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Polyhedral monocarbaborane chemistry ☆ Reactions of the [6-Ph-*nido*-6-CB_9H_{11}]$^-$ anion with two-electron donors to yield a series of neutral *arachno* and *closo* ten-vertex monocarbaborane derivatives

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Abstract

Reaction of the ten-vertex [6-Ph-*nido*-6-CB_9H_{11}]$^-$ anion (**1**) with two-electron donor ligands L, where L is SMe_2, NH_2Ph, NC_5H_5, NC_5H_4-*para*-CH_2Ph, NC_5H_4-*para*-Ph or NC_9H_7 (where NC_9H_7 is quinoline) in the presence of {$FeCl_3(OH_2)_6$} gives the six neutral *arachno* ten-vertex monocarbaboranes [6-Ph-9-L-*arachno*-6-CB_9H_{12}], compounds **2**, **3, 4**, **7**, **9** and **11**, respectively, isolatable in yields of up to 63%. On prolonged treatment with {$FeCl_3(OH_2)_6$} oxidative cluster closure of the four compounds **4**, **7**, **9** and **11** that have pyridine-type ligands gives the neutral *closo* ten-vertex monocarbaboranes [1-Ph-6-L-*closo*-1-CB_9H_8], compounds **6**, **8**, **10** and **12**, respectively, in yields of 49–92%. All new species **2**, **3**, **4**, **6**, **7**, **8**, **9**, **10**, **11** and **12** are characterised by single-crystal X-ray diffraction analysis and NMR spectroscopy. [This paper is an annotated exposition of parts of an oral presentation at the Third Pan-European Meeting of Boron Chemists, EUROBORON-3, Pruhonice, The Czech Republic, September 2004, of which the proceedings constitute this volume of *Journal of Organometallic Chemistry*.]

Keywords: Boron-containing cluster compounds; Monocarbaboranes; *closo* Ten-vertex monocarbaboranes; *arachno* Ten-vertex monocarbaboranes; Ligand adducts of moncarbaboranes; Single-crystal X-ray diffraction analysis; Crystal and molecular structure; NMR spectroscopy

1. Introduction

The chemistry of the monocarbaboranes – boron hydride cluster compounds that also 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 also contain two carbon atoms in the cluster. In the past this was mainly due to the lack of convenient syntheses of these compounds. The relatively recent discovery of the Brellochs reaction, between *nido*-$B_{10}H_{14}$ and aldehydes in alkaline solution, for the generation of {CB_9} cluster species, now offers a convenient one-step entry into monocarbaborane chemistry, with the choice of aldehyde making a variety of

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C-substituted monocarbaboranes available [1–6]. There is some ongoing interest in the synthesis of species that combine carbaborane units with organyl systems to generate interesting molecular frameworks, for example in the construction of rod-like units, due in part to their potential applicability in areas such as nanoarchitectural construction [7–13] and effect chemistry such as liquid-crystal behaviour [14,15]. As a contribution to these areas, we report here on a potentially generic route to neutral monocarbaborane derivatives that is afforded by the reaction of the [6-Ph-*nido*-6-CB_9H_{11}]$^-$ anion **1** with two-electron donor species, which we here exemplify principally by pyridine-type species. Anion **1** is the product of the Brellochs reaction between *nido*-$B_{10}H_{14}$ and PhCHO. The commercial availability of many pyridine derivatives that can be used as two-electron donors permits the ready synthesis of systematically related series of compounds. The resulting neutral species described, of which the molecules have an extended bent aspect, complement recently reported monoanionic and dianionic rod-like species that are also constructed from combinations of monocarbaborane and organic units [16].

A previous study of a number of neutral pyridine-borane compounds, specifically a series with general formulation [6,9-(NC_5H_4R)$_2$-*arachno*-$B_{10}H_{12}$], made use of Kitaigorodskii's *Aufbau* Principle (KAP) for the systematic analysis and visualisation of any similarities or variations among their extended crystal structures [17,18]. This method of approach to the delineation of crystal packing allows trends in packing behaviour and specific lower-energy intermolecular solid state interactions of interest to be identified easily and systematically. The cumulative effect of such lower-energy interactions is one of the principal driving forces behind the supramolecular assembly of larger molecules, an area of currently expanding interest and activity. One intention behind this present work is that the generation and crystallographic analysis of systematic sequences of structurally related smaller compounds that are suitable for such systematic KAP analyses will better enable the study and understanding of such weaker interactions.

2. 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 the literature methods [1,2]. We now report that, in the presence of iron(III) chloride hexahydrate – {$FeCl_3(OH_2)_6$} – anion **1** reacts with two-electron donor species such as dimethylsulfide, aniline and pyridine to form compounds such as [6-Ph-9-(SMe_2)-*arachno*-6-CB_9H_{12}] (**2**), [6-Ph-9-(NH_2Ph)-*arachno*-6-CB_9H_{12}] (**3**) and [6-Ph-9-(NC_5H_5)-*arachno*-6-CB_9H_{12}] (**4**). Note that, for convenience in this text, we use the formulation {$FeCl_3(OH_2)_6$} to describe iron(III) chloride hexahydrate, rather than the more exact, but more cumbersome, solid-state formulation [$FeCl_2(OH_2)_4$]$Cl(OH_2)_2$; we acknowledge an (inexact) comment from a referee about this. We have been able to obtain compounds **2** and **3** in yields of 88% and 58%, respectively, although it has so far only been possible to obtain the NC_5H_5 compound **4** in a yield of 14% in a pure state due to its very ready further reaction under the conditions used (see below). The crystallographically determined molecular structures are shown in Fig. 1. Each of the compounds **2**, **3** and **4** exhibits 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, with the phenyl and ligand groups bound *exo* to the cluster in the C(6)- and B(9)-positions, respectively. Characterisation of these compounds was further substantiated by ^{11}B and ^{1}H NMR spectroscopy. These three *arachno* compounds **2**, **3** and **4** have similar ^{11}B NMR spectra, with six resonances corresponding to the chemically inequivalent sets of atoms B(1,3), B(2), B(4), B(5,7), B(8,10) and B(9). Full assignments for both ^{11}B and ^{1}H NMR spectra are given in Section 4.

The crystallographically determined molecular structure of [6-Ph-9-(NC_5H_5)-*arachno*-6-CB_9H_{12}] (**4**) was found to be 50:50 disordered as a result of pseudo-symmetry across the molecular framework. In the crystallographic solution, the disorder results in an averaging of the interatomic distances associated with the C(6) and B(9) positions in the monocarbaborane cluster. These distances are therefore in this case averaged in the crystallographic solution, even though carbon-to-boron connectivities in carbaborane cluster compounds are generally shorter than their corresponding boron-to-boron connectivities. For comparison, Table 1 tabulates relevant cluster-connectivity lengths for compounds **2**, **3** and **4** and for the closely related series of analogous substituted monocarbaboranes [6-Ph-9-(NC_5H_4-*para*-CH_2Ph)-*arachno*-6-CB_9H_{12}] (**7**), [6-Ph-9-(NC_5H_4-*para*-Ph)-*arachno*-6-CB_9H_{12}] (**9**) and [6-Ph-9-(NC_9H_7)-*arachno*-6-CB_9H_{12}] (**11**) (where NC_9H_7 is quinoline). Compounds **7**, **9** and **11** are synthesised and characterised as described below. One consequence of the disorder in the crystal of compound **4** is that the crystallographically derived molecular structure is very similar to that of the long-known isostructural species [6,9-(NC_5H_5)$_2$-*arachno*-$B_{10}H_{12}$] (**5**) [18,19]. In accord with this molecular similarity, the overall three-dimensional crystal structures of compounds **4** and **5** are also very much alike, and essentially isomorphous, as reflected in very similar unit-cell dimensions for both species (Table 2).

If the {$FeCl_3(OH_2)_6$} is present in excess in the reaction with pyridine, an oxidation of the initially formed [6-Ph-9-(NC_5H_5)-*arachno*-6-CB_9H_{12}] species **4** can

