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Macropolyhedral boron-containing cluster chemistry

Models for intermediates en route to globular and discoidal megaloborane assemblies. Structures of [*nido*-$B_{10}H_{12}$(*nido*-B_5H_8)$_2$] and [($CH_2CH_2C_5H_4N$)-*arachno*-$B_{10}H_{10}$(NC_5H_4-*closo*-$C_2B_{10}H_{10}$)] as determined by synchrotron X-ray diffraction analysis[1]

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Abstract

A {$B_{20}H_{28}$} species, from the oligomerisation of B_5H_9, has a central *nido* {$B_{10}H_{12}$} core with two *nido* {B_5H_8} units bound to it at mutually adjacent positions. [($CH_2CH_2C_5H_4N$)-*arachno*-$B_{10}H_{10}$(NC_5H_4-*closo*-$C_2B_{10}H_{10}$)], a by-product from the reaction of [$B_{10}H_{12}(NCMe)_2$] with *ortho*-ethynyl-pyridine, has mutually linked *closo* {C_2B_{10}} and *arachno* {B_{10}} cluster units conjoined to a central aromatic pyridine unit; the *arachno* {B_{10}} residue is also fused to an organyl double-ring structure involving a second pyridyl moiety. Both species model possible steps to globular megaloborane synthesis via the assembly of boron hydride units around a central cluster core, as well as having other interesting features. The small size of the crystals for both compounds necessitated the use of synchrotron X-radiation for sufficient diffracted-beam intensity for crystallographic analysis. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Boron cluster compounds; Macropolyhedral; Megaloborane; Triple cluster fusion; Synchrotron X-ray diffraction analysis; X-ray structures

Molecules of highly condensed macropolyhedral boron-containing cluster compounds such as [$(PMe_3)_4(CO)Ir_2B_{26}H_{24}$] [1], [$(C_5Me_5)_3Ir_3B_{18}H_{15}(OH)$] [2], [$(PMe_2Ph)_4Pt_2B_{18}H_{16}$] [3], and [$(PPh_3)_4(PPh_2)_2Pd_4B_{20}H_{16}$] [4] have highly condensed cluster cores that are perceived to mimic structural features in elemental boron [4–6]. This perception leads to the concept that families of larger globular 'megaloborane' structures will be based on fragments of polyboron domains from elemental boron structures, these fragments having their peripheral valencies bound with hydrogen [4]. Their

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[1] A cursive IUPAC nomenclature for compound **4** is 5-(*nido*-pentaboran-2-yl)-6-(*nido*-pentaboran-1-yl)-*nido*-decaborane, and, for compound **5**, [6-*spiro*{N,C(2)}-{1-(*ortho*-pyridyl)-*closo*-1,2-dicarbadodecaboranyl}-μ-8{C},9{N}-(*ortho*-pyridylethyl)-*arachno*-decaborane]. This article was freely submitted for publication without royalty. By acceptance of this paper, the publisher and/or recipient acknowledges the right of the authors to retain non-exclusive, royalty-free license in and to any copyright covering this paper, along with the right to reproduce all or part of the copyrighted paper.

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structures could thence be visualised as central borons-only cores fused with surrounding boron-hydride units that are themselves fused together to give a boron hydride skin covering the central core [4–7]. This hypothesis is supported by structural calculations, based on fragments of the β-rhombohedral boron lattice, that suggest that species such as $B_{27}H_{21}$ (species **1**, Fig. 1, left) and $B_{84}H_{54}$ (species **2**, Fig. 1, right) are at energetic minima on a multidimensional structure-energy continuum, and therefore may be inherently isolatable [4].

The filled-ball architectural principles of such globular 'megaloborane' species will be quite different to those of the hollow fullerenes, and their novel properties will consequently complement those of the hollow carbon cages. The construction of such new large molecular nanoglobules, and their tailoring by substituent chemistry to modify and enhance interactions important for host–guest interlocking, for crevice and anchor generation for molecular recognition, and to tune hydrophilic versus lipophilic character, and so on, will therefore be of high interest. Implicit in this is the development of clean *Aufbau* techniques from simple boron-containing starting substrates. However, generic routes for the required intimate cluster condensations are as yet lacking. Similar problems in principle arise in carbon hydride chemistry, but in practice syntheses of polycondensed aromatics from smaller hydrocarbons such as benzene are not required. This is because condensed hydrocarbon feedstock compounds are readily available, albeit, when their origins in primordial forests in the carboniferous era are considered, in very low yield and from very inefficient processes.

