# Macropolyhedral boron-containing cluster chemistry. A synthetic approach *via* the auto-fusion of $[6,9-(SMe_2)_2$ -*arachno*- $B_{10}H_{12}]^{\dagger}$

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In an attempt to build up borane-based multicluster assemblies, thermolysis of  $[6,9-(SMe_2)_2$ -*arachno*- $B_{10}H_{12}]$  **1** in inert hydrocarbon solution, followed by chromatographic separation, has resulted in the isolation not only of the previously established single-cluster product from this reaction,  $[5-(SMe_2)-nido-B_{10}H_{12}]$  **2** (30%), but also the two two-cluster species  $[6,9-(SMe_2)_2$ -*arachno*- $B_{10}H_{11}$ -1-(*6'-nido*- $B_{10}H_{13}$ )] **3** (20%) and  $[1,6'-(nido-B_{10}H_{13})_2]$  **6** (*ca.* 0.5%) and the two three-cluster species  $[6,9-(SMe_2)_2$ -*arachno*- $B_{10}H_{10}$ -1,5-(*6'-nido*- $B_{10}H_{13}$ )<sub>2</sub>] **4** (5%), characterized crystallographically, and  $[6,9-(SMe_2)_2$ -*arachno*- $B_{10}H_{10}$ -1,3-(*6'-nido*- $B_{10}H_{13}$ )<sub>2</sub>] **5** (<1%), identified by NMR spectroscopy. An improved crystallographic investigation of  $[5-(SMe_2)-nido-B_{10}H_{12}]$  **2** is also presented. The feasibility of the stability of species resulting from multiple adjacent substitution of *nido*-decaboranyl units on the  $[6,9-(SMe_2)_2$ -*arachno*- $B_{10}H_{12}$ ] skeleton is tested by DFT calculations. In an extension, to attempt the use of pre- $\sigma$ -linked two-cluster compounds as starting substrates, two-cluster  $[5-(SMe_2)-4-(2'-nido-B_{10}H_{13})-nido-B_{10}H_{11}]$  **7** (0.6%) has been isolated from the reaction of SMe<sub>2</sub> with  $[1,5'-(nido-B_{10}H_{13})_2]$ , other identified products being compound **1** (39%) and compound **3** (10.5%).

# Introduction

Extension of polyhedral boron-containing cluster chemistry to include contiguous clusters of more than about twelve vertices requires the intimate fusion of smaller clusters.<sup>1,2</sup> Compounds that have two or more clusters intimately fused together so that they have two or more framework atoms held in common between individual pairs of clusters have been dubbed 'macropolyhedral' species. Although redox fusion, mediated by transition-element centres, has been advocated as a general method of 'designed' fusion to achieve inter-cluster fusion,<sup>3</sup> so far this has been reported to be successful only to an upper limit of about fourteen vertices. Meanwhile, there is merit in exploring for other routes to macropolyhedral boron-containing cluster species. Of such other routes, thermolyses of arachno nine-vertex boron-containing cluster compounds have, to date, proved to be one of the most successful general routes for achieving intercluster fusion. Although there is as yet no consistent pattern to the products, several interesting macropolyhedral boranes, heteroboranes and metallaboranes of between eighteen and twenty-six vertices have been obtained by this general method.<sup>1,2,4–15</sup>

There is a fascination about the formation of new 'borons-only' clusters because they have an aura of fundamental elegance. In terms of borons-only macropolyhedral species, the nine-vertex arachno cluster compounds  $[(SMe_2)B_9H_{13}]$  and  $[(O^nBu_2)B_9H_{13}]$ have been found to yield the *anti* isomer of  $B_{18}H_{22}$  upon simple thermolysis; this is long known.<sup>16</sup> In these reactions, the ready dissociation of the weak SMe2 and O<sup>n</sup>Bu2 ligands to generate the known reactive  $\{B_9H_{13}\}$  species,<sup>17</sup> or possibly a related intermediate, is probably very significant. With this in mind, we have been interested to see whether the related<sup>18</sup> arachno species [6,9-(SMe<sub>2</sub>)<sub>2</sub>-arachno-B<sub>10</sub>H<sub>12</sub>] (compound 1, schematic structure  $I, L = SMe_2$ , with ten rather than nine boron vertices, could also similarly be induced readily to undergo cluster fusion. We have been encouraged to examine for this, not only in the light of the  $[(SMe_2)B_0H_{13}]$  cluster-fusion reaction, but also because, in previous work, compound 1 has been reasonably supposed to give a 'reactive' isomer of  $\{(SMe_2)B_{10}H_{12}\}$  in its thermolytic reactions with acetylenes to give  $\{C_2B_{10}\}$  dicarbaboranes.<sup>19,20</sup> Thence we surmised that this reactive intermediate might be active towards homofusion in the absence of alternative substrates. Here we also noted that the thermolysis of [6,9-(SMe<sub>2</sub>)<sub>2</sub>-arachno-B<sub>10</sub>H<sub>12</sub>] (compound 1), to give the 'stable' isomer of  $[(SMe_2)B_{10}H_{12}]$ , viz. [5-(SMe\_2)*nido*- $B_{10}H_{12}$ ] (compound 2, Fig. 1, schematic structure II, L = SMe<sub>2</sub>),<sup>21-30</sup> is also known to yield higher, though unspecified, 'polymeric' by-products,<sup>21</sup> which might well be uncharacterised multi-cluster species. Additionally, in the reaction of 1-octyne with compound 1, a by-product has been tentatively identified as containing three decaboranyl residues per molecule.18 In the context of these considerations, we here report results on some higher borane products from a preliminary investigation of the simple thermolysis of [6,9-(SMe<sub>2</sub>)<sub>2</sub>-arachno-B<sub>10</sub>H<sub>12</sub>] (compound 1)