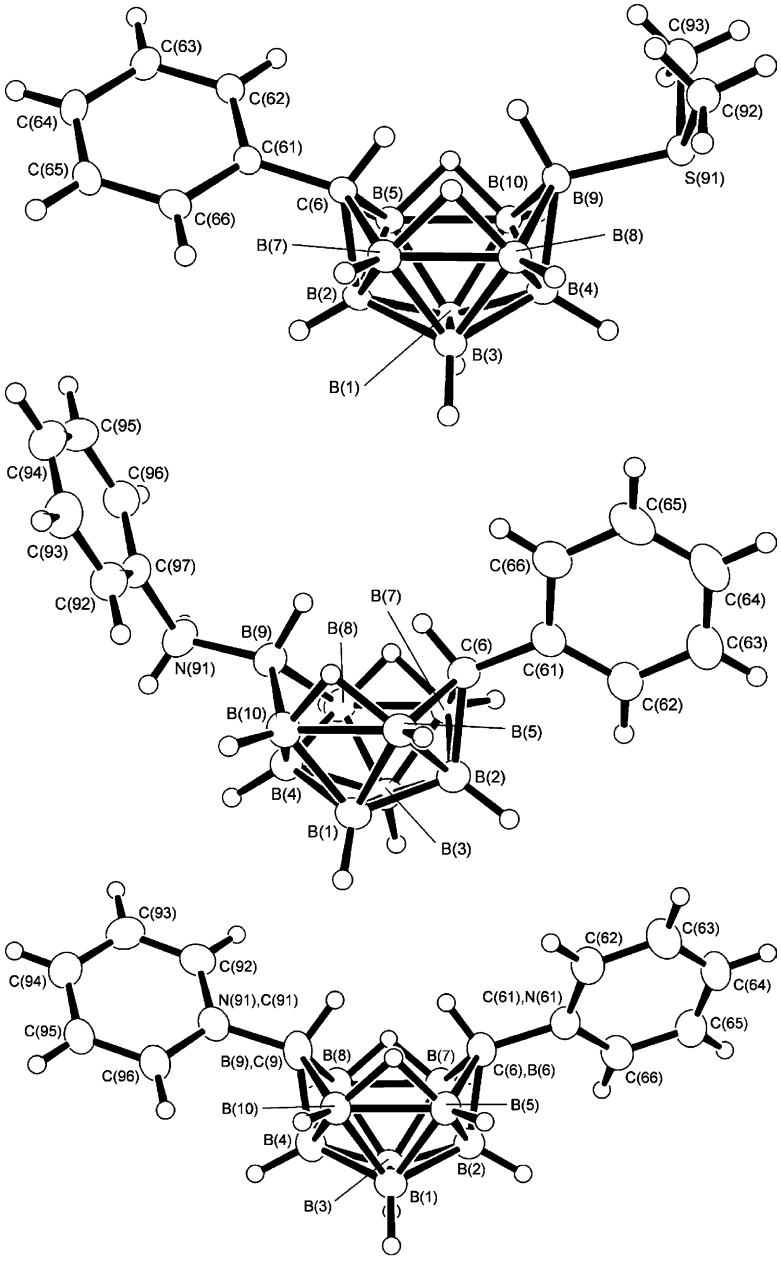


Fig. 1. ORTEP diagrams illustrating the crystallographically determined molecular structures of (top) [6-Ph-9-(SMe_2)-*arachno*-6-CB_9H_{12}] (**2**), (centre) [6-Ph-9-(NH_2Ph)-*arachno*-6-CB_9H_{12}] (**3**) and (bottom) [6-Ph-9-(NC_5H_5)-*arachno*-6-CB_9H_{12}] (**4**). Anisotropic displacement parameters are shown at the 50% probability level. There are two crystallographically independent molecules of [6-Ph-9-(SMe_2)-*arachno*-6-CB_9H_{12}] in the asymmetric unit; but both have similar intramolecular dimensions, therefore only one is shown here. Selected interatomic distances (in Å) are as follows: for **2**, B(5)–C(6) 1.771(4), C(6)–B(7) 1.725(4), B(7)–B(8) 1.889(4), B(8)–B(9) 1.870(4), B(9)–B(10) 1.853(4), B(10)–B(5) 1.861(4), C(6)–C(61) 1.508(4) and B(9)–S(91) 1.912(3); for **3**, B(5)–C(6) 1.739(2), C(6)–B(7) 1.758(2), B(7)–B(8) 1.873(3), B(8)–B(9) 1.890(3), B(9)–B(10) 1.890(3), B(10)–B(5) 1.863(3), C(6)–C(61) 1.495(2) and B(9)–N(91) 1.604(2); and for **4**, B(5)–C(6) 1.822(4), C(6)–B(7) 1.792(4), B(7)–B(8) 1.876(4), B(8)–B(9) 1.811(4), B(9)–B(10) 1.805(4), B(10)–B(5) 1.873(4), C(6)–C(61) 1.543(3) and B(9)–N(91) 1.547(3).

occur. Specifically, a four-electron oxidation results in closure of the monocarbaborane cluster, to yield the corresponding *closo* congener [1-Ph-6-(NC_5H_5)-*closo*-1-CB_9H_8] (**6**). Overall, the {$FeCl_3(OH_2)_6$} first facilitates the binding of the two-electron donor species to the monocarbaborane cluster to yield the [6-Ph-9-(NC_5H_5)-*arachno*-6-CB_9H_{12}] species **4**, and thence, when present in excess, it oxidises this *arachno* monocarbaborane cluster to the *closo* congener **6** (Scheme 1).

Stoichiometries as in Eqs. (1) and (2) can be written for the reaction of anion **1** with pyridine and for the subsequent oxidation of the intermediate *arachno* species **4** to the final *closo* product **6**. Under conditions that we have attempted so far, we have not been able to induce cluster

Table 1
Comparison of connectivity distances for the disordered [6-Ph-9-(NC_5H_5)-*arachno*-6-CB_9H_{12}] structure (compound **4**) with those for related species [6-Ph-9-L-*arachno*-6-CB_9H_{12}], where L is SMe_2 (compound **2**), NH_2Ph (compound **3**), NC_5H_4-*para*-CH_2Ph (compound **7**), NC_5H_4-*para*-Ph (compound **9**) and NC_9H_7 (quinoline, compound **11**)

Connection	Distance (in Å) for [6-Ph-9-L-*arachno*-6-CB_9H_{12}]					
	L = NC_5H_5 (**4**)	L = SMe_2 (**2**)	L = NH_2Ph (**3**)	L = $NC_5H_4CH_2Ph$ (**7**)	L = NC_5H_4Ph (**9**)	L = NC_9H_7 (**11**)
C,B(6)–B(2)	1.688(4)	1.672(4), 1.673(4)	1.674(2)	1.673(3)	1.667 (2)	1.672(2)
C,B(9)–B(4)	1.685(5)	1.737(4), 1.730(4)	1.721(2)	1.745(3)	1.733(2)	1.736(2)
C,B(6)–B(5)	1.822(4)	1.771(4), 1.732(4)	1.734(2)	1.759(3)	1.740(2)	1.736(2)
C,B(9)–B(10)	1.809(4)	1.853(4), 1.852(4)	1.890(3)	1.871(3)	1.901(2)	1.890(2)
C,B(6)–B(7)	1.795(4)	1.725(4), 1.763(4)	1.758(2)	1.732(3)	1.752(2)	1.755(2)
C,B(9)–B(8)	1.813(4)	1.870(4), 1.886(4)	1.890(3)	1.874(3)	1.867(2)	1.895(2)
C,B(6)–C,N(61)	1.541(4)	1.508(4), 1.501(4)	1.495(2)	1.503(2)	1.508(2)	1.504(2)
C,B(9)–C,N(91)	1.545(4)	1.912(3)[a], 1.909(3)[a]	1.604(2)	1.580(3)	1.569(2)	1.580(2)

Standard uncertainties are given in parentheses.
[a] *Note*: The atoms involved in this instance are B(9) and S(91), therefore the distance is greater.

Table 2
Comparison of unit-cell dimensions for the two isostructural species [6-Ph-9-(NC_5H_5)-*arachno*-6-CB_9H_{12}] (compound **4**), and [6,9-(NC_5H_5)$_2$-*arachno*-$B_{10}H_{12}$] (compound **5**) [18,19][a]

	Compound **4**	Compound **5** [a]
Space group	*C*2/*c*	*C*2/*c*
Z	8	8
a	15.3090(4)	15.1401(5)
b	13.6837(4)	13.7539(3)
c	15.7206(5)	15.6420(5)
β	100.874(1)	101.582(2)

Standard uncertainties are given in parentheses.
[a] *Note*: Compound **5** can also be induced to crystallise with $P2_1/c$ morphology [18,19].

closure from *arachno* to *closo* for the SMe_2 and NH_2Ph species **2** and **3**. It is not clear at present why the pyridine species should undergo closure the more readily.

$$[\text{6-Ph-}\textit{nido}\text{-6-}CB_9H_{11}]^- + H_2O + NC_5H_5 \rightarrow \text{6-Ph-9-}(NC_5H_5)\text{-}\textit{arachno}\text{-6-}CB_9H_{12} + OH^- \quad (1)$$

Although the stoichiometry of Eq. (1) does not involve an iron(III) species, the reaction nevertheless does not proceed in the absence of the added {$FeCl_3(OH_2)_6$}. It is not evident to us what the role of the {$FeCl_3(OH_2)_6$}

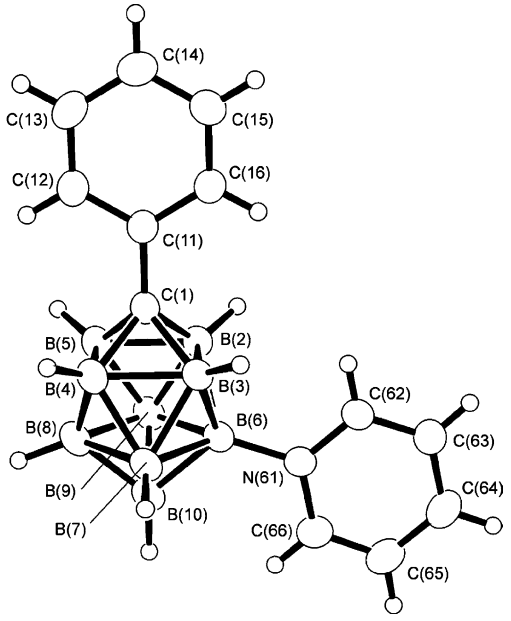
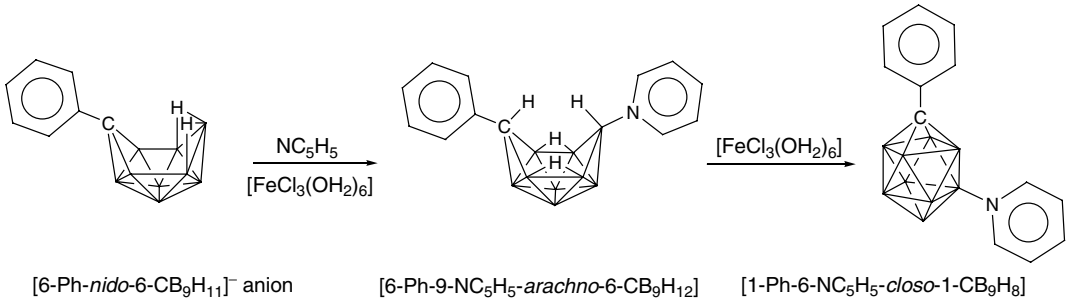


Fig. 2. ORTEP diagram illustrating the crystallographically determined molecular structure of [1-Ph-6-(NC_5H_5)-*closo*-1-CB_9H_8] (compound **6**). Anisotropic displacement parameters are shown at the 50% probability level. Selected interatomic distances (in Å) are as follows: C(1)–C(11) 1.4871(16), C(1)–B(2) 1.6105(17), C(1)–B(3) 1.6082(17), B(2)–B(3) 1.8431(18), B(2)–B(6) 1.7988(18), B(3)–B(6) 1.8047(18) and B(6)–N(61) 1.5501(16).