A possible route for syntheses of the larger globular filled-ball megaloboranes is suggested by the structure of $B_{84}H_{54}$ mentioned above (Fig. 1, right). This globular structure can be regarded as constructed of a central *closo* $[B_{12}H_{12}]^{2-}$ unit, of which the twelve *exo*-hydrogen atoms are replaced by twelve apically bound *nido* B_6H_{10} type units, of which the pentagonal bases are themselves mutually fused via dihydrogen loss to create the outer $\{B_{60}H_{54}\}$ skin. This leads to the supposition that a synthetic route may be constructed similarly, viz. by the stepwise assembly of boron hydride units about a central cluster followed by their ultimate cross-linking (e.g. schematic **I**). An initial feasibility step along this pathway has recently been reported, in that the thermolysis of $[B_{10}H_{12}(SMe_2)_2]$ gives [6,9-$(SMe_2)_2$-*arachno*-$B_{10}H_{10}$-1,5-(6′-*nido*-$B_{10}H_{13})_2$] (compound **3**, schematic cluster structure **II**) [7], in which two *nido*-decaboranyl units are assembled on adjacent sites around an *arachno*-decaboranyl core. In the development of the general feasibility of this type of experimental pathway, it is necessary to establish other paradigms and principles for various intermediate structural possibilities, as

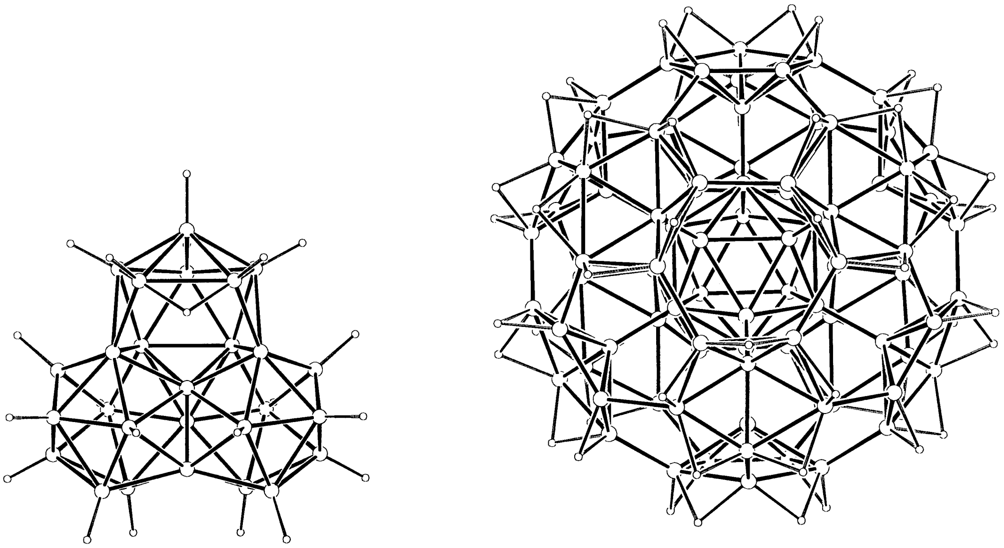
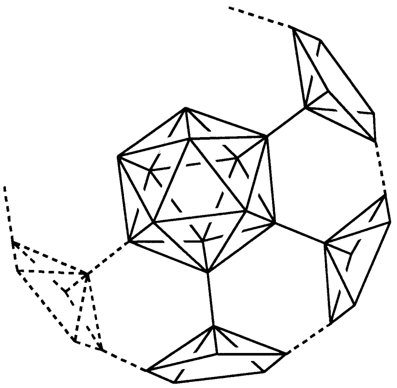


Fig. 1. Left: a representation of the STO-3G ab-initio calculated structure of neutral $[B_{27}H_{21}]$ (species **1**), in which the $\{B_{27}\}$ unit has many similarities with the $\{B_{27}\}$ unit in the β-rhombohedral allotrope of elemental boron. There is a seven-atom 'borons-only' core, with a boron-hydride skin consisting of 20 peripheral boron atoms with 20 *exo*-hydrogen atoms and one bridging hydrogen atom. Right: a representation of the AM-1 semi-empirical energy-minimized structure of neutral $[B_{84}H_{54}]$ (species **2**), in which the $\{B_{84}\}$ unit mimics that in β-rhombohedral boron. There are 24 atoms in the borons-only core, and a $\{B_{60}H_{54}\}$ boron hydride skin. Its architecture may be visualized as an icosahedral $\{B_{12}\}$ unit, like that in the $[closo\text{-}B_{12}H_{12}]^{2-}$ anion, fused to twelve *nido*-hexaboranyl units that are themselves fused together (see schematic **I**). Data for both species are from Ref. [4].

well as principles and paradigms behind the final targets.