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<sup>†</sup> IUPAC nomenclature for crystallographically determined species: compound **2**, 5-dimethyl sulfide-*nido*-decaborane; compound **3**, 6,9bis(dimethyl sulfide)-5-(6'-*nido*-decaboranyl)-*arachno*-decaborane; compound **4**, 6,9-bis(dimethyl sulfide)-1,5-bis(6'-*nido*-decaboranyl)-*arachno*decaborane; and compound **7**, 5-dimethyl sulfide-4-(2'-*nido*-decaboranyl)*nido*-decaborane.

in refluxing hydrocarbon solvents. Preliminary reports on some aspects of this and closely related work have been made.<sup>25,26</sup>



## **Results and discussion**

The heating for 6 h of a sample of [6,9-(SMe<sub>2</sub>)<sub>2</sub>-arachno-B<sub>10</sub>H<sub>12</sub>] (compound 1) at reflux in toluene solution at a concentration of ca. 0.020 M, followed by thin-layer chromatographic separation (TLC), resulted in the isolation of [5-(SMe<sub>2</sub>)-nido-B<sub>10</sub>H<sub>12</sub>] (compound 2) in 30% yield as a white air-stable solid. This was identified by single-crystal X-ray diffraction analysis (Fig. 1) and NMR spectroscopy. Selected interatomic dimensions for this compound and the other species reported here are listed in Table 1. NMR and single-crystal X-ray diffraction work on compound 2 has been previously reported,<sup>21-23</sup> but we were able to glean a somewhat better crystallographic data set in this present work. Results from this latter X-ray work, and additional NMR and structural considerations with regard to compound 2 that arise from our present study, are briefly discussed below. Other products were also apparent from this reaction, and mass spectrometric assessment of these indicated that they were higher boranes. Additional siting experiments and assessments of TLC characteristics of some of these additional products were therefore conducted.

Thence, a thermolytic reaction at lower temperature, using a ca. 0.022 M solution of compound 1 in 50 : 50 benzene-hexane at reflux for 6 h, followed by TLC separation, gave an isolated yield of the bis(decaboranyl) species  $[6,9-(SMe_2)_2-arachno-B_{10}H_{11} 1-(6'-nido-B_{10}H_{13})$ ] (compound 3, schematic structure III, Fig. 2) in yields of up to 20% as a pale yellow solid. Compound 3, previously unreported, was characterized by a single-crystal Xray diffraction analysis and by NMR spectroscopy as discussed below. This linked cluster species is the first compound yet reported that has the classical *nido* and *arachno* decaborane  $\{B_{10}\}$  skeletons  $\sigma$ -bound. The monocluster species 2 was again isolated, now in the smaller yield of 11%. Additional products, which mass spectrometry indicated were still higher borane species, were again apparent, but in our hands could not readily be separated by TLC work. Further experiments were therefore conducted with HPLC separation in mind.



Thus, the heating at reflux of 10 ml of a ca. 0.04 M solution of compound 1 in benzene for 6 h, followed by repeated TLC



**Fig. 1** Left-hand diagram: the crystallographically determined molecular structure of  $[5-(SMe_2)-nido-B_{10}H_{12}]$  (compound **2**; compare also references 23 and 24). Right-hand diagram: Lowest energy DFT-minimized structure for compound **2**. Note the good conformational approximation to the crystallographically determined structure in the right-hand diagram: clearly for this compound packing forces do not overcome the *ca*. 10 kJ mol<sup>-1</sup> energy barrier to the contra-rotation of the SMe<sub>2</sub> unit *vs*. the cluster unit about the S(5)–B(5) bond (see Fig. 6, below).

Table 1	Selected interatomic	c distances (Å) with	s.u.s in parenthese	es for compounds 2,	3, 4, 6 and 7
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		3		4			6		7	
	2	Primed	Unprimed	a	b	c	Primed	Unprimed	Primed	Unprimed
B(5)-B(10)	2.034(3)	1.955(6)	1.898(6)	1.874(5)	1.969(5)	1.980(6)	1.972(3)	1.981(3)	1.986(3)	1.840(2)
B(7) - B(8)	1.830(3)	1.984(6)	1.890(6)	1.861(5)	1.993(5)	1.979(6)	1.996(3)	1.989(3)	1.984(3)	2.038(3)
B(5) - B(6)	1.771(3)	1.845(6)	1.867(5)	1.876(5)	1.804(5)	1.806(5)	1.801(2)	1.796(2)	1.783(3)	1.660(2)
B(6) - B(7)	1.654(3)	1.834(6)	1.889(5)	1.858(5)	1.810(5)	1.806(5)	1.802(3)	1.796(3)	1.781(3)	1.783(3)
B(8) - B(9)	1.791(3)	1.788(6)	1.881(6)	1.853(5)	1.776(6)	1.776(7)	1.785(3)	1.792(3)	1.791(3)	1.779(3)
B(9) - B(10)	1.785(3)	1.813(7)	1.852(5)	1.860(5)	1.803(6)	1.789(3)	1.794(3)	1.793(3)	1.794(3)	1.790(3)
S–B	1.883(2)	1.943(4)		1.924(3) [S6]		~ ~ ~	~ /			1.8890(18) [S5]
S–B	~ /			1.927(3) [S9]						
B–B			1.693(5)		1.688(5)	1.676(5)		1.686(2)		1.695(2)
conjuncto										. ,



Fig. 2 The crystallographically determined molecular structure of  $[6,9-(SMe_2)_2$ -*arachno*- $B_{10}H_{11}$ -1-(6-*nido*- $B_{10}H_{13})]$  (compound 3).