Scheme 1. Schematic diagram exemplifying the formation of *arachno* and *closo* monocarbaborane products from the reaction of the [6-Ph-*nido*-6-$CB_9H_{11}]^-$ anion (**1**) with pyridines.

might be, whether perhaps as a Lewis acid catalyst – which is unlikely as the metal centre will be coordinatively unsaturated in its hydrated form, or perhaps as a generator of mild protic acidity under the quasi-aqueous conditions, which may assist the reaction in some way. An interesting quasi-converse of this type of phenomenon is involved in the reaction of the *nido* ten-vertex $[PhCB_9H_{11}]^-$ anion (**1**) to give the *closo* ten-vertex $[PhCB_9H_9]^-$ anion by ostensibly simple dihydrogen loss, which we have found proceeds best with the presence of elemental sodium metal [2], which is odd because the closure is a formal oxidation, whereas elemental sodium is a strong reducing agent.

The crystallographically determined molecular structure of **6** is shown in Fig. 2. It can be seen that the phenyl-substituted carbon atom is at the apical 1-position, with the pyridine unit bound to the boron atom in the 6-position. As with all new compounds reported in this paper, this crystallographically determined structure is consistent with the ^{11}B and ^{1}H NMR spectra recorded

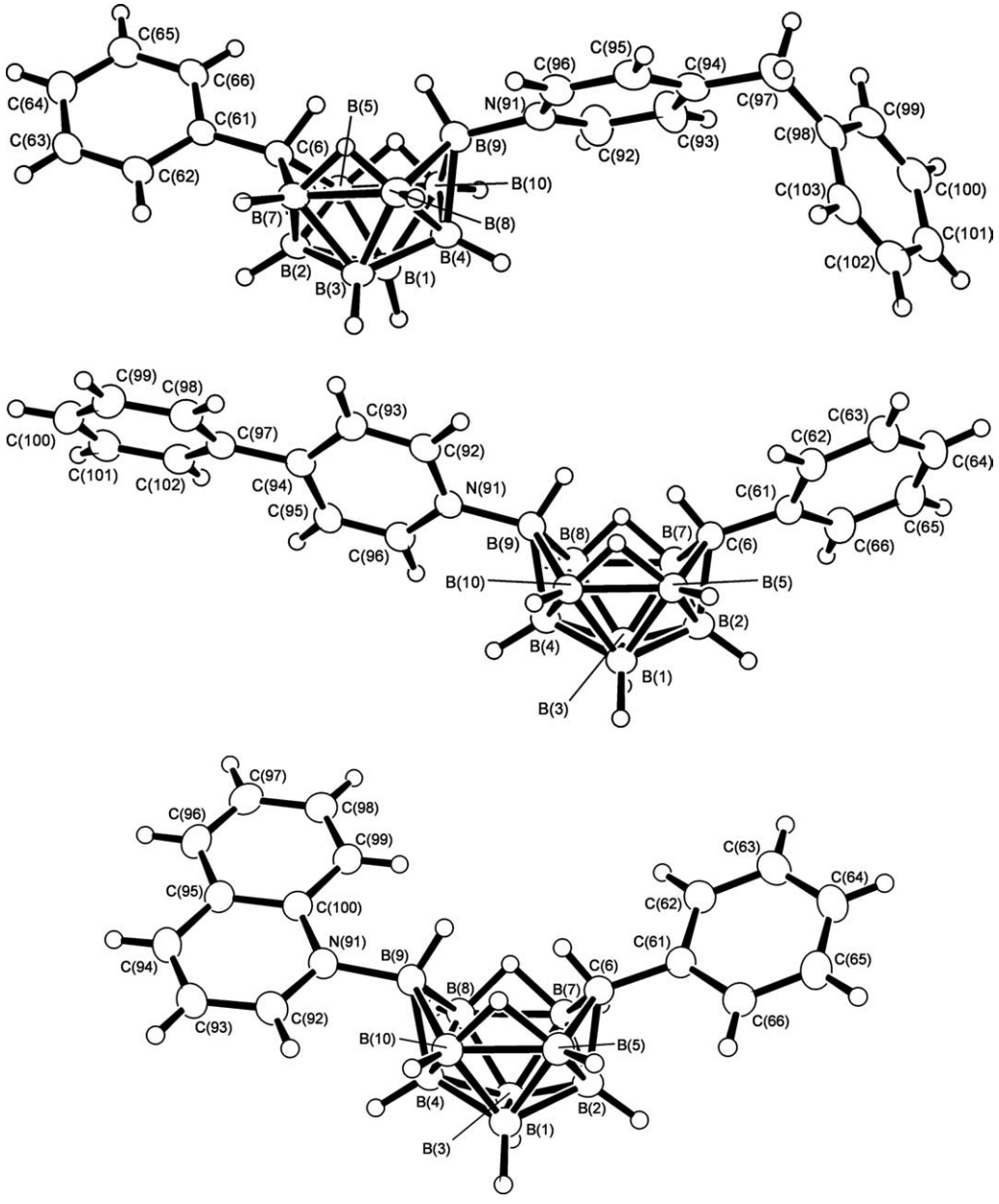


Fig. 3. ORTEP diagrams illustrating the crystallographically determined molecular structures of (top) [6-Ph-9-(NC_5H_4-*para*-CH_2Ph)-*arachno*-6-CB_9H_{12}] (compound **7**), (centre) [6-Ph-9-(NC_5H_4-*para*-Ph)-*arachno*-6-CB_9H_{12}] (compound **9**), and (bottom) [6-Ph-9-(NC_9H_7)-*arachno*-6-CB_9H_{12}] (compound **11**). Anisotropic displacement parameters are shown at the 50% probability level. Selected interatomic distances (in Å) are as follows: for **7**, B(5)–C(6) 1.759(3), C(6)–B(7) 1.732(3), B(7)–B(8) 1.867(3), B(8)–B(9) 1.874(3), B(9)–B(10) 1.871(3), B(10)–B(5) 1.870(3), C(6)–C(61) 1.503(2) and B(9)–N(91) 1.580(3); for **9**, B(5)–C(6) 1.7396(19), C(6)–B(7) 1.7523(19), B(7)–B(8) 1.875(2), B(8)–B(9) 1.867(2), B(9)–B(10) 1.901(2), B(10)–B(5) 1.863(2), C(6)–C(61) 1.5077(17) and B(9)–N(91) 1.5685(17); and for **11**, B(5)–C(6) 1.7361(18), C(6)–B(7) 1.7554(19), B(7)–B(8) 1.870(2), B(8)–B(9) 1.895(2), B(9)–B(10) 1.890(2), B(10)–B(5) 1.876(2), C(6)–C(61) 1.5036(17) and B(9)–N(91) 1.5789(17).

for the bulk sample, confirming that the single crystals selected for the X-ray work were representative. Thus, this *closo* ten-vertex monocarbadecaborane [1-Ph-6-(NC_5H_5)-*closo*-1-CB_9H_8] (**6**) shows six resonance centres in its ^{11}B NMR spectrum, arising from the inequivalent B(2,3), B(4,5), B(6), B(7,9), B(8) and B(10) positions. As expected, the B(6) resonance for the pyridine-substituted position appears as a singlet in the ^{11}B NMR spectrum, whereas the other signals appear as doublets arising from couplings $^1J(^{11}B–^1H)$.

Pyridine-substitution on the lower belt of boron atoms, i.e., those more distal from the C(1) cluster carbon centre, is in accord with observations made in previous studies of substitution reactions of ten-vertex monocarbaboranes, such as in reactions of the [*closo*-1-$CB_9H_{10}]^-$ and [1-Ph-*closo*-1-$CB_9H_9]^-$ anions. For example, it has been reported that halogenation of these two anions occurs also initially at the 6-position [2,20,21].

$$\text{6-Ph-9-}(NC_5H_5)\text{-}arachno\text{-6-}CB_9H_{12} + 4Fe^{3+} \rightarrow \text{1-Ph-6-}(NC_5H_5)\text{-}closo\text{-6-}CB_9H_8 + 4Fe^{2+} + 2H_2 \quad (2)$$

In this reaction of the [6-Ph-*nido*-6-$CB_9H_{11}]^-$ anion (**1**) with pyridine, the second step (Eq. (2)) of the overall reaction occurs very readily, and, under conditions that we have used so far, proceeds before the first step (Eq. (1)) is complete. It is only when the concentration of {$FeCl_3(OH_2)_6$} is relatively low, e.g., ca. 0.9 mol equivalents relative to 1 mol of the $[NEt_4]^+$ salt of anion **1**, that the [6-Ph-9-(NC_5H_5)-*arachno*-6-CB_9H_{12}] species **4** is observed as a major reaction product, and even then significant quantities of [1-Ph-6-(NC_5H_5)-*closo*-1-CB_9H_8] (**6**) (from step 2) are present. The mixture of compounds **4** and **6** was not easily separable into its components by recrystallisation and chromatography, although ultimately we did manage successfully to obtain a pure sample of the *arachno* compound **4** and characterise it by NMR spectroscopy and a single-crystal X-ray diffraction analysis. The *closo* species **6** is much easier to obtain in a pure state because reaction with an excess of {$FeCl_3(OH_2)_6$} drives the second step to completion, and the *arachno* species **4** is then not present in the final product mixture. The second step (Eq. (2)) does not occur so readily with the substituted pyridines that we have investigated as part of this work, and all the other *closo* and *arachno* monocarbaboranes reported below can thence be isolated more easily as individual major reaction products.