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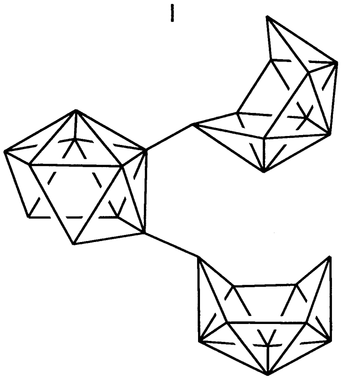

II

In this context, we present initial results on the isolation and characterisation of two more triple-fusion products that examine and extend the structural principles for such intermediates. One product, [*nido*-$B_{10}H_{12}$(*nido*-B_5H_8)$_2$] (compound **4**), represents the first steps on assembling smaller *nido* clusters, here based on B_5H_9, around the central boron core, rather than the larger {$B_{10}H_{14}$}-derived clusters of compound **3**, thus approximating more closely to the {*nido*-B_6H_{10}}-based construction of compound **1**. The other product, [($CH_2CH_2C_5H_4N$)-*arachno*-$B_{10}H_{10}$(NC_5H_4-*closo*-$C_2B_{10}H_{10}$)] (compound **5**), introduces the concept of the ultimate assembly of borane units to encapsulate carbon-based, rather than boron-based cores. It also illustrates the principle of linking the peripheral encapsulating units. Although both are obtained only in low yield, the essential structural concepts are nevertheless clearly indicated. Both compounds only yielded very small crystals, so that synchrotron X-ray radiation was required to generate sufficiently strong diffracted intensity for their characterisation by single-crystal diffraction analysis.

For the isolation of compound **4**, it was noted that a sample of B_5H_9 that had been sealed under vacuum in pyrex glass, and had been stored under ambient lighting and temperature conditions for 23 years, had deposited a clear viscous pale reddish material. This material dissolved cleanly in CH_2Cl_2, and was subjected to HPLC separation (Lichrosorb SI 60 7 μm, 25 × 2.1 cm, 100% CH_2Cl_2, 10 ml min^{-1}), giving a number of partially separated components. Collection of a fraction between R_T 7 min and R_T 11 min, which contained the major component, followed by slow sublimation under vacum using 40°C/20°C hot–cold conditions in a sealed tube, then engendered a few very small colourless crystals. This compound was shown by single-crystal X-ray diffraction analysis[2] to be 5-(2-*nido*-B_5H_8)-6-(1-*nido*-B_5H_8)-*nido*-$B_{10}H_{12}$ (compound **4**, Fig. 2, schematic cluster skeleton **III**); synchrotron radiation was required for sufficient diffraction intensity for the analysis.

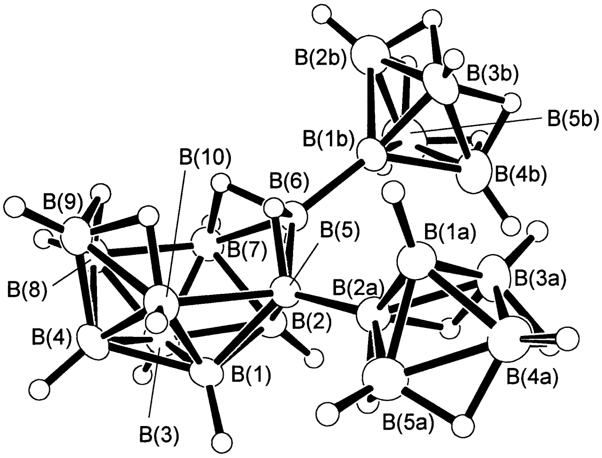

Fig. 2. Representation of the crystallographically determined molecular structure of [*nido*-$B_{10}H_{12}$(*nido*-B_5H_8)$_2$] **4**, drawn with 40 % probability ellipsoids for non-hydrogen atoms, and with a small arbitrary radius for hydrogen atoms. Selected interatomic distances (Å) are as follows: B(6)–B(1b) 1.6728(14), B(5)–B(2a) 1.6921(16), B(5)–B(10) 2.0027(15) and B(7)–B(8) 1.9604(17); other interboron distances from B(1b) are in the range 1.6865(19) to 1.6941(18), and interboron distances from B(1a) are in the range 1.6826(18) to 1.6987(16); hydrogen-bridged interboron distances in the {B_5H_8} units are in the range 1.785(2) to 1.832(17), those involving B(2a) being at the higher end of this range, and in the {$B_{10}H_{12}$} unit 1.787(2) to 1.8098(15).