and thence HPLC separation, yielded, in addition to the monocluster compound **2** and the two-cluster compound **3**, small quantities of identifiable higher borane species. We have isolated and identified two of these as the isomeric three-cluster compounds  $[6,9-(SMe_2)_2$ -*arachno*- $B_{10}H_{10}$ -1,5-(*6'-nido*- $B_{10}H_{13}$ )<sub>2</sub>] (compound **4**, schematic structure **IV**, Fig. 3, 13% yield) and  $[6,9-(SMe_2)_2$ -*arachno*- $B_{10}H_{10}$ -1,3-(*6'-nido*- $B_{10}H_{13}$ )<sub>2</sub>] (compound **5**, schematic structure **V**, Fig. 4, *ca*. 0.5% yield). A repeat reaction with two added equivalents of  $B_{10}H_{14}$  showed a small amount of  $[1,6'-(nido-B_{10}H_{13})_2]$  (compound **6**, Fig. 5, *ca*. 2% yield). Compound **4** was identified by a single-crystal X-ray diffraction analysis allied with <sup>11</sup>B and <sup>1</sup>H single-resonance and multiple-



Fig. 3 The crystallographically determined molecular structure of  $[6,9-(SMe_2)_2$ -*arachno*- $B_{10}H_{10}$ -1,5-(6'-*nido*- $B_{10}H_{13}$ )<sub>2</sub>] (compound 4).

resonance NMR spectroscopy. Compound 5 was identified by <sup>11</sup>B and <sup>1</sup>H NMR spectroscopy, allied with DFT calculations of structure and thence of <sup>11</sup>B nuclear shielding, all in general comparison with compound 4. Compounds 4 and 5 extend the concept embodied in the structure of compound 3, in that the structure of compound 3 has one nido decaboranyl unit bound to an arachno decaboranyl unit, whereas compounds 4 and 5 have two such *nido* units bound to the *arachno* decaboranyl unit. Exhaustive investigation by HPLC revealed trace amounts of other two-cluster species both with and without bound SMe<sub>2</sub> groups but we have not been able to demonstrate, in this or other related product mixtures resulting from the thermolysis of compound 1, the presence of any four-cluster species, consisting, for example, of three nido decaboranyl units bound to a central decaboranyl substrate. The steric feasibility of having more than two nidodecaboranyl units bound in adjacent positions on a central nidodecaboranyl skeleton is discussed below.



The crystallographically determined molecular structure of [5- $(SMe_2)$ -*nido*- $B_{10}H_{12}$ ] (compound **2**) is in Fig. 1. It is of classical *nido* ten-vertex constitution as adequately discussed elsewhere.<sup>19,21,23</sup> Formally, it is related to the [*nido*- $B_{10}H_{13}$ ]<sup>-</sup> anion<sup>27,28</sup> by the replacement of a formally anionic *exo*-terminal {:H}<sup>-</sup> unit by a neutral :SMe<sub>2</sub> ligand. Starting from [6,9-(SMe<sub>2</sub>)<sub>2</sub>-*arachno*- $B_{10}H_{12}$ ] (compound **1**), there has been a formal loss of the two-electron ligand SMe<sub>2</sub> to give a classical *arachno*  $\rightarrow$  *nido* two-electron conversion. The SMe<sub>2</sub> unit and some of the hydrogen atoms have concomitantly repositioned themselves about the open face of the classical *nido/arachno* boat-shaped skeleton. It has been demonstrated that there is probably no re-arrangement of the boron atom positions within the skeleton during this process.<sup>24</sup>

The crystallographic determination of compound **2** has previously been reported.<sup>23</sup> In this previous report, however, it was only possible to solve the structure as a racemic twin in space group  $P2_12_12_1$ . In our present work, we were able to get good



**Fig. 4** The molecular structure of  $[6,9-(SMe_2)_2$ -*arachno*- $B_{10}H_{10}$ -1,3-(6-*nido*- $B_{10}H_{13})_2$ ] (compound **5**), as determined by DFT calculations.



Fig. 5 The crystallographically determined structure of  $[1,6'-(nido-B_{10}H_{13})_2]$  compound 6.

single-crystal X-ray diffraction data at 150 K. Using anomalous dispersion we were then able to solve and refine the absolute structure with improved molecular dimensions, a selection of which is given in Table 1. Of these dimensions, the shorter distance B(6)-B(7) of 1.654(3) Å, noted before,<sup>23</sup> again is worth emphasizing, because it leads to the suggestion that the broad appearance of the two <sup>11</sup>B NMR resonances arising from these two sites derives from a large interboron internuclear coupling constant  ${}^{1}J({}^{11}B-{}^{11}B)$  between these two positions. Otherwise, the <sup>11</sup>B spectrum itself has previously been assigned and discussed, and its similarity to that of the  $[nido-B_{10}H_{13}]^-$  anion noted.<sup>23</sup> As part of this present work we now have additionally measured and assigned the <sup>1</sup>H NMR chemical shifts of the cluster hydrogen atoms. However, there is nothing exceptional about these within the context of the generally expected parallels between the <sup>1</sup>H and <sup>11</sup>B chemical shifts for directly bound BH(exo) units within a particular compound, with {BH(endo)} and {BHB} bridging proton resonances lying to higher shielding of this general trend.<sup>29</sup>

Because of the chiral nature of compound **2**, the two methyl groups of the  $SMe_2$  ligand are chemically inequivalent and have different chemical shifts,<sup>20</sup> even though there may be relatively free rotation about the boron-sulfur bond. This rotation has previously been examined at the extended-Hückel level.<sup>20</sup> This last study

gave a rotational energy barrier  $\Delta G^{\dagger}$  of *ca.* 23 kJ mol<sup>-1</sup>, with the minimum energy conformer (schematic VI) corresponding approximately to the crystallographically determined configuration (Fig. 1). This low  $\Delta G^{\dagger}$  value implies that any differentiation of individual rotamers would not be detectable by NMR spectroscopy down to less than -100 °C, in accord with observation. The various energetic maxima from this study correspond to conformations in which the methyl groups of the SMe<sub>2</sub> moiety approximately eclipse the adjacent BH(1), BH(2), BH(6) and BH(10) positions as in schematics VII, VIII and IX. Because we have become interested in how rotamers about exo-cluster linkages may affect cluster geometry and cluster electronic structure, and thence how they may affect cluster NMR shielding behaviour,<sup>27</sup> we have repeated this calculation using the DFT approach at the B3LYP/6-31G\* level, and have calculated the <sup>11</sup>B nuclear shieldings by the GIAO approach.