Thus, utilising the same reaction, but using a series of substituted pyridines, two series of compounds with general formulae [6-Ph-9-L-*arachno*-6-CB_9H_{12}] and [1-Ph-6-L-*closo*-1-CB_9H_8], where L = NC_5H_5 (compounds **4** and **6**, respectively), NC_5H_4-*para*-CH_2Ph (**7** and **8**, respectively), NC_5H_4-*para*-Ph (**9** and **10**, respectively) and NC_9H_7 (quinoline, compounds **11** and **12**, respectively), have been prepared in reasonable yields, isolated and fully characterised. All compounds were synthesised by the reaction of [NEt_4][6-Ph-*nido*-6-CB_9H_{11}], i.e., the $[NEt_4]^+$ salt of anion **1**, with the appropriate pyridine or quinoline derivative in the presence of {$FeCl_3(OH_2)_6$} as oxidant. The crystallographically determined molecular structures are shown in Figs. 3 and 4, and preparative details are given in Section 4. The *arachno* compounds **7**, **9** and **11** all have characteristic ^{11}B NMR spectra very similar to that of the simple parent (i.e., unsubstituted) pyridine derivative [6-Ph-9-(NC_5H_5)-*arachno*-6-CB_9H_{12}] (**4**) described above. Likewise, the *closo* species **8**, **10** and **12** exhibit ^{11}B NMR spectra analogous to that of [1-Ph-6-(NC_5H_5)-*closo*-1-CB_9H_8] (**6**), also described above. Assignments for all ^{11}B and ^1H NMR spectra are given in Section 4.

The compounds [6-Ph-9-(NC_5H_4-*para*-CH_2Ph)-*arachno*-6-CB_9H_{12}] (**7**), [6-Ph-9-(NC_5H_4-*para*-Ph)-*arachno*-6-CB_9H_{12}] (**9**), [1-Ph-6-(NC_5H_4-*para*-CH_2Ph)-*closo*-1-CB_9H_8] (**8**) and [1-Ph-6-(NC_5H_4)-*para*-Ph)-*closo*-1-CB_9H_8] (**10**) can be envisaged as being rod-like in character, having tip-to-tip van der Waals lengths ranging from ca. 14.9 to 17.5 Å, and approximate along-the-molecule lengths ranging from ca. 17.5 to 19.7 Å (see Table 3). In contrast to other reported rod-like monocarbaborane derivatives, such as those based on the icosahedral {CB_{11}} cluster [16], the species presented here have an inherent degree of angularity. In the cases of the *closo* compounds this angularity arises from the mutual '*meta*'-type positionings of the C(1)-phenyl and B(6)-pyridyl(ene) groupings: the angles between the C(1)–C(11) and B(6)–N(61) bonding vectors for all the *closo* compounds **6**, **8**, **10**, and **12** are given in Table 4. For the *arachno* species, the angularity arises from the non-colinearity of the *exo*-terminal bonding vectors at the cluster C(6) and B(9) positions; the relevant angles between the C(6)–C(61) and B(9)–N(91) vectors for the *arachno* species **4**, **7**, **9** and **11** are given in Table 5. The two *para*-benzylpyridine species **7** and **8** have additional angularity associated with them, arising from the tetrahedral {CH_2} methylene group present.

3. Conclusion

The new neutral monocarbaborane derivatives **2**–**4** and **6**–**12** reported here and characterised as summarised above are readily synthesised. As well as having interesting molecular frameworks that may have potential interest from a standpoint of nanoarchitectural construction, they also constitute series of compounds that vary systematically in that they have successively more condensed aromatic residues in the nitrogen-do-

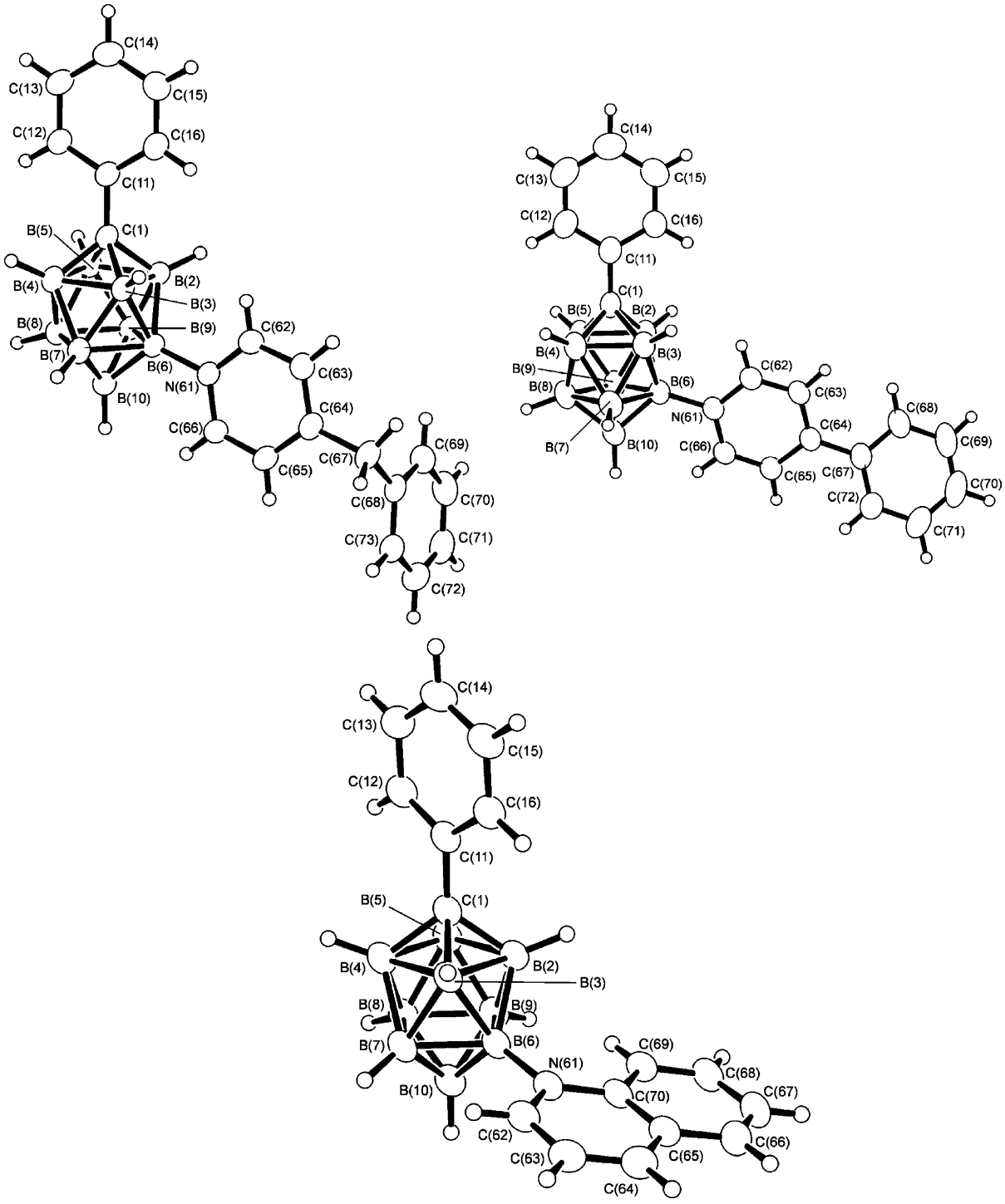


Fig. 4. ORTEP diagrams illustrating the crystallographically determined molecular structures of (top) [1-Ph-6-(NC_5H_4-*para*-CH_2Ph)-*closo*-1-CB_9H_8] (compound **8**), (centre) [1-Ph-6-(NC_5H_4-*para*-Ph)-*closo*-1-CB_9H_8] (compound **10**) and (bottom) [1-Ph-6-(NC_9H_7)-*closo*-1-CB_9H_8] (compound **12**). Anisotropic displacement parameters are shown at the 50% probability level. There are two crystallographically independent molecules of [1-Ph-6-(NC_5H_4-*para*-Ph)-*closo*-1-CB_9H_8] (**10**) in the asymmetric unit; however, both have similar intramolecular dimensions, therefore only one is shown here. Selected interatomic distances (in Å) are as follows: for **8**, C(1)–C(11) 1.4868(18), C(1)–B(2) 1.6121(18), C(1)–B(3) 1.6126(19), B(2)–B(3) 1.847(2), B(2)–B(6) 1.808(2), B(3)–B(6) 1.800(2) and B(6)–N(61) 1.5507(16); for **10**, C(1)–C(11) 1.4908(19), C(1)–B(2) 1.606(2), C(1)–B(3) 1.6023(19), B(2)–B(3) 1.845(2), B(2)–B(6) 1.795(2), B(3)–B(6) 1.799(2) and B(6)–N(61) 1.5438(18); and for **12**, C(1)–C(11) 1.490(2), C(1)–B(2) 1.609(2), C(1)–B(3) 1.608(2), B(2)–B(3) 1.845(3), B(2)–B(6) 1.805(3), B(3)–B(6) 1.811(3) and B(6)–N(61) 1.556(2).

nor ligands bonded to the monocarbaborane cluster. Specifically, there is an effective condensation that progresses from the *para*-benzylpyridine derivatives, in which the non-pyridyl aromatic ring is bound to the pyridyl {NC_5} skeleton by a {CH_2} link, through *para*-phenylpyridine, which has the non-pyridyl aro-