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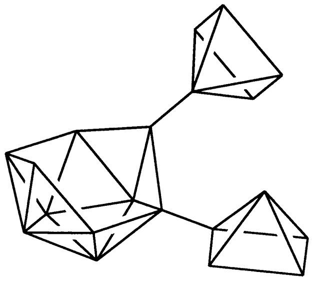
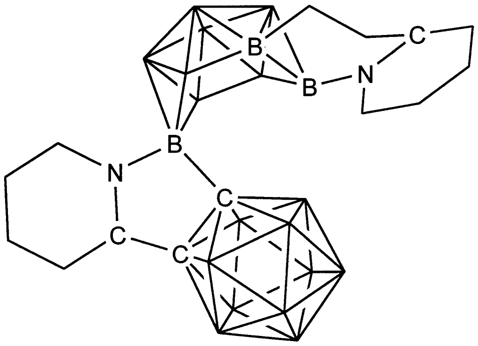
[2] Crystal data for [*nido*-$B_{10}H_{12}$(*nido*-B_5H_8)$_2$] (compound **4**), $H_{28}B_{20}$: $M = 244.42$, orthorhombic (colourless blocks, from slow sublimation in vacuo from 313 to 293 K), 0.24 × 0.18 × 0.12 mm, Space Group *Pbca*, $a = 10.2481(6)$, $b = 17.4188(11)$, $c = 19.9508(13)$Å, $U = 3561.4(4)$ Å^3, $D_{calc} = 0.912$ Mg m^{-3}, $Z = 8$, synchrotron wiggler-generated radiation,[8] $\lambda = 0.6883$ Å, $\mu = 0.034$ mm^{-1}, $T = 150(2)$ K, $R_1 = 0.0646$ for 4020 reflections with $I > 2\sigma(I)$, and $wR_2 = 0.1773$ for all 4663 unique reflections; CCDC reference number 173670. Crystal data for [($CH_2CH_2C_5H_4N$)-*arachno*-$B_{10}H_{10}$(NC_5H_4-*closo*-$C_2B_{10}H_{10}$)] (compound **5**), $C_{14}H_{32}B_{20}N_2$: $M = 444.62$, monoclinic (pale red needles from *n*-C_5H_{12}/C_6H_6/CH_2Cl_2 at 283 K), 0.35 × 0.05 × 0.03 mm, space group $P2_1/n$, $a = 19.0578(3)$, $b = 7.3280(11)$, $c = 20.198(3)$ Å, $\beta = 115.08(2)$, $U = 2554.8(5)$ Å^3, $D_{calc} = 1.156$ Mg m^{-3}, $Z = 4$, synchrotron wiggler-generated radiation [9], $\lambda = 0.6883$ Å, $\mu = 0.055$ mm^{-1}, $T = 150(2)$ K, $R_1 = 0.0795$ for 4074 reflections with $I > 2\sigma(I)$, and $wR_2 = 0.2045$ for all 5431 unique reflections; CCDC reference number 173671. Methods and programs were standard [9–12].

Seventy-electron-volt EI mass spectrometry gave a high-mass envelope corresponding to icosaboranyl fragments, with a highest mass cut-off corresponding to an apparent $[M-1]^+$ ion, and also indicated ready fragmentation to give pentadecaboranyl, decaboranyl and pentaboranyl units. The compound clearly exhibits two *nido*-pentaboranyl units sigma-bound with two-electron two-centre bonds to adjacent open-face sites around a *nido*-decaboranyl core (schematic cluster structure **III**), in accord with the first steps of the *Aufbau* type of a synthetic approach implied in schematic **I**. One pentaboranyl unit is conjoined at its apical position, and the other conjoined at one of its a basal positions. The relatively high incidence of this specific $\{(B_5)(B_{10})(B_5)\}$ three-cluster aggregation is of interest, and suggests that a first borane substituent, $\{$*nido*-$B_5H_8\}$ in this case, may activate the cluster to further addition, as surmised for the successive addition of $\{$*nido*-$B_{10}H_{13}\}$ units to a $\{B_{10}\}$ cage as previously entertained for compound **3** [7]. Its stability in air is also noteworthy, as the parent *nido*-pentaboranyl unit, *nido*-B_5H_9 itself, is notorious for its spontaneous inflammability.



