is propagated in the direction of the *ac* unit-cell diagonal. Within each single chain, molecules **A** are related by successive *ac* translations, molecules of type **B** likewise. Application of inversion symmetry (● represents an inversion centre relating molecules of same type) generates an equivalent chain running anti-parallel to the original one. In addition to the inversion symmetry that relates molecules of the same type, molecules of types **A** and **B** in neighbouring chains are related by non-crystallographic "pseudo- inversion centres" (○ represents a non-crystallographic pseudo-inversion centre relating individual pairs of molecules of types **A** and **B**). The lower diagram shows the double chain consisting of alternating independent molecules of types **C** and **D**. Each chain can be described as a sequence of molecules weakly interacting via longer BH···HN dihydrogen interactions (2.297 and 2.438 Å in length) between amine-group hydrogen atoms and the BH(3) vertex. The chain is propagated in the direction of the $\bar{a}c$ unit cell diagonal. Molecules **C** along each chain are related by successive $\bar{a}c$ translations, as are molecules of type **D**. Application of inversion symmetry (● designates the inversion centre relating molecules of same type) generates an equivalent chain running anti-parallel to the original one. The significant difference in rotation of the pyridine rings for molecules of types **C** and **D** means that there is no additional pseudo-inversion symmetry in the manner of the double chains that consist of molecules of types **A** and **B**

respectively that have been quoted for BH–HN dihydrogen bonding[18]. The two chains are related by true crystallographic inversion centres that relate individual pairs of molecules **AA** and **BB** in adjacent chains, as well as by the 'pseudo' inversion centres that relate **AB** and **BA** pairs (Fig. 5, upper diagram).

Molecules of types **C** and **D** also form double chains, propagating now along the $\bar{a}c$ unit-cell diagonal. The conformations of types **C** and **D** are much less alike than those of types **A** and **B**, with different B–$NC_5H_4NH_2$ rotamer angles providing the principal difference. In contrast to **A** and **B**, therefore, **C** and **D** are not describable as being related in terms of a pseudo inversion centre. Within the double chains, each of the single chains consists of alternating molecules of types **C** and **D**, with the two chains being related by inversion centres between molecules of the same type (Fig. 5, lower diagram). In these **CD** double chains the BH–HN intermolecular interhydrogen distances are longer than the otherwise corresponding **AB** distances, and take values of 2.297 Å (between NH in molecules **C** and BH(3) in molecules **D**) and of 2.438 Å (between NH in molecules **D** and BH(3) in molecules **C**). These last distances exceed the sum of the van der Waals distances for two hydrogen atoms and so are probably too long to be characterised as definitive BH–HN dihydrogen bonds and may therefore reflect looser electrostatic influences on the intermolecular assembly. This weaker interaction is also manifest in the BHH and HHN angles of 111.5 and 131.0° respectively in the first case, and 112.2 and 119.7° respectively in the second, which now deviate more than the **AB** angles from the typical mean values of 120 and 149° respectively that have been quoted for BH–HN dihydrogen bonding[18].

CONCLUSION

The new neutral amine-functionalised monocarbaborane derivatives **4**, **5**, **7** and **8** reported and characterised here are readily synthesised. These new species incorporate the functionality of a primary amine group into a system of neutral monocarbaboranes, as opposed to anionic monocarbaboranes[15]. The utilisation of such amino functionalities on a neutral monocarbaborane species should now assist the development of further structural chemistry, effect chemistry and reaction chemistry for monocarbaborane systems. For example, reactions of {-NH_2} units with carboxylic acids, acid chlorides and aldehydes, generating peptide or imine linkages, etc., are classical features of traditional organic chemistry that have recent precedent of application in anionic monocarbaborane systems[11–14]. The