The results gave energy maxima in positions similar to those found in the earlier extended-Hückel study, which is reasonable. The maxima are approximately represented by structures **VII**, **VIII** and **IX**, respectively corresponding to calculated energies at *ca*. 9.8, 2.8 and 7.6 kJ mol<sup>-1</sup> relative to the lowest energy conformer **VI**. The geometries arising from the calculation showed that there was little effect on cluster geometry associated with the rotation about the boron–sulfur link. There was also little effect on the CSC interatomic angle of *ca*. 101° as the SMe<sub>2</sub> ligand was rotated. The principal change was in the boron-to-sulfur distance, which maximized in the eclipsed positions **VII**, **VIII** and **IX** at 1.941, 1.923 and 1.937 Å, respectively. However, these extensions over the value of 1.915 Å for the ground-state conformation **VII** are very small. They are presumably induced principally by the steric effects of the eclipsing.

Corresponding to these minimal geometrical changes, there is also little variation in the calculated <sup>11</sup>B nuclear shieldings of the cluster as the SMe<sub>2</sub> group is rotated relative to the cluster (Fig. 6). The maximum variations are those for  ${}^{11}B(1)$  and  ${}^{11}B(10)$ , with variations over ranges of 5.7 and 5.4 ppm, respectively. These small variations suggest only minor intra-cluster electronic changes associated with the rotation; they are similar to, but somewhat less than, those calculated as arising from P-phenyl rotation about the phosphorus-carbon linkage in [7-Ph-nido-7,8,10-PC<sub>2</sub>B<sub>8</sub>H<sub>10</sub>], the only other species examined for this type of phenomenon, where the variations range over more than 6 ppm.<sup>30</sup> For compound 2, there is reasonable correlation between calculated and experimental <sup>11</sup>B chemical shifts. This correlation adds confidence to the use of this DFT-GIAO procedure for the definitions of the structures of related compounds for which crystallographically established structures are not available.<sup>31,32</sup> This consideration applies particularly for compounds 4 and 5 in this present work as discussed below.

The crystallographically determined structure of  $[6,9-(SMe_2)_2-arachno-B_{10}H_{11}-1-(6'-nido-B_{10}H_{13})]$  (compound **3**, schematic **III**) is in Fig. 2. This is seen to have the *arachno* ten-vertex



**Fig. 6** Variation in the molecular energy, given as  $\Delta H$  in kJ mol<sup>-1</sup> (upper diagram), and in the calculated <sup>11</sup>B NMR shielding, given as  $\delta$ (<sup>11</sup>B) in ppm (lower diagram), at the various cluster sites in [5-(SMe<sub>2</sub>)-*nido*-B<sub>10</sub>H<sub>12</sub>] (compound **2**), as determined by DFT/GIAO calculations, as the SMe<sub>2</sub> group and the {B<sub>10</sub>H<sub>12</sub>} moiety mutually contra-rotate about the S(5)–B(5) bond.

 $6,9-(SMe_2)_2$ -substituted constitution of the starting species [6,9- $(SMe_2)_2$ -arachno- $B_{10}H_{12}$ ] (compound 1), but with a pendant nidodecaboranyl  $\{B_{10}H_{13}\}$  group  $\sigma$ -bound by its open-face 6-position to the apical 1-position of the arachno-decaboranyl unit. The intercluster  $\sigma$  bond B(1)–B(6') at 1.693(5) Å is comparable to the intercluster linkage in, for example, the  $[(nido-B_{10}H_{13})_2]$  isomers, in which it ranges from 1.679(3)-1.704(3) Å,<sup>33-35</sup> and is similar to the other  $\sigma$ -linked interboron distances listed in Table 1 for the other new compounds reported here. The individual arachno and nido ten-boron clusters have straightforward geometries, with dimensions corresponding closely to those of unsubstituted [6,9- $(SMe_2)_2$ -arachno- $B_{10}H_{12}$ ] (compound 1) itself,<sup>36</sup> and to those of unsubstituted B<sub>10</sub>H<sub>14</sub> itself,<sup>37</sup> respectively. As far as we are aware, compound 3 is the first reported species that links together the classical38 and otherwise well-examined nido and arachno tenboron clusters. Linked {ten-vertex closo : ten-vertex closo} and {ten-vertex *nido* : ten-vertex *nido*} bis(decaboranyl) systems are, by contrast, well recognized.31-35,39

The formation of compound **3** from compound **1** is of interest, because a *nido*-decaboranyl  $\{B_{10}H_{13}\}$  cluster is generated from an *arachno* [(SMe<sub>2</sub>)<sub>2</sub>B<sub>10</sub>H<sub>12</sub>] unit. This implies inter-cluster transfer of a hydrogen atom as well as loss of the two SMe<sub>2</sub> ligands. In view of the knowledge of the existence of a 'reactive' {(SMe<sub>2</sub>)B<sub>10</sub>H<sub>12</sub>} isomer that is readily formed from compound **1** under mild thermolytic conditions,<sup>29,30</sup> it is reasonable to postulate a dissociation

from compound 1 of one  $SMe_2$  unit, say that at the 6-position. This dissociation would give either an incipient or intermediate 'reactive' isomer of compound 2 with a  $\{9-(SMe_2)B_{10}H_{12}\}$  formulation; compared to compound 1 it would now have a reactive site at the 6-position instead of SMe<sub>2</sub>, (schematic X). This 6position, having lost SMe<sub>2</sub>, would be electrophilic, and would attack the 1-position of a second [(SMe<sub>2</sub>)<sub>2</sub>B<sub>10</sub>H<sub>12</sub>] molecule via B-H addition. There would be a consequent rearrangement of hydrogen atoms around the open face together with concomitant loss of  $SMe_2$  from the 9-position (schematic **X**). This would be consistent with the general supposition that the 1,3 positions of the arachno decaboranyl cluster have a high electron density,40 and be thereby most susceptible to electrophilic attack by the vacant 6-position of the reactive  $\{9-(SMe_2)B_{10}H_{12}\}$  moiety. However, as we note below, isomerisations of the nido ten-vertex cluster are also feasible in this type of system, such that positions initially in the open face of the cluster may end in basal positions. In this regard it is noted that any general rearrangement tendencies for the ostensibly rigid nido-decaboranyl unit are far from thoroughly investigated or established.