III



IV

Compound **5** was isolated from the residues of the reaction of [*arachno*-$B_{10}H_{12}$-6,9-$(NCMe)_2$] with 2-ethynyl-pyridine, a reaction that gives *ortho*-(1,2-dicarbadodecaboranyl)-pyridine, [2-$(HCB_{10}H_{10}C)C_5H_4N$] [8]. TLC on the residual yellow CH_2Cl_2-soluble solid (silica gel G, Fluka GF254; 100% CH_2Cl_2) revealed several components, colourless, yellow and orange. A yellow–orange mixture of components with R_F ca. 0.4 was subjected to HPLC separation. Thence, a pale orange–pink component (R_T 22.6 min, Lichrosorb SI 60 7 μm 25 × 2.1 cm, 35% CH_2Cl_2/hexane, 20 ml min^{-1}) was crystallized via pentane diffusion through a benzene layer into a CH_2Cl_2 solution, and identified by single-crystal X-ray diffraction analysis[2] as of formulation $[(CH_2CH_2C_5H_4N)$-*arachno*-$B_{10}H_{10}(NC_5H_4$-*closo*-$C_2B_{10}H_{10})]$, the structure being of formal description [6-*spiro*$^{N,C(2)}$-{1-(2-$C_5H_4N^B$)-*closo*-1,2-$CC^BB_{10}H_{10}$}-μ-$8^C,9^N$-{(2-$C_5H_4N^B)CH_2C^BH_2$}-*arachno*-$B_{10}H_{10}$] (compound **5**, ca. 0.4%, Fig. 3, schematic skeletal structure **IV**). Seventy-electron-volt EI mass spectrometry gave a highest-mass envelope with m/z (max.) ca. 438, consistent with a molecular ion with some dihydrogen loss. We hope to be able to report on the other low-yield components of this residue at some future date. The crystal needles of compound **5** were small, of ca. 30 micron cross-section, and, as with compound **4** above, required synchrotron X-radiation for the observation of sufficient diffracted-beam intensity for the structural analysis.

The structure of compound **5** has several features of interest (Fig. 3 and structure **IV**). In terms of borane-based clusters around a central core, it can be seen that an *arachno* decaboranyl unit (atoms 1′a–10′a) and a *closo* dicarbadocaboranyl unit (atoms 1, 2a, 3a and 4–12) are both linked to the same core pyridyl unit (atoms 21a–26a) in adjacent sites. This leads to the idea of a group of six boron-hydride cluster units around an aromatic carbon core; their interfusion by cross-linking would then generate discoidally shaped megaloboranes with carbon-based cores, rather than the more spherical boron-cored globules of Fig. 1. Interestingly, in this compound the two boron-containing clusters are in fact already interlinked by the C(2a)–B(6′a) two-electron two-centre sigma link, demonstrating the feasibility of intercluster linking implied in schematic cluster structure **I**. At the other end of the *arachno* decaboranyl unit, the 2-ethynyl pyridine substrate has undergone a reductive cycloboronation to give a boat-cyclohexane-like unit that is fused both to the *arachno* subcluster and to the terminal pyridine unit that consists of atoms 92a–96a. In this regard, the compound can be regarded as fusing no fewer than six cluster-type units together: viz. an *arachno* $\{NC_5\}$ pyridyl skeleton fused with two atoms, N(91) and C(92a), in common with a boat $\{NB_2C_3\}$ azadiboracyclohexane unit, which is fused, in turn, with two atoms, B(8′a) and B(9′a), in common with an *arachno* $\{B_{10}\}$ unit, which is fused, with the one B(6′a atom in common, with a $\{NBC_4\}$ azaboracyclopentane unit that is fused in turn to two more units: an *arachno* $\{NC_5\}$ pyridyl unit with two atoms, N(22a) and C(21a), in common, and a *closo* $\{C_2B_{10}\}$ unit with two atoms, C(1) and C(2a), in common. This type of complex fused