Table 3
The overall tip-to-tip van-der-Waals lengths (in Å) of the rod-like compounds [6-Ph-9-(NC_5H_4-*para*-CH_2Ph)-*arachno*-6-CB_9H_{12}] (compound **7**), [6-Ph-9-(NC_5H_4-*para*-Ph)-*arachno*-6-CB_9H_{12}] (compound **9**), [1-Ph-6-(NC_5H_4-*para*-CH_2Ph)-*closo*-1-CB_9H_8] (compound **8**) and [1-Ph-6-(NC_5H_4-*para*-Ph)-*closo*-1-CB_9H_8] (compound **10**): first column, through space; second column, approximately along the spine of the molecule

Compound		Length	Length
7	[6-Ph-9-(NC_5H_4-*para*-CH_2Ph)-*arachno*-6-CB_9H_{12}]	19.93	22.07
9	[6-Ph-9-(NC_5H_4-*para*-Ph)-*arachno*-6-CB_9H_{12}]	19.82	20.49
8	[1-Ph-6-(NC_5H_4-*para*-CH_2Ph)-*closo*-1-CB_9H_8]	18.07	21.51
10	[1-Ph-6-(NC_5H_4-*para*-Ph)-*closo*-1-CB_9H_8]	17.29, 17.72	19.95, 19.96

Table 4
Angles (in degrees) between the C(1)–C(11) and B(6)–N(61) bonding vectors for compounds [1-Ph-6-(NC_5H_5)-*closo*-1-CB_9H_8] (compound **6**), [1-Ph-6-(NC_5H_4-*para*-CH_2Ph)-*closo*-1-CB_9H_8] (compound **8**), [1-Ph-6-(NC_5H_4-*para*-Ph)-*closo*-1-CB_9H_8] (compound **10**), and [1-Ph-6-(NC_9H_7)-*closo*-1-CB_9H_8] (compound **12**)

Compound		Angle C(1)–C(11) / B(6)–N(61)
6	[1-Ph-6-(NC_5H_5)-*closo*-1-CB_9H_8]	109.32
8	[1-Ph-6-(NC_5H_4)-*para*-CH_2Ph)-*closo*-1-CB_9H_8]	109.23
10	[1-Ph-6-(NC_5H_4)-*para*-Ph)-*closo*-1-CB_9H_8]	107.15 and 111.56
12	[1-Ph-6-(NC_9H_7)-*closo*-1-CB_9H_8]	107.68

Table 5
Angles (in degrees) between the C(6)–C(61) and B(9)–N(91) bonding vectors for compounds [6-Ph-9-(NC_5H_5)-*arachno*-6-CB_9H_{12}] (compound **4**), [6-Ph-9-(NC_5H_4-*para*-CH_2Ph)-*arachno*-6-CB_9H_{12}] (compound **7**), [6-Ph-9-(NC_5H_4-*para*-Ph)-*arachno*-6-CB_9H_{12}] (compound **9**), and [6-Ph-9-(NC_9H_7)-*arachno*-6-CB_9H_{12}] (compound **11**)

Compound		Angle C(6)–C(61) / B(9)–N(91)
4	[6-Ph-9-(NC_5H_5)-*arachno*-6-CB_9H_{12}]	144.29
7	[6-Ph-9-(NC_5H_4-*para*-CH_2Ph)-*arachno*-6-CB_9H_{12}]	151.68
9	[6-Ph-9-(NC_5H_4-*para*-Ph)-*arachno*-6-CB_9H_{12}]	145.89
11	[6-Ph-9-(NC_9H_7)-*arachno*-6-CB_9H_{12}]	149.93

matic ring more intimately linked by a direct *sigma*-bond, to quinoline in which the second benzenoid group is now very intimately fused to the $\{NC_5\}$ pyridyl residue with two atoms in common. As mentioned in the Introduction, one intent behind the work is the generation of systematic sequences of such structurally related smaller molecular species that are suitable for a systematic study of variations of solid-state packing patterns to assess weaker intermolecular interaction modes. In this context, we currently explore for the synthesis of other closely related systematic series, for example the series with general formula [1-Ph-6-(NC_5H_4-*para*-R)-*closo*-1-CB_9H_8], where R = H, Me, Et, *iso*Pr and *tert*-Bu, which exhibits incremental increase of steric bulk at the pyridine *para*-site. The factors that influence solid-state crystal packing are not very well understood, and so these systematic synthetic studies, combined with a methodical stepwise crystallographic analysis, for example by the KAP approach, should result in a better appreciation of a range of weaker solid state interactions that could have useful implications for designed crystal engineering that involves boron-containing clusters [22]. We hope to report on our applications of this approach when we have crystallographically substantiated a larger library of compounds.

4. Experimental

4.1. General

Reagents and solvents were obtained commercially; solvents were dried and deoxygenated before use, and reagents were used as obtained commercially. As mentioned above, 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 $[FeCl_2(OH_2)_4]Cl(OH_2)_2$. The $[NEt_4]^+$ salt 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 [2,23]. Reactions were carried out under dry dinitrogen, with subsequent manipulations conducted in air. Thin-layer chromatography (TLC) was carried out using 1 mm layers of silica gel GF254 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, in most cases, elemental analytical data and single-crystal X-ray diffraction analysis for the crystal and molecular structures, and also in most cases by mass-spectrometric confirmation of molecular weight and empirical formula, although the *arachno* species described generally exhibited double dihydrogen loss from the parent ion. Single-resonance NMR spectroscopy, and one-dimensional and two-dimensional double resonance correlation NMR spectroscopy, were generally performed at 294–299 K and at ca. 5.9 T (the field $\boldsymbol{B}_0$ corresponding to ^{1}H frequencies at ca. 250 MHz), although some work was done at ca. 11.8 T (the field $\boldsymbol{B}_0$ corresponding to ^{1}H frequencies at ca. 500 MHz), as indicated. Commercially available instrumentation was used, with techniques and procedures as adequately described and enunciated elsewhere [24–28]. Chemical shifts δ are given in ppm relative to $\Xi = 100$ MHz for $\delta(^{1}H)$ (±0.05 ppm) (nominally TMS) and $\Xi = 32.083972$ MHz for $\delta(^{11}B)$ (±0.5 ppm) (nominally $[BF_3(OEt_2)]$ in $CDCl_3$) [28]. Ξ is as defined by McFarlane [29]. 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 these experimentally observed splittings will generally be lower than the actual coupling constants $^{1}J(^{11}B–^{1}H)$, particularly in cases of overlap of proximate resonance lines [28]. For the non-cluster ^{1}H NMR data, numberings of the non-cluster hydrogen atoms are according to those used for the crystallographic data.

4.2. Preparation of [6-Ph-9-(SMe_2)-*arachno*-6-CB_9H_{12}] (compound **2**)

$[NEt_4][6\text{-Ph-}nido\text{-}6\text{-}CB_9H_{11}]$ (300 mg, 0.92 mmol) and $\{FeCl_3(OH_2)_6\}$ (0.5 g, 1.8 mmol) were dissolved in CH_2Cl_2 (20 cm^3). Dimethyl sulfide (2 cm^3, 27 mmol) was added and the reaction mixture was stirred at room temperature under an N_2 atmosphere for 18 h. The reaction mixture was then evaporated, and the resultant yellow-brown residue was acidified with aqueous hydrochloric acid (5%, 50 cm^3) and the aqueous layer extracted with diethyl ether (3×30 cm^3). The ethereal layers were combined and evaporated, and the solid washed with *n*-hexane (20 cm^3) and dried to yield [6-Ph-9-(SMe_2)-*arachno*-6-CB_9H_{12}] (**2**) as a white crystalline solid (0.21 g, 0.81 mmol, 88%). Crystals (m.p./dec. 120–122 °C) suitable for single-crystal X-ray work were obtained by the overlayering of a concentrated solution of compound **2** in CH_2Cl_2 in a 5 mm tube with a tenfold excess of hexane, and allowing slow diffusion. NMR data: $\delta(^{11}B)$ ($CDCl_3$): +1.5, d(130), B(4); −4.0, d, B(2); −8.7, d(150), B(5,7); −20.2, d(118), B(9); −26.1, d(132), B(8,10); −38.6, d(149), B(1,3). $\delta(^{1}H)$ ($CDCl_3$): +7.22, m, H(62,63,65,66); +7.12, m, H(64); +2.99, H(2); +2.80, H(4); +2.76, H(5,7); +2.57, s, H(92,93); +1.60, H(8,10); +0.91, H(1,3); +0.50, H(9); −0.18, H(6); −3.19, H_μ. Microanalyses: values for C and H were found to be consistently low for this species; typically found values were C, 40.4; H, 8.0%; $C_9H_{23}B_9S$ requires C, 41.5; H, 8.9%; however, NMR spectroscopy showed no impurities, and the single-crystal X-ray work showed no solvent in the crystal matrix.