new ten-vertex *closo*-1-monocarbadecaboranes **5** and **7** are additionally interesting in that they exhibit the unexpected positioning of a substituent at B(2), i.e. on the belt of boron atoms adjacent to the apical cluster carbon atom (schematic **IV**). Previous precedent would predict a 6-substituted isomeric configuration **III**, but the 6-substituted isomer **6** expected on this basis was only detectable in trace quantities in the reaction mixture and we have not been able to isolate it from the reaction. Further interest derives from the observation of the BH–HN dihydrogen bonding that the amine groups engender, particularly the BH–HN bonding that induces the extended chain structures in the crystals of compound **8**. These observations may be conduced to the understanding of processes of intermolecular self-assembly as in crystal engineering, host–guest chemistry and molecular recognition, areas in which the use of polyhedral boron-containing cluster compounds is attracting healthy contemporary attention[29–34].

EXPERIMENTAL

General

Reagents and solvents were obtained commercially; solvents were dried and deoxygenated before use, and reagents were used as obtained commercially. The $[NEt_4]^+$ salt **1a** of the [6-Ph-*nido*-6-CB_9H_{11}]$^-$ anion **1** was prepared by the Brellochs reaction between *nido*-$B_{10}H_{14}$ and PhCHO as described in the literature[5]. Reactions were carried out under dry nitrogen, with subsequent manipulations conducted in air. Evaporations were carried out at room temperature using a thin-film rotary evaporator at water-pump pressure. Thin-layer chromatography (TLC) was carried out using 1-mm layers of silica gel GF254 supported on glass plates of dimensions 20 × 20 cm, made from aqueous slurries followed by drying in air at 80 °C. Criteria of identity and purity for new species were clean ^{11}B and ^{1}H NMR spectra together with, for products obtained in non-trace quantities, single-crystal X-ray diffraction analysis for the crystal and molecular structures, as well as elemental analytical data, and also in most cases by mass-spectrometric confirmation of molecular weight and empirical formula (although in their mass spectra the hydrogen-richer *arachno* species **4** and **8** exhibited ready double dihydrogen loss from the parent ion). Single-resonance NMR spectroscopy, and one-dimensional and two-dimensional double-resonance correlation NMR spectroscopy, were performed at 294–299 K and at ca. 5.9 T (the field $\boldsymbol{B}_0$ corresponding to ^{1}H Larmour frequencies at ca. 250 MHz). Commercially available instrumentation was used, with techniques and procedures as adequately described and enunciated elsewhere[35–39]. Chemical shifts δ are given in ppm relative to Ξ = 100 MHz (nominally TMS) for δ(^{1}H) (±0.05 ppm) and Ξ = 32.083972 MHz (nominally [$BF_3(OEt_2)$] in $CDCl_3$ (ref.[39])) for δ(^{11}B) (±0.5 ppm). Ξ is as defined by McFarlane[40], and is the resonance frequency at the polarising field strength $\boldsymbol{B}_0$ at which the protons in TMS resonate at *exactly* 100 MHz. Resonance-line separations arising from couplings *J* are given in Hz. Separations of the doublets observed for {BH} units in the ^{11}B spectra are given ±4 Hz, although it should be pointed out that, because of natural linewidth and overlap of the two components of the doublets, these experi-

mentally observed splittings will often be lower than the actual coupling constants $^1J(^{11}B\text{-}^1H)$, particularly in cases of broader resonance lines and overlap of proximate resonances[39]. For the non-cluster ^1H NMR data, numberings of the non-cluster hydrogen atoms are according to those used for the crystallographic data.