The process of additive attack by such a  $\{9-(SMe_2)B_{10}H_{12}\}$ intermediate should, in principle, be repeatable, to give multicluster species. The isolation and characterisation of the two threecluster isomers [6,9-(SMe<sub>2</sub>)<sub>2</sub>-arachno-B<sub>10</sub>H<sub>10</sub>-1,5-(6'-nido-B<sub>10</sub>H<sub>13</sub>)<sub>2</sub>] (compound 4, schematic structure IV) and [6,9-(SMe<sub>2</sub>)<sub>2</sub>-arachno- $B_{10}H_{10}-1,3-(6'-nido-B_{10}H_{13})_2$  (compound 5, schematic structure V) from the same system that yields the two-cluster compound 3 thence suggest that this is indeed the case. Of these two threecluster compounds, we have been able to establish the structure of  $[6,9-(SMe_2)_2$ -arachno- $B_{10}H_{10}-1,5-(6'-nido-B_{10}H_{13})_2]$  (compound 4) by an X-ray diffraction analysis (Fig. 3 above). Obtainable crystals under our conditions were only very small fibres of ca.  $0.08 \times 0.02$  mm cross section, and required the use of synchrotrongenerated X-irradiation for sufficient diffraction intensity for the analysis, as reported in a preliminary note.25 The diffraction analysis revealed the *arachno*  $\{(SMe_2)_2B_{10}\}$  configuration as in compounds 1 and 3, but now with two pendant open decaboranyl groups rather than just the one of compound 3. These are on the B(1) and B(5) positions, and are established as  $\{nido-B_{10}H_{13}\}$ moieties both by their bridging hydrogen-atom positions and by the general *nido*-type molecular dimensions established by the single-crystal X-ray work. Their nido character was also apparent from the results of <sup>11</sup>B and <sup>1</sup>H single-resonance and doubleresonance NMR spectroscopy. These results show that each {nido- $B_{10}H_{13}$  unit is bound by its 6-position, as in compound 3 described above. The NMR data were also consistent with the arachno character of the central  $\{(SMe_2)_2 B_{10} H_{10}\}$  unit. DFT/GIAO molecular geometry and nuclear shielding calculations on the molecular structure of compound 4 gave  $\delta(^{11}B)$  values that closely corresponded to those measured experimentally, which gave confidence in the use of this method for the establishment of the structure of its isomeric compound 5 (see next paragraph) for which single-crystal X-ray work was not feasible. A comparison diagram of the experimental and calculated spectrum for compound **4** is shown in Fig. 7.



**Fig. 7** NMR spectra for  $[6,9-(SMe_2)_2$ -*arachno*- $B_{10}H_{10}-1,5-(6'-nido-<math>B_{10}H_{13})_2]$  (compound 4): upper trace, the <sup>11</sup>B spectrum as calculated by DFT B3LYP/ 6-31G\* with no <sup>1</sup>H coupling; lower trace, the measured room-temperature 128 MHz <sup>11</sup>B–{<sup>1</sup>H(broad-band noise)} spectrum (CDCl<sub>3</sub>). Selective line-broadening has been applied to appropriate resonance lines in the calculated spectrum in order to mimic experimental linewidths.

As just mentioned, crystals of compound **5** suitable for singlecrystal X-ray work have not yet been obtained. However, NMR spectroscopy shows a symmetrical bis(*nido*-decaboranyl)-*arachno*decaborane constitution for this species. Detailed <sup>11</sup>B and <sup>1</sup>H single and multiple resonance work readily establishes the (1,3) substituent pattern as in schematic cluster structure V above, giving the overall formulation [6,9-(SMe<sub>2</sub>)<sub>2</sub>-*arachno*-B<sub>10</sub>H<sub>10</sub>-1,3-(6'-*nido*-B<sub>10</sub>H<sub>13</sub>)<sub>2</sub>]. This structural conclusion was also supported by DFT/GIAO structural and nuclear shielding calculations, which gave  $\delta$ (<sup>11</sup>B) values corresponding very reasonably with those measured and assigned experimentally (see Experimental section).

Compounds 4 and 5 are the first tridecaboranyls definitively identified. The resultant  $\{B_{30}\}$  units, as far as we are aware, constitute the biggest molecular all-boron skeletal assemblies yet unequivocally characterized. Although a sample of  $B_{30}H_{38}$ , bis(*nido*-decaboranyl)-*nido*-decaborane,  $[B_{10}H_{12}(B_{10}H_{13})_2]$ , was reported a quarter of a century ago to be isolated from the products from the thermolysis in refluxing toluene solution of  $nido-B_{10}H_{14}$ in the presence of 0.03 mol%  $[6,9-(SC_4H_8)_2-arachno-B_{10}H_{12}]$  as catalyst, this was an unspecified and unspecifiable mixture of isomers,<sup>41</sup> of which some 546 are in principle possible. A closer structural parallel for compounds 4 and 5 is perhaps the bis(nidodecaboranyl)-arachno-diplatinadecaborane, [6,9-(PMe<sub>2</sub>Ph)<sub>2</sub>- $\mu(5^{\rm C},\!6^{\rm P}),\!\mu(8^{\rm C},\!9^{\rm P})-(PMe_2\text{-}{\it ortho-C_6H_4})_2\text{-}{\it arachno-6,}9\text{-}Pt_2B_8H_8\text{-}2,\!4\text{-}$  $(6'-nido-B_{10}H_{13})_2$  [schematic cluster structure XI, in which M is  ${Pt(PMe_2Ph) (PMe_2C_6H_4)}].^{42}$  This last species has two pendant nido-decaboranyl units also bound by their 6-positions, but they are now bound to a central *arachno* ten-vertex  $\{Pt_2B_8\}$  unit, rather than to a central *arachno* ten-vertex  $\{B_{10}\}$  unit as in compounds 4