4.3. Preparation of [6-Ph-9-(NH_2Ph)-*arachno*-6-CB_9H_{12}] (compound **3**)

$[NEt_4][6\text{-Ph-}nido\text{-}6\text{-}CB_9H_{11}]$ (500 mg, 1.5 mmol) was dissolved in $CHCl_3$ (40 cm^3), and aniline (NH_2Ph, 4.5 cm^3, 49 mmol) and $\{FeCl_3(OH_2)_6\}$ (1.4 g, 5.2 mmol) were added. The reaction mixture was stirred at reflux temperature under a nitrogen atmosphere for 72 h, and then allowed to cool. Evaporation of $CHCl_3$ resulted in a brown residue which was acidified with aqueous hydrochloric acid (5%, 50 cm^3). The aqueous mixture was extracted with diethyl ether (3×30 cm^3), and the ethereal layers were combined and evaporated, leaving a pale brown residue containing mostly the [6-Ph-9-NH_2Ph-*arachno*-6-CB_9H_{12}] product **3** (260 mg, 0.89 mmol, 58%). Preparative TLC (CH_2Cl_2:hexane, 7:3) yielded pure **3** as a white crystalline solid (220 mg, 0.75 mmol, 49%, $R_F = 0.15$). Slow evaporation of a solution of **3** in $CHCl_3$ yielded single crystals (m.p. 189–191 °C) suitable for study by single-crystal X-ray diffraction analysis. NMR data: $\delta(^{11}B)$ ($CDCl_3$): +0.9, d(135), B(4); ca. −8.2, B(2); ca. −8.6, d(113), B(2) and B(5,7); −15.2, d(96), B(9); −26.9, d(123), B(8,10); −39.6, d(147), B(1,3). $\delta(^{1}H)$ ($CDCl_3$): +7.50, m, H(63-65); +7.37, d, H(62,66); +7.15, m, H(93,97,95); +7.08, m, H(94,96); +5.98, s, H(91); ca. +2.70, H(4); ca. +2.65, H(2); ca. +2.57, H(5,7); +1.35, H(8,10); ca. +0.68, H(1,3) and H(9); −0.48, H(6); −3.47, H_μ. Microanalysis: $C_{13}H_{24}B_9N$ requires C, 53.5; H, 8.3; N, 4.8; found C, 53.6; H, 8.3; N, 4.8%. Mass spectrometry: $m/z = 286.9$, envelope maximum, $[M]^+ - 4H$.

4.4. Formation and isolation of [6-Ph-9-(NC_5H_5)-*arachno*-6-CB_9H_{12}] (compound **4**)

$[NEt_4][6\text{-Ph-}nido\text{-}6\text{-}CB_9H_{11}]$ (250 mg, 0.76 mmol) was dissolved in CH_2Cl_2 (40 cm^3), and pyridine (NC_5H_5, 4 cm^3, 49 mmol) and $\{FeCl_3(OH_2)_6\}$ (180 mg, 0.67 mmol) were added. The reaction mixture was stirred at room temperature under a dinitrogen atmosphere for 72 h. The dichloromethane and excess pyridine were removed under vacuum, and the resulting brown residue was acidified with aqueous hydrochloric acid (5%, 30 cm^3). The aqueous mixture was extracted with diethyl ether (3×30 cm^3), and the ethereal layers were combined and evaporated, leaving a pale brown solid (110 mg). ^{11}B

NMR spectroscopy showed that this solid contained both the *closo* and *arachno* pyridine species [1-Ph-6-(NC_5H_5)-*closo*-1-CB_9H_8] (**6**) and [6-Ph-9-(NC_5H_5)-*arachno*-6-CB_9H_{12}] (**4**), along with [4-Ph-*arachno*-4-CB_8H_{13}] arising from acidification of the [NEt_4][6-Ph-*nido*-6-CB_9H_{11}] starting material [2] and also the [1-Ph-*closo*-1-CB_9H_9]$^-$ anion [2], in approximately 2:3:1:1 molar ratio. Preparative TLC (CH_2Cl_2: hexane, 4:1) was carried out, and the mixture of compounds **4** and **6** (49 mg, $R_F = 0.67$) was separated from the other products. In a 5 mm tube, slow diffusion of hexane across a benzene interface into a solution of this mixture in CH_2Cl_2 thence yielded single crystals of **4** (m.p./dec. 200–205 °C) suitable for study by single-crystal X-ray diffraction analysis and for NMR spectroscopy. NMR data: $\delta(^{11}B)$, 160.5 MHz) ($CDCl_3$): +1.3, d(131), B(4); −7.1, d(148), B(2); −9.1, d(147), B(5,7); −12.2, d(123), B(9); −25.3, d(119), B(8,10); −39.1, d(147), B(1,3). $\delta(^1H)$ ($CDCl_3$): +8.87, d, H(92,96); +8.12, t, H(94); +7.66, t, H(93,95); +7.24, d, H(62,66); +7.20, t, H(63,65); +7.11, t, H(64); +2.77, H(2); ca. +2.66, H(4) and H(5,7) accidentally coincident; +1.54, H(8,10); +1.38, H(9); +0.75, H(1,3); −0.22, H(6); −3.14, H_μ. Microanalysis: $C_{13}H_{24}B_9N$ requires C 51.9, H 8.0, N 5.1; found C 51.7, H 7.8 and N 5.1%. Mass spectrometry: $m/z = 273.3$, envelope maximum, $[M]^+ - 4H$.

4.5. Preparation of [1-Ph-6-(NC_5H_5)-closo-1-CB_9H_8] (compound **6**)

[NEt_4][6-Ph-*nido*-6-CB_9H_{11}] (350 mg, 1.07 mmol) and {$FeCl_3(OH_2)_6$} (1 g, 3.7 mmol) were dissolved in CH_2Cl_2 (20 cm^3). Pyridine (2 cm^3, 25 mmol) was added and the reaction mixture was stirred at room temperature under an N_2 atmosphere for 96 h. The reaction mixture was then evaporated, and the resultant brown residue was acidified with aqueous hydrochloric acid (5%, 50 cm^3) and the aqueous layer extracted with diethyl ether (3×30 cm^3). The ethereal layers were combined and evaporated. The yellowish solid was recrystallised from CH_2Cl_2/*n*-hexane, to yield [1-Ph-6-(NC_5H_5)-*closo*-1-CB_9H_8] (**6**) as a white crystalline solid (270 mg, 0.99 mmol, 92%). In a 5 mm tube, slow diffusion of hexane into a solution of **6** in CH_2Cl_2 yielded single crystals (m.p. 195–198 °C) suitable for study by single-crystal X-ray diffraction analysis. NMR data: $\delta(^{11}B)$ ($CDCl_3$): +25.2, d(156), B(10); −5.1, s, B(6); −11.1, d(155), B(4,5); −16.6, d(154), B(2,3); −20.3, d(145), B(7,9); −24.8, d(142), B(8). $\delta(^1H)$ ($CDCl_3$): +8.58, d, H(62,66); +8.15, t, H(64); +7.93, d, H(11,16); +7.66, t, H(63,65); +7.41, t, H(13,15); +7.35, t, H(14); +5.38, H(10); +2.29, H(4,5); +2.17, H(2,3); +1.87, H(7,9); +1.09, H(8). Microanalyses: over several attempts, values for C and H and N were found to be consistently erratic for this species, usually with found values being high; however, NMR spectroscopy showed no impurities, and the single-crystal X-ray work showed no solvent in the crystal matrix, and the m.p. was constant.

4.6. Preparation of [6-Ph-9-(NC_5H_4-para-CH_2Ph)-arachno-6-CB_9H_{12}] (compound **7**)

[NEt_4][6-Ph-*nido*-6-CB_9H_{11}] (500 mg, 1.5 mmol) was dissolved in CH_2Cl_2 (30 cm^3), and *para*-benzylpyridine NC_5H_4-*para*-CH_2Ph, (10 cm^3, 63 mmol) and {$FeCl_3(OH_2)_6$} (1.5 g, 5.5 mmol) were added. The reaction mixture was stirred at room temperature under a dinitrogen atmosphere for 96 h, and subsequent evaporation yielded a brown residue which was then acidified with aqueous hydrochloric acid (5%, 50 cm^3). The aqueous mixture was extracted with diethyl ether (3×30 cm^3), and the ethereal layers were combined and evaporated. The resulting residue was washed with hexane, leaving a pale yellow solid containing mostly the [6-Ph-9-(NC_5H_4-*para*-CH_2Ph)-*arachno*-6-CB_9H_{12}] product (**7**) (74 mg, 0.20 mmol, 13%). In a 5 mm tube, slow diffusion of hexane across a benzene interface into a solution of this residue in CH_2Cl_2 yielded single crystals of **7** (m.p./dec. 199–204 °C) suitable for study by single-crystal X-ray diffraction analysis. NMR data: $\delta(^{11}B)$ ($CDCl_3$): +0.9, d(111), B(4); ca. −.6, B(2); ca. −.2, d(127), B(5,7); −12.3, d, B(9); −25.5, d(120), B(8,10); −39.3, d(146), B(1,3). $\delta(^1H)$ ($CDCl_3$): +8.69, d, H(92,96); +7.35, m, unresolved ArH; +7.10, m, unresolved ArH; +4.14, s, H(97); ca. +2.75, H(4); ca. +2.62, H(2) and H(5,7) accidentally coincident; +1.48, H(8,10); +1.30, H(9); +0.71, H(1,3); −0.24, H(6); −3.21, H_μ. Microanalysis: $C_{19}H_{28}B_9N$ requires C 62.1, H 7.7, N 3.8; found C 61.9, H 7.6 and N 3.7%. Mass spectrometry: $m/z = 363.3$, envelope maximum, $[M]^+ - 4H$.