Preparation of [6-Ph-9-(NC_5H_4-2-NH_2)-*arachno*-6-CB_9H_{12}] (**4**)

[NEt_4][6-Ph-*nido*-6-CB_9H_{11}] (**1a**; 250 mg, 760 μmol) was dissolved in $CHCl_3$ (30 cm^3), and NC_5H_4-2-NH_2 (1 g, 10.6 mmol) and {$FeCl_3(OH_2)_6$} (250 mg, 925 μmol) were added. The reaction mixture was stirred at reflux temperature under a nitrogen atmosphere for 18 h. The reaction mixture was then filtered, and the solid residue washed with $CHCl_3$. The $CHCl_3$ solutions were combined and then evaporated, and the residue redissolved in CH_2Cl_2 (30 cm^3). The CH_2Cl_2 solution was washed with water (3 × 30 cm^3), the water layers were combined and extracted with CH_2Cl_2 (3 × 30 cm^3), and the CH_2Cl_2 solutions combined and evaporated, leaving a pale brown residue. Preparative TLC (CH_2Cl_2:C_6H_{14}, 3:1) yielded pure [6-Ph-9-(NC_5H_4-2-NH_2)-*arachno*-6-CB_9H_{12}] (**4**) as a white crystalline solid (138 mg, 470 μmol, 62%, R_F 0.48). Slow diffusion between C_6H_{14} and a solution of **4** in CH_2Cl_2 in a 5-mm glass tube yielded single crystals (m.p. (dec.) 227–235 °C) suitable for study by single-crystal X-ray diffraction analysis. NMR data: $\delta(^{11}B)$ ($CDCl_3$): +1.3, d(138), B(4); –6.7 (1 × B) and –8.7 (2 × B), d(149), B(2) and B(5,7); –16.6, d(117), B(9); –26.2, d(129), B(8,10); –38.9, d(148), B(1,3). $\delta(^1H)$ ($CDCl_3$): +8.24, d, H(96); +7.69, t, H(94); +7.24, d, H(62,66); +7.20, t, H(63,65); +7.11, t, H(64); +6.80, d and t, H(93,95); +6.05, H(97); +2.78, H(2); +2.65, 3 × H, H(4), H(5) and H(7) accidentally coincident; +1.47, H(8,10); +0.75, H(1,3); +0.69, H(9); –0.26, H(6); –3.35, μH(5,10;7,8). Microanalysis: for $C_{12}H_{23}B_9N_2$ (292.6) calculated: 49.3% C, 7.9% H, 9.6% N; found: 49.0% C, 7.8% H, 9.4% N. Mass spectrometry: envelope maximum *m/z* 288.1, $[M]^+ - 4$ H.

Formation and Isolation of [1-Ph-2-(NC_5H_4-2-NH_2)-*closo*-1-CB_9H_8] (**5**) and [1-Ph-2-(NC_5H_4-2-NH_2)-4-Cl-*closo*-1-CB_9H_7] (**7**)

[NEt_4][6-Ph-*nido*-6-CB_9H_{11}] (**1a**; 250 mg, 760 μmol) and NC_5H_4-2-NH_2 (1.2 g, 12.8 mmol) were dissolved in $CHCl_3$ (30 cm^3) and {$FeCl_3(OH_2)_6$} (800 mg, 2.96 mmol) was added. The reaction mixture was stirred at reflux temperature under an atmosphere of dry nitrogen for 3 days The reaction mixture was then cooled and filtered, and the solid residue washed with CH_2Cl_2 (30 cm^3). The filtrate was evaporated, and the residue redissolved in a smaller amount of CH_2Cl_2 (5 cm^3). A small amount of a residual white solid, identified as crude [1-Ph-2-(NC_5H_4-2-NH_2)-4-Cl-*closo*-1-CB_9H_7] (**7**), was filtered off and dried (5 mg, 17 μmol, 2%). Evaporation of the CH_2Cl_2 solution gave a brown residue, which was washed with water, and redissolved in CH_2Cl_2 (10 cm^3). This solution washed with water (3 × 20 cm^3) and the organic layer was then evaporated to yield a white solid. Preparative TLC (CH_2Cl_2:C_6H_{14}, 4:1) thence yielded pure [1-Ph-2-(NC_5H_4-2-NH_2)-*closo*-1-CB_9H_8] (**5**) as a white crystalline solid (145 mg, 500 μmol, 66%, R_F 0.41). Slow diffusion between C_6H_{14} and a solution of **7** in Me_2CO in a 5-mm glass tube yielded a small number of single crystals of **7** suitable for study by single-crystal X-ray diffraction analysis, and slow diffusion between C_6H_{14} and a CH_2Cl_2 solution of **5** in a 5-mm glass tube similarly yielded single crystals of **5** (m.p. 214–217 °C) suitable for study by single-crystal X-ray diffraction analysis. For **7**, NMR data: $\delta(^{11}B)$ ($(CD_3)_2CO$): +27.8, d(162), B(10); –5.4, s, B(2); –8.00, s, B(4); –14.3, d(157), B(3,5); –19.7, d(158), B(6,9); –21.8, d(152), B(7,8). $\delta(^1H)$ ($(CD_3)_2CO$): +7.75, m, H(12,16,26); +7.4, m, H(13-15,24); +7.24, H(27); +7.03, d, H(23); +6.85, t, H(25); +5.59, H(10); +3.05, H(3,5);