and **5**. In the platinaborane these are bound at the (2,4) positions on the *arachno* central cluster, rather than the (1,5) and (1,3) positions as in compounds **4** and **5**, respectively. These different positionings could suggest different mechanisms of cluster conjunction. This would not be unexpected, because the method of synthesis of the  $[(PMe_2Ph)_2(PMe_2C_6H_4)_2Pt_2B_8H_6(B_{10}H_{13})_2]$ species, from the reaction of the nine-vertex *arachno* platinaborane  $[(PMe_2Ph_2)_2PtB_8H_{12}]$  with and in molten  $B_{10}H_{14}$ , used as a reacting solvent, at +128 °C,<sup>42</sup> is quite different from the procedure with compound **2** in this present work, although it is of interest to note that all of the pendant *nido*-decaboranyl clusters resulting from these fusion reactions are joined by the (6)-positioned vertices of the *nido*-decaboranyl cluster.



A small amount of the two-cluster species  $[1,6'-(nido-B_{10}H_{13})_2]$ (compound 6, Fig. 5, ca. 0.5%), identified by single-crystal Xray diffraction analysis, was also isolated from the mixture of products from this reaction, together with small amounts of other unidentified two-cluster compounds. The nido:nido compound 6 exhibits the same (1,6') cluster linkage as found in the arachno:nido compound 3. However, given the small yield, no definitive mechanistic conclusions may be drawn here, although it should be noted in this context that, as borane cluster-substituent chemistry is being developed and thence effective labelling becoming available, it is becoming increasingly apparent that in many cases the products ostensibly resulting from reactions on rigid borane cages in fact involve borane-cluster rearrangements.<sup>43</sup> The (1,6')-linked compound **6** is the eighth characterised  $[(B_{10}H_{13})_2]$  isomer out of the eleven possible geometric isomers, the other seven being the (1,1'), (1,2'), (1,5'), (2,2'), (2,5'), (2,6') and (5,5') analogues.<sup>33-35</sup>

It is of interest in terms of approaches to new fused macropolyhedral assemblies that, in both compounds 4 and 5, the two nido-decaboranyl substituents are in adjacent positions on the central arachno decaboranyl nucleus. In prognostications for possible structures of large very condensed boron-containing cluster species,1,2,42,44-46 it has been proposed that large globular boron-hydride species can consist of borons-only cores surrounded by outer boron-hydride skins.<sup>1,2,42</sup> One fundamental architectural principle visualised here is that the central boron cores of such species will themselves be based on known simpler boron-hydride species, but with the exo-terminal boron-hydrogen bonds formally replaced by interboron bonds to outer recognisable boron-hydride cluster units. Thus, for example, the framework of the computed species  $B_{84}H_{54}$  (schematic XII),<sup>1,2,26</sup> based on a fundamental structural fragment of  $\beta$ -rhombohedral boron with peripheral valencies bound by hydrogen, is seen to consist of a central  $\{B_{12}\}$  core with a *nido*-type pentagonal pyramidal six-vertex  $\{B_6\}$  unit bound to each of the twelve boron atoms, with the twelve  $\{B_6\}$  units mutually fused to generate the sixtyboron-atom basis of the outer boron-hydride skin. This structural perception suggests a general strategy for the synthesis of such species by the multiple substitution of  $\{BH(exo)\}$  hydrogen atoms on starting borane substrates by boron–hydride units. These outer moieties might then be induced to cross-link, perhaps by thermal dihydrogen elimination, to generate a contiguous outer boron– hydride skin (schematic **XIII**). Here the peralkylation of the closed  $\{C_2B_{10}\}$  and related carbaborane skeletons<sup>47-49</sup> offers an interesting related paradigm: however, as far as we are aware, no attempts have yet been made directly to interlink the outer carbon atoms in these latter peralkylated  $\{C_2B_{10}\}$  species, although the results of straightforward thermolysis experiments would be interesting. In any event, it is clear that compounds **4** and **5**, each with its two adjacent  $\{B_{10}H_{13}\}$  substituents on a ten-boron core (Fig. 3 and 4, schematics **IV** and **V**), represent initial steps on the required multi-cluster accumulation.



In this regard it is of interest to ascertain whether multiple adjacent substitution is indeed a valid further target along this strategic pathway. To assess this possibility, a DFT calculation of a five-cluster tetrakis(*nido*-decaboranyl)-substituted  $\{(SMe_2)_2B_{10}\}$ arachno species, specifically [6,9-(SMe<sub>2</sub>)<sub>2</sub>-arachno-B<sub>10</sub>H<sub>8</sub>-1,2,3,4- $(6'-nido-B_{10}H_{13})_4$ ], was carried out. This symmetrically substituted (1,2,3,4) species was chosen for convenience of calculation. Also for convenience of calculation, a  $C_{2v}$  symmetry constraint was adopted. This five-cluster system minimised energetically without any disruption to the individual nido-decaboranyl and arachnodecaboranyl geometries (Fig. 8), strongly supporting the concept that multiple decaboranyl substitution on adjacent sites on deltahedral borane clusters is in principle feasible, at least as far as steric considerations in the product are concerned. We currently examine for compounds that may induce or exhibit such multiple substitution in this and related systems.