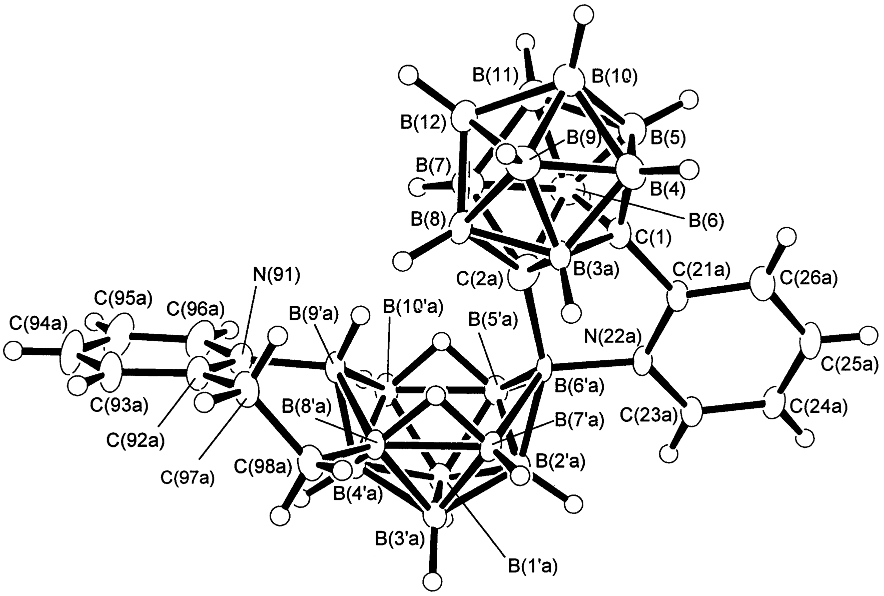


Fig. 3. Representation of the crystallographically determined molecular structure of [$(CH_2CH_2C_5H_4N)$-*arachno*-$B_{10}H_{10}(NC_5H_4$-*closo*-$C_2B_{10}H_{10})$] **5**, drawn with 40% probability ellipsoids for non-hydrogen atoms, and with a small arbitrary radius for hydrogen atoms. Selected interatomic distances (Å) are as follows: C(1)–C(2a) 1.717(14), with C(1)–C(21a) and C(1)–B(3a) short at 1.490(4) and 1.635(3) respectively, C(2a)–B(6′a) 1.747(4), B(5′a)–B(10′a) 1.900(8), B(7′a)–B(8′a) 1.882(4), B(8′a)–C(98a) 1.590(4), B(9′a)–N(91) 1.578(4), B(8′a)–B(9′a) 1.867(5) and B(9′a)–B(10′a) 1.852(5); distances from C(2a) to its other adjacent boron atoms are in the range 1.760(4) to 1.796(4) and from C(1) to its other adjacent boron atoms being shorter, in the range 1.693(4) to 1.735(4). Angles C(1)–C(2a)–B(6′a) and C(2a)–C(1)–C(21a) are 103.78(18) and 105.8(2) ° respectively, whereas B(5)–C(1)–C(21a) and B(8)–C(2a)–B(6′a) are 124.3(2)° and 138.2(2) ° respectively, indicating distortion at the C(1)C(2a) site; C(1)–C(21a)–N(22a) is 114.7 2° and C(21a)–N(22a)–B(6′a) is 116.7 2°; N(22a)–B(6′a)–C(2a) is 98.27(19) °, B(2′a)–B(6′a)–N(22a) is 107.3 2°, and B(4′a)–B(9′a)–N(91) is 106.7(2)°.

architecture, intimately intermingling structural elements of chain and ring carbon-hydride chemistry with the cluster features of boron-hydride chemistry, points the way to whole series of interesting hybrid molecules. For example, the parabiosis of borane and carbane clusters could in principle engender biologically active or otherwise medically useful applications.

In sum, it is clear that the two new structures of compounds **4** and **5** reported here have interesting implications not only for future synthetic directions for megaloborane formation, but also in several other new aspects of boron-containing cluster chemistry.

Supplementary material

Crystallographic data for [*nido*-$B_{10}H_{12}$(*nido*-$B_5H_8)_2$] (compound **4**), and [$(CH_2CH_2C_5H_4N)$-*arachno*-$B_{10}H_{10}(NC_5H_4$-*closo*-$C_2B_{10}H_{10})$] (compound **5**) are deposited at the Cambridge Crystallographic Data Centre, CCDC, deposition nos. 173670 and 173671 respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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