+1.34, H(6,9); +1.27, H(7,8). For **5**, NMR data: δ(^{11}B) ($CDCl_3$): +30.3, d(163), B(10); –5.5, s, B(2); –15.4, d(156), B(3,4,5); –20.4, d(145), B(6,9); –24.6, d(141), B(7,8). δ(^{1}H) ($CDCl_3$): +7.74, d, H(26); +7.67, d, H(12,16); +7.62, t, H(24); +7.28, m, H(13–15); +6.71, t, H(25); +6.65, d, H(23); +6.04, H(27); +5.78, H(10); +2.63, H(3,5); +1.94, H(4); +1.35, H(6,9); +1.10, H(7,8). Microanalysis: for $C_{12}H_{19}B_9N_2$ (288.6) calculated: 49.9% C, 6.6% H, 9.7% N; found: 50.0% C, 6.7% H, 9.7% N. Mass spectrometry: envelope maximum *m/z* 288.1, $[M]^+$.

Preparation of [6-Ph-9-(NC_5H_4-4-NH_2)-*arachno*-6-CB_9H_{12}] (**8**)

[NEt_4][6-Ph-*nido*-6-CB_9H_{11}] (**1a**; 250 mg, 760 μmol) and NC_5H_4-4-NH_2 (1 g, 10.6 mmol) were dissolved in $CHCl_3$ (30 cm^3) and {$FeCl_3(OH_2)_6$} (1 g, 3.70 mmol) was added. The reaction mixture was stirred at reflux temperature under an atmosphere of dry nitrogen for 5 days, then filtered and evaporated to dryness. The brown residue was washed with water, dissolved in CH_2Cl_2 (10 cm^3) and washed with water (3 × 20 cm^3). The organic layer was evaporated to yield a yellow residue, which was dissolved in a minimum amount of CH_2Cl_2 and filtered through flash silica. The filtrate was evaporated to give a white solid which was recrystallised from $CHCl_3$ to yield [6-Ph-9-(NC_5H_4-4-NH_2)-*arachno*-6-CB_9H_{12}] (**8**; 95 mg, 320 μmol, 43%). This crystallisation also afforded single crystals (m.p. (dec.) 183–186 °C) suitable for study by single-crystal X-ray diffraction analysis. NMR data: δ(^{11}B) ($CDCl_3$): –0.06, d(128), B(4); –9.2, d(132), B(2) and B(5,7) accidentally coincident; –12.3, d(117), B(9); –26.1, d(125), B(8,10); –39.6, d(146), B(1,3). δ(^{1}H) ($CDCl_3$): +8.27, d, H(92,96); +7.24, d, H(62,66); +7.19, t, H(63,65); +7.10, t, H(64); +6.61, d, H(93,95); +5.00, H(97); +2.69, H(2); +2.51, H(4); +2.58, H(5,7); +1.39, H(8,10); +1.15, H(9); +0.66, H(1,3); –0.32, H(6); –3.25, μH(5,10;7,8). Microanalysis: for $C_{12}H_{23}B_9N_2$ (292.6) calculated: 49.3% C, 7.9% H, 9.6% N; found: 49.0% C, 8.1% H, 9.3% N. Mass spectrometry: envelope maximum *m/z* 288.1, $[M]^+$ – 4 H.