In the general context of building bigger borane-based assemblies, there is also interest in determining whether this intercluster coupling based on transient SMe<sub>2</sub>-containing species might



**Fig. 8** The molecular structure of the as yet hypothetical species  $[6,9-(SMe_2)_2$ -*arachno*- $B_{10}H_8$ -1,2,3,4-(6'-*nido*- $B_{10}H_{13}$ )<sub>4</sub>] as determined by DFT calculations. For economy of computing time, the energetic minimum was constrained to  $C_{2v}$  symmetry, but the stereochemical feasibility of having four adjacent *nido*-decaboranyl units bound to the four adjacent sites on a typical borane four-boron deltahedral 'diamond' is nevertheless readily demonstrated.

be extendable to bigger starting borane substrates. Here, in preliminary siting experimentation, we find that the heating at reflux of  $[1,5'-(nido-B_{10}H_{13})_2]^{33}$  in SMe<sub>2</sub> solution for 5 h, followed by TLC and HPLC separation, gave single-cluster  $[6,9-(SMe_2)_2-arachno-B_{10}H_{12})]$  (compound 1) and two-cluster  $[6,9-(SMe_2)_2-arachno-B_{10}H_{11}-1-(6'-nido-B_{10}H_{13})]$  (compound 3, described above, schematic cluster structures III and XIV) as the principle products, in isolated yields of 39 and 10.5%, respectively. No three-cluster species were detected, but a small amount of the previously unreported two-cluster species [5-(SMe\_2)-4-(2'-nido-B\_{10}H\_{13})-nido-B\_{10}H\_{11}] (compound 7, 0.6% yield) was also isolated. Compound 7 was characterised by a single-crystal X-ray diffraction analysis (Fig. 9, schematic cluster structure XV) and by NMR spectroscopy (see Experimental section below).



Fig. 9 The crystallographically determined molecular structure of  $[5-(SMe_2)-4-(2'-nido-B_{10}H_{13})-nido-B_{10}H_{11}]$  (compound 7).

Compound 7 features a subcluster comparable to that found in the single-cluster species,  $[5-(SMe_2)-nido-B_{10}H_{12}]$  (compound 2) and, although 7 is formed in modest yield, it nevertheless does suggest the possible presence in the reaction mixture of reactive intermediates of the type  $\{(SMe_2)B_{10}H_{11}(B_{10}H_{13})\}$ , based on the 'reactive' isomer of  $[(SMe_2)B_{10}H_{12}]$ , but with an additional  $\{nido-B_{10}H_{13}\}$  moiety appended. This augurs well for the isolation of four-cluster species, as well as alternative three-cluster species, from this type of reaction system.



The (1,6')- $\sigma$  linkage in the major product  $[6,9-(SMe_2)_2$ arachno- $B_{10}H_{11}$ -1-(6'-nido- $B_{10}H_{13}$ )] (compound 3, schematic cluster structure **XIV**) and the (4,2')- $\sigma$  linkage in the minor product  $[5-(SMe_2)-4-(2'-nido-B_{10}H_{13})-nido-B_{10}H_{11}]$  (compound 7, schematic cluster structure XV) are clearly different to the starting configuration in  $[1,5'-(nido-B_{10}H_{13})_2]$  (schematic cluster structure XVI). The formation of the single-cluster species [6,9-(SMe<sub>2</sub>)<sub>2</sub>-arachno- $B_{10}H_{12}$ ] 1 (39%) shows that much cluster de-linking occurs in the reaction system, possibly implying the formation of the twocluster compounds 3 and 7 via cluster fusion through a reactive *nido*-type { $(SMe_2)B_{10}H_{12}$ } isomer, as seen for the formation of compounds 4 and 5 as well as for compound 3 as reported above. However, this reaction to give 3 and 7 from  $[1,5'-(nido-B_{10}H_{13})_2]$ was carried out at lower temperature, in refluxing SMe<sub>2</sub> (38 °C), in contrast to the reactions in refluxing benzene (80 °C) or toluene (111 °C) to give 3, 4 and 5 as discussed above. Further, loss of SMe<sub>2</sub> from 1 to form the 'reactive' intermediate  $\{(SMe_2)B_{10}H_{12}\}$ has been shown<sup>19</sup> to be retarded by excess SMe<sub>2</sub>, thus limiting the likelihood of its formation in this system, which uses neat refluxing SMe<sub>2</sub> as solvent. Additionally, the production of the two-cluster compound 3, which has only one appended borane ligand, in significant quantity, in solution in neat refluxing SMe<sub>2</sub>, suggests that this reaction of two-cluster  $[1,5'-(nido-B_{10}H_{13})_2]$ to give compound 3 may proceed differently to that of the single decaboranyl cluster discussed above (near schematic cluster structures III, V and V). The observed products may therefore result from direct attack by SMe2 on the original undissociated double-clusters rather than through a cluster-coupling process. Consequently, a succeeding cluster isomerisation would then be required to yield the observed isomer composition. In this regard,

it may be noted that it is increasingly recognised that, under some conditions, for example in the presence of Lewis base, openfaced borane, metalladecaborane, and carbadecaborane clusters do have a tendency to exhibit isomerisation. General mechanisms for ten-vertex clusters are proposed to proceed through 'vertexflip' processes, in which a 'prow' B(6) or B(9) vertex may be regarded as moving around the open face of the ten-vertex cluster.<sup>43,50,51</sup> Thus, for example, it is possible in principle to convert the configuration of an initial  $[6,9-(SMe_2)_2-arachno-B_{10}H_{11}-1-(5'-nido-B_{10}H_{13})]$  product into the final (1,6') configuration in **3**, through a vertex flip on one *nido*-decaboranyl subcluster (schematics **XVII**  $\rightarrow$  **XIX**).