4.7. Preparation of [1-Ph-6-(NC_5H_4-para-CH_2Ph)-closo-1- CB_9H_8] (compound **8**)

[NEt_4][6-Ph-*nido*-6-CB_9H_{11}] (1 g, 3.1 mmol) was dissolved in $CHCl_3$ (40 cm^3), and 4-benzylpyridine (NC_5H_4-*para*-CH_2Ph, 12.5 cm^3, 79 mmol) and {$FeCl_3(OH_2)_6$} (3 g, 0.011 mol) were added. The reaction mixture was stirred at reflux temperature under a dinitrogen atmosphere for 14 days, and then allowed to cool. The $CHCl_3$ was removed under vacuum, and the resulting brown residue was acidified with aqueous hydrochloric acid (5%, 50 cm^3). The aqueous mixture was extracted with diethyl ether (4×30 cm^3), and the ethereal layers were combined and evaporated, leaving a pale yellow solid consisting mostly of [1-Ph-6-(NC_5H_4-*para*-CH_2Ph)-*closo*-1-CB_9H_8] (**8**) (720 mg, 2.0 mmol, 64%). Preparative TLC (CH_2Cl_2:hexane, 3:2) thence yielded pure **8** as a white crystalline solid (650 mg, 1.8 mmol, 58%, $R_F = 0.45$). In a 5 mm tube,

slow diffusion of hexane, across a benzene interface, into a solution of **8** in CH_2Cl_2 yielded single crystals (m.p. 151–152 °C) suitable for study by single-crystal X-ray diffraction analysis. NMR data: $\delta(^{11}B)$ ($CDCl_3$): +25.0, d(155), B(10); −5.3, s, B(6); −11.1, d(143), B(4,5); −16.7, d(154), B(2,3); −20.1, d(141), B(7,9); −24.9, d(140), B(8). $\delta(^1H)$ ($CDCl_3$): +8.42, d, H(62,66); +7.92, d, H(12,16); +7.4, m, H(13-15,63,65,70-72); +7.13, d, H(69,73); +5.34, H(10); +4.11, s, H(67); +2.24, H(4,5); +2.08, H(2,3); +1.80, H(7,9); +1.03, H(8). Microanalysis: $C_{19}H_{24}B_9N$ requires C, 62.8; H, 6.7; N, 3.9; found C, 62.6; H, 6.7; N, 3.6%. Mass spectrometry: m/z = 364.3, envelope maximum, $[M]^+$

4.8. Preparation of [6-Ph-9-(NC_5H_4-para-Ph)-arachno-6-CB_9H_{12}] (compound **9**)

$[NEt_4][6\text{-Ph-}nido\text{-}6\text{-}CB_9H_{11}]$ (500 mg, 1.5 mmol) and 4-phenylpyridine (NC_5H_4-*para*-Ph, 3.2 g, 21 mmol) were dissolved in $CHCl_3$ (40 cm^3), and $\{FeCl_3(OH_2)_6\}$ (1.2 g, 4.4 mmol) was added. The reaction mixture was stirred at reflux temperature under a dinitrogen atmosphere for 28 h, and then allowed to cool. The $CHCl_3$ was removed under vacuum, and the resulting brown residue was acidified with aqueous hydrochloric acid (5%, 50 cm^3). The aqueous mixture was extracted with CH_2Cl_2 (3×30 cm^3), and the organic layers were combined and evaporated, leaving a pale yellow solid consisting mostly of [6-Ph-9-(NC_5H_4-*para*-Ph)-*arachno*-6-CB_9H_{12}] (**9**) (300 mg, 0.84 mmol, 56%). Preparative TLC (CH_2Cl_2:hexane, 4:1) thence yielded pure **9** as a white crystalline solid (230 mg, 0.65 mmol, 43%, R_F = 0.5). In a 5 mm tube, slow diffusion of hexane, across a benzene interface, into a solution of **8** in CH_2Cl_2 yielded single crystals (m.p./dec. 231–240 °C) suitable for study by single-crystal X-ray diffraction analysis. NMR data: $\delta(^{11}B)$ ($CDCl_3$): +0.9, d(122), B(4); ca. −.2, B(2); ca. −.2, d(129), B(5,7); −12.4, d, B(9); −25.4, d(115), B(8,10); −39.2, d(146), B(1,3). $\delta(^1H)$ ($CDCl_3$): +8.84, d, H(92,96); +7.81, d, H(93,95); +7.72, m, H(62,66); +7.60, m, H(63-65); +7.20, m, H(99-101); +7.09, d, H(98,102); ca. +2.80, H(2); ca. +2.73, H(4); ca. +2.66, H(5,7); +1.54, H(8,10); +1.36, H(9); +0.75, H(1,3); +0.19, H(6); −3.13, H_μ. Microanalysis: $C_{18}H_{26}B_9N$ requires C 61.1, H 7.4, N 4.0; found C 60.9, H 7.7 and N 4.1%. Mass spectrometry: m/z = 349.4, envelope maximum, $[M]^+ - 4H$.

4.9. Preparation of [1-Ph-6-(NC_5H_4-para-Ph)-closo-1-CB_9H_8] (compound **10**)

$[NEt_4][6\text{-Ph-}nido\text{-}6\text{-}CB_9H_{11}]$ (800 mg, 2.4 mmol) and 4-phenylpyridine (NC_5H_4-*para*-Ph, 5 g, 032 mmol) were dissolved in $CHCl_3$ (40 cm^3), and $\{FeCl_3(OH_2)_6\}$ (2 g, 7.40 mmol) was added. The reaction mixture was stirred at reflux temperature under a dinitrogen atmosphere for 14 days, and then allowed to cool. The $CHCl_3$ was removed under vacuum, and the resulting brown residue was acidified with aqueous hydrochloric acid (5%, 70 cm^3). The aqueous mixture was extracted with diethyl ether (3×40 cm^3), and the ethereal layers were combined and evaporated, leaving a pale yellow solid consisting principally of [1-Ph-6-(NC_5H_4-*para*-Ph)-*closo*-1-CB_9H_8] (**10**) (540 mg, 1.5 mmol, 63%). Preparative TLC (CH_2Cl_2:hexane, 3:2) thence yielded pure **10** as a white crystalline solid (420 mg, 1.2 mmol, 49%, R_F = 0.6). In a 5 mm tube, slow diffusion, across a benzene interface, between hexane and a solution of **10** in CH_2Cl_2 yielded single crystals (m.p. 177–179 °C) suitable for study by single-crystal X-ray diffraction analysis. NMR data: $\delta(^{11}B)$ ($CDCl_3$): +25.0, d(155), B(10); −5.2, s, B(6); −11.0, d(142), B(4,5); −16.6, d(155), B(2,3); −20.1, d(139), B(7,9); −24.8, d(141), B(8). $\delta(^1H)$ ($CDCl_3$): +8.57, d, H(62,66); +7.97, d, H(12,16); +7.79, d, H(63,65); +7.67, m, H(68,72); +7.59, m, H(69-71); +7.38, m, H(13-15); +5.41, H(10); +2.27, H(4,5); +2.14, H(2,3); +1.85, H(7,9); +1.07, H(8). Microanalysis: $C_{18}H_{22}B_9N$ requires C, 61.8; H, 6.3; N, 4.0; found C, 61.8; H, 6.2; N, 4.0%. Mass spectrometry: m/z = 349.3, envelope maximum, $[M]^+$.

4.10. Preparation of [6-Ph-9-(NC_9H_7)-arachno-6-CB_9H_{12}] (compound **11**)

$[NEt_4][6\text{-Ph-}nido\text{-}6\text{-}CB_9H_{11}]$ (0.4 g, 1.22 mmol) was dissolved in $CHCl_3$ (80 cm^3), quinoline (2 cm^3, 17 mmol) and $\{FeCl_3(OH_2)_6\}$ (0.4 g, 1.48 mmol) were added, and the reaction mixture was stirred at reflux temperature under an atmosphere of dinitrogen for 24 h, then allowed to cool to room temperature. The reaction mixture was acidified with aqueous hydrochloric acid (5%, 50 cm^3) and extracted with CH_2Cl_2 (3×30 cm^3). The organic layers were combined and evaporated, yielding a yellow residue. Preparative TLC (CH_2Cl_2:hexane, 4:1) yielded pure [6-Ph-9-(NC_9H_7)-*arachno*-6-CB_9H_{12}] (**11**) as a white crystalline solid (190 mg, 48%, R_F = 0.7). Single crystals of **11** (m.p./dec. 226–228 °C) suitable for study by single-crystal X-ray diffraction analysis were grown by slow diffusion of *n*-hexane into a concentrated solution of **11** in CH_2Cl_2 in a 5 mm tube. NMR data: $\delta(^{11}B)$ ($CDCl_3$): +1.7, d(128), B(2); ca. −.4, B(4); ca. −.7, d, B(5,7); −14.0, d, B(9); −25.2, d(117), B(8,10); −38.9, d(147), B(1,3). $\delta(^1H)$ ($CDCl_3$): +9.41, d, H(99); +9.35, d, H(92); +8.63, d, H(94); +8.10, t, H(98); +8.08, m, H(96); +7.85, t, H(97); +7.70, t, H(93); +7.33, d, H(62,66); +7.23, t, H(63,65); +7.13, t, H(64); ca. +2.80, H(2) and H(4) accidentally coincident; +2.75, H(5,7); +1.56, H(8,10); +1.53, H(9); +0.78, H(1,3); +0.01, H(6), −2.98, H_μ. Microanalysis: $C_{16}H_{24}B_9N$ requires C, 58.7; H, 7.4; N, 4.3; found C, 58.5; H, 7.5; N, 4.1%.