Single-Crystal X-ray Diffraction Analyses

For all compounds a conventional sealed-tube X-ray source was used, and methods and programs were standard[41–43]. Display programs were ORTEP-3 and X-seed-1.5 [44,45]. Selected crystallographic data are given below. Full data for all the previously crystallographically unreported species discussed in this present paper are deposited at the Cambridge Crystallographic Data Centre, CCDC. CCDC 272531 (**4**), 272532 (**5**), 272533 (**7**), 272534 (**8**) contain the supplementary crystallographic data for this present paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

[6-Ph-9-(NC_5H_4-2-NH_2)-arachno-6-CB_9H_{12}] (**4**): $C_{12}H_{23}B_9N_2$, M = 292.61, monoclinic, non-centrosymmetric space group Cc, a = 8.2967(2) Å, b = 20.3316(6) Å, c = 10.5257(4) Å, β = 108.3570(10)°, U = 1685.18(9) Å^3, D_{calc} = 1.153 Mg m^{-3}, Z = 4, MoKα, λ = 0.71073 Å, μ = 0.06 mm^{-1}, T = 150(2) K, R_1 = 0.0608 for 2813 reflections with $I > 2\sigma(I)$, and wR_2 = 0.1627 for all 2972 unique reflections.

[1-Ph-2-(NC_5H_4-2-NH_2)-closo-1-CB_9H_8] (**5**): $C_{12}H_{19}B_9N_2$, M = 288.58, orthorhombic, space group $Pna2_1$, a = 17.7374(2) Å, b = 17.6794(2) Å, c = 10.2808(1) Å, U = 3223.92(6) Å^3, D_{calc} = 1.189 Mg m^{-3}, Z = 8, MoKα, λ = 0.71073 Å, μ = 0.062 mm^{-1}, T = 150(2) K, R_1 = 0.0373 for 5987 reflections with $I > 2\sigma(I)$, and wR_2 = 0.0948 for all 6319 unique reflections.

[1-Ph-2-(NC$_5$H$_4$-2-NH$_2$)-4-Cl-closo-6-CB$_9$H$_7$] (**7**): $C_{12}H_{18}B_9ClN_2$, M = 323.02, orthorhombic, space group $Pna2_1$, a = 13.3673(6) Å, b = 8.4604(3) Å, c = 14.8624(5) Å, U = 1680.83(11) Å^3, D_{calc} = 1.276 Mg m^{-3}, Z = 4, MoKα, λ = 0.71073 Å, μ = 0.22 mm^{-1}, T = 150(2) K, R_1 = 0.0453 for 2849 reflections with $I > 2\sigma(I)$, and wR_2 = 0.1143 for all 3236 unique reflections.

[6-Ph-9-(NC$_5$H$_4$-4-NH$_2$)-arachno-6-CB$_9$H$_{12}$] (**8**): $C_{12}H_{23}B_9N_2$, M = 292.61, triclinic, space group $P\bar{1}$, a = 10.5559(2) Å, b = 17.2624(3) Å, c = 18.9484(3) Å, α = 86.310(1)°, β = 89.8100(10)°, γ = 80.5480(10)°, U = 3398.75(10) Å^3, D_{calc} = 1.144 Mg m^{-3}, Z = 8, MoKα, λ = 0.71073 Å, μ = 0.059 mm^{-1}, T = 150(2) K, R_1 = 0.0925 for 9146 reflections with $I > 2\sigma(I)$, and wR_2 = 0.271 for all 13 294 unique reflections.

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