4.11. Preparation of [1-Ph-6-(NC_9H_7)-closo-1-CB_9H_8] (compound **12**)

[NEt_4][6-Ph-*nido*-6-CB_9H_{11}] (0.32 g, 0.976 mmol) was dissolved in $CHCl_3$ (40 cm^3), quinoline (NC_9H_7, 3.5 cm^3, 30 mmol) and {$FeCl_3(OH_2)_6$}] (0.85 g, 3.14 mmol) were added, and the reaction mixture stirred at reflux temperature under an atmosphere of dry nitrogen for 12 days. The reaction mixture was then cooled and evaporated, acidified with aqueous hydrochloric acid (5%, 30 cm^3), and then extracted with CH_2Cl_2 (3 × 30 cm^3). The CH_2Cl_2 extracts were combined and evaporated, to yield a pale brown residue. Preparative TLC (CH_2Cl_2:hexane, 3:1) yielded [1-Ph-6-(NC_9H_7)-*closo*-1-CB_9H_8] (**12**) as a white crystalline solid (154 mg, 49%; R_F = 0.74). Slow diffusion of hexane into solution of compound **12** in CH_2Cl_2, held in a 5 mm tube, thence yielded single crystals (m.p. 81–83 °C) suitable for study by single-crystal X-ray diffraction analysis. NMR data: $\delta(^{11}B)$ ($CDCl_3$): +25.9, d(148), B(10); −5.5, s, B(6); −10.9, d(147), B(4,5); −15.4, d(148), B(2,3); −19.9, d(137), B(7,9); −24.9, d(140), B(8). $\delta(^1H)$ ($CDCl_3$): +8.72, d, H(62); +8.63, d, H(69); +8.55, d, H(64); +8.00, d, H(66); +7.95, t, H(68); +7.89, d, H(12,16); +7.79, t, H(67); +7.63, t, H(63); +7.37, t, H(13,15); +7.30, t, H(14); +5.30, H(10); +2.32, H(4,5); +2.26, H(2,3); +2.12, H(7,9); +1.21, H(8). Microanalyses: over several attempts, values for C and H and N were found to be consistently erratic for this species; however, NMR spectroscopy showed no impurities, and the single-crystal X-ray work showed no solvent in the crystal matrix, and the m.p. was consisitent. Mass spectrometry: m/z = 322.0, envelope maximum, $[M]^+$.

5. Single-crystal X-ray diffraction analyses

For all compounds except **7**, a conventional sealed-tube X-ray source was used. Obtainable crystals for compound **7** were small and required use of higher-intensity synchrotron-generated X-radiation to achieve sufficient diffraction intensity for crystallographic analysis [30–32]. Otherwise, methods and programs were standard [33–35]. 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. The CCDC deposition numbers for the individual compounds are as indicated in data summaries below. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]. Data for compound **8** are previously reported and deposited [16], but are included here for convenience of reference. Diagrams in Figs. 1–4 were prepared with the aid of the ORTEP-3 program [36].

5.1. [6-Ph-9-(SMe_2)-arachno-6-CB_9H_{12}] (compound **2**)

$C_9H_{23}B_9S$, M = 260.62, monoclinic, space group $P2_1/c$, a = 12.8311(2), b = 16.0183(3), c = 19.4141(3) Å, β = 128.993(1)°, U = 3101.29(9) $Å^3$, D_{calc} = 1.116 Mg m^{-3}, Z = 8, Mo Kα, λ = 0.71073 Å, μ = 0.183 mm^{-1}, T = 150(2) K, R_1 = 0.0629 for 5452 reflections with $I > 2\sigma(I)$, and wR_2 = 0.1566 for all 6079 unique reflections; CCDC 254031.

5.2. [6-Ph-9-(NH_2Ph)-arachno-6-CB_9H_{12}] (compound **3**)

$C_{13}H_{24}B_9N$, M = 291.62, orthorhombic, space group $Pna2_1$, a = 10.4683(3), b = 10.1286(3), c = 16.3132(5) Å, U = 1729.68(9) $Å^3$, D_{calc} = 1.12 Mg m^{-3}, Z = 4, Mo Kα, λ = 0.71073 Å, μ = 0.056 mm^{-1}, T = 150(2) K, R_1 = 0.0378 for 3002 reflections with $I > 2\sigma(I)$, and wR_2 = 0.0895 for all 3322 unique reflections; CCDC 254032.

5.3. [6-Ph-9-(NC_5H_5)-arachno-6-CB_9H_{12}] (compound **4**)

$C_{12}H_{22}B_9N$, M = 277.6, monoclinic, space group $C2/c$, a = 15.3090(4), b = 13.6837(4), c = 15.7206(5) Å, β = 100.874(1)°, U = 3234.08(16) $Å^3$, D_{calc} = 1.14 Mg m^{-3}, Z = 8, Mo Kα, λ = 0.71073 Å, μ = 0.057 mm^{-1}, T = 150(2) K, R_1 = 0.0719 for 2758 reflections with $I > 2\sigma(I)$, and wR_2 = 0.1624 for all 3167 unique reflections; CCDC 254033.

5.4. [1-Ph-6-(NC_5H_5)-closo-1-CB_9H_8] (compound **6**)

$C_{12}H_{18}B_9N$, M = 273.56, orthorhombic, space group $Pbca$, a = 13.5552(3), b = 14.6399(4), c = 15.5854(5) Å, U = 3092.87(15) $Å^3$, D_{calc} = 1.175 Mg m^{-3}, Z = 8, Mo Kα, λ = 0.71073 Å, μ = 0.059 mm^{-1}, T = 150(2) K, R_1 = 0.0419 for 2657 reflections with $I > 2\sigma(I)$, and wR_2 = 0.113 for all 3028 unique reflections; CCDC 254034.

5.5. [6-Ph-9-(NC_5H_4-para-CH_2Ph)-arachno-6-CB_9H_{12}] (compound 7)

$C_{19}H_{28}B_9N$, M = 367.71, orthorhombic, space group $P2_12_12_1$, a = 7.9947(9), b = 12.8714(13), c = 20.585(2) Å, U = 2118.3(4) $Å^3$, D_{calc} = 1.153 Mg m^{-3}, Z = 4, λ = 0.684 Å [wiggler-generated from 2-GeV electrons at 150-250 mA on the synchrotron radiation source (SRS) at station 9.8, CCLRC, Daresbury, UK] [28–30], μ = 0.059 mm^{-1}, T = 150(2) K, R_1 = 0.0475 for 3759 reflections with $I > 2\sigma(I)$, and wR_2 = 0.116 for all 4666 unique reflections; CCDC 254035.

5.6. [1-Ph-6-(NC_5H_4-para-CH_2Ph)-closo-1-CB_9H_8] (compound **8**)

$C_{19}H_{24}B_9N$, $M = 363.68$, monoclinic, space group $P2_1/c$, $a = 9.9181(2)$, $b = 10.8545(3)$, $c = 19.3643(4)$ Å, $\beta = 97.272(1)°$, $U = 2067.91(8)$ Å^3, $D_{calc} = 1.168$ Mg m^{-3}, $Z = 4$, Mo Kα, $\lambda = 0.71073$ Å, $\mu = 0.06$ mm^{-1}, $T = 150(2)$ K, $R_1 = 0.0434$ for 3360 reflections with $I > 2\sigma(I)$, and $wR_2 = 0.1216$ for all 4050 unique reflections; CCDC 204007.

5.7. [6-Ph-9-(NC_5H_4-para-Ph)-arachno-6-CB_9H_{12}] (compound **9**)

$C_{18}H_{26}B_9N$, $M = 353.69$, monoclinic, space group $P2_1/c$, $a = 10.8914(2)$, $b = 10.6922(2)$, $c = 18.8063(3)$ Å, $\beta = 113.952(1)°$, $U = 2001.46(6)$ Å^3, $D_{calc} = 1.174$ Mg m^{-3}, $Z = 4$, Mo Kα, $\lambda = 0.71073$ Å, $\mu = 0.06$ mm^{-1}, $T = 150(2)$ K, $R_1 = 0.0415$ for 3200 reflections with $I > 2\sigma(I)$, and $wR_2 = 0.1096$ for all 3922 unique reflections; CCDC 254036.

5.8. [1-Ph-6-(NC_5H_4-para-Ph)-closo-1-CB_9H_8] (compound **10**)

$C_{18}H_{22}B_9N$, $M = 349.66$, triclinic, space group $P\bar{1}$, $a = 10.7917(1)$, $b = 12.0346(1)$, $c = 17.3083(3)$ Å, $\alpha = 76.450(1)$, $\beta = 88.690(1)$, $\gamma = 65.703(1)°$, $U = 1984.89(4)$ Å^3, $D_{calc} = 1.17$ Mg m^{-3}, $Z = 4$, Mo Kα, $\lambda = 0.71073$ Å, $\mu = 0.06$ mm^{-1}, $T = 150(2)$ K, $R_1 = 0.0434$ for 6381 reflections with $I > 2\sigma(I)$, and $wR_2 = 0.1184$ for all 7773 unique reflections; CCDC 254037.

5.9. [6-Ph-9-(NC_9H_7)-arachno-6-CB_9H_{12}] (compound **11**)

$C_{16}H_{24}B_9N$, $M = 327.65$, monoclinic, space group $P2_1/c$, $a = 11.7278(2)$, $b = 11.4555(2)$, $c = 14.3034(3)$ Å, $\beta = 106.469(1)°$, $U = 1842.79(6)$ Å^3, $D_{calc} = 1.181$ Mg m^{-3}, $Z = 4$, Mo Kα, $\lambda = 0.71073$ Å, $\mu = 0.06$ mm^{-1}, $T = 150(2)$ K, $R_1 = 0.0423$ for 2953 reflections with $I > 2\sigma(I)$, and $wR_2 = 0.1169$ for all 3608 unique reflections; CCDC 254038.

5.10. [1-Ph-6-(NC_9H_7-closo-1-CB_9H_8] (compound **12**)

$C_{16}H_{20}B_9N$, $M = 323.62$, monoclinic, space group $P2_1/c$, $a = 14.2254(3)$, $b = 10.5672(2)$, $c = 12.9679(2)$ Å, $\beta = 114.1070(10)°$, $U = 1779.35(6)$ Å^3, $D_{calc} = 1.208$ Mg m^{-3}, $Z = 4$, Mo Kα, $\lambda = 0.71073$ Å, $\mu = 0.062$ mm^{-1}, $T = 150(2)$ K, $R_1 = 0.0615$ for 2810 reflections with $I > 2\sigma(I)$, and $wR_2 = 0.1681$ for all 3482 unique reflections; CCDC 254039.

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