Two such cluster isomerisations, one for each sub-cluster, for example as in schematics  $XX \rightarrow XXI$  and  $XXII \rightarrow XXIII$ , would be required to afford the (4,2') configuration observed for compound 7. However, deuterium-labelling experiments<sup>24</sup> have been taken to suggest that there is no cluster isomerisation either during the formation of  $[(SMe_2)_2B_{10}H_{12}]$  1 itself from *nido*-B<sub>10</sub>H<sub>14</sub> in SMe<sub>2</sub> solution at ambient temperature, or during the subsequent highertemperature formation of the proposed reactive  $\{(SMe_2)B_{10}H_{12}\}$ intermediate. That isomerisations occur in the present system implies that the presence of an effective borane substituent on a borane subcluster affects the course of the reaction in the twocluster compound. A precedent for this type of substituent effect is that the heating of the chlorine-substituted decaboranyl cluster species [2,4-Cl<sub>2</sub>-nido-B<sub>10</sub>H<sub>12</sub>] in SMe<sub>2</sub> solution at reflux gives [6,9- $(SMe_2)_2$ -1,7-Cl<sub>2</sub>-arachno-B<sub>10</sub>H<sub>10</sub>] as one of the products, also via a postulated 'vertex flip' during the course of the reaction.<sup>43,50</sup> On the other hand, the monohalogenated species  $[2-Br-nido-B_{10}H_{13}]$ yields an apparently unrearranged species [6,9-(SMe<sub>2</sub>)<sub>2</sub>-2-Brarachno-B<sub>10</sub>H<sub>11</sub>].<sup>52</sup> The high yield of the single-cluster product  $[(SMe_2)_2B_{10}H_{12}]$  1 here may be a consequence of cluster vertex motility promoting cluster de-linking. This may impose a kinetic limit on the number of decaboranyl clusters that may be conjoined in this type of system. The overall reaction system is clearly complex and contains competing processes: in the auto-reaction of  $[6,9-(SMe_2)_2$ -arachno- $B_{10}H_{12}]$  (compound 1) in refluxing benzene

dealt with earlier in this account, the presence of the reactive intermediate promotes cluster oligomerisation; on the other hand, the reactions in SMe<sub>2</sub> as solvent suggest that free SMe<sub>2</sub> will promote cluster isomerisation and de-linking of inter-cluster  $\sigma$  linkages. We hope to investigate these differential types of processes further.

#### Conclusion

One initial objective, of achieving intimate intercluster fusion to give contiguous new borane skeletons of more then twenty vertices with more than one vertex in common, so that the multicentre bonding extends over both subclusters, was not observed in this approach. Nevertheless, the achieved results of two or more clusters conjoined by two-electron two-centre  $\sigma$  linkages, in good yield for a thermolytic conjoining reaction, has some interesting auguries. First, the ready attack of the 'reactive'  $\{(SMe_2)B_{10}H_{12}\}$ isomer at the electrophilic site of  $[6,9-(SMe_2)_2-arachno-B_{10}H_{12}]$ (compound 1) suggests that the method could be of more general use in co-thermolysis reactions of compound 1 with other boranes in order to link the versatile nido-decaboranyl residue to other borane residues. Reaction with the  $[closo-B_{12}H_{12}]^{2-}$  dianion to give  $[B_{12}H_{11}(B_{10}H_{13})]^{2-}$ , which might be precursive, via further oxidation, to the relatively recently reported<sup>53,54</sup> very interesting fused-cluster species [B<sub>22</sub>H<sub>22</sub>]<sup>2-</sup>, would be an attractive target here. Second, the multiple addition of nido-decaboranyl residues in adjacent sites is of potential use in the synthesis of higher more condensed boranes. Here, the close proximity of the nidodecaboranyl residues on the central borane substrate might imply that coupling reactions among them, with dihydrogen loss, may be readily effected (schematic structure XIII above). The close proximity also suggests that the adjacent open *nido*-decaboranyl clusters may be linkable by bonding to a common heteroatom, such as a transition-element centre. We are currently devising experiments that may generate larger quantities of the adjacently substituted bis(decaboranyl) species 4 and 5 in order to test these hypotheses. In more general cluster construction terms, these could be steps towards the feasibility of building up big filledball globular species based on the concept of borons-only cores surrounded by boron hydride sheaths (schematic structures XII and XIII above).<sup>1,2,45</sup> These latter 'filled-ball' architectures may be those that ultimately typify big borane chemistry. Their 'filled-ball' constitution<sup>2,42,44,45</sup> contrasts to the 'hollow-ball' architectures of the fullerenes.

## Experimental

#### General

Reactions were carried out in dry solvents (toluene, benzene, hexane, cyclohexane and dichloromethane) under dry dinitrogen, but subsequent manipulatory and separatory procedures were carried out in air. [6,9-(SMe<sub>2</sub>)<sub>2</sub>-arachno-B<sub>10</sub>H<sub>12</sub>] (compound 1)<sup>55,56</sup> and  $[1,5'-(nido-B_{10}H_{13})_2]^{31-35}$  was prepared essentially as in literature methods. Preparative thin-layer chromatography (TLC) was carried out using 1 mm layers of silica gel G (Fluka, type GF254) made from water slurries on glass plates of dimensions  $20 \times 20 \,\mathrm{cm}^2$ , followed by drying in air at 80 °C; components were located

visually with ambient or ultra-violet irradiation. HPLC was performed on a silica-gel column (Lichosorb SI 60,  $25 \times 2.12$  cm). Mass spectrometry was carried out on a VG Autospec instrument using electron-impact ionisation at 70 eV. NMR spectroscopy was performed at ca. 5.9 and 11.8 T (fields corresponding to 250 and 500 MHz <sup>1</sup>H frequencies, respectively) using commercially available instrumentation and using techniques and procedures as adequately described and enunciated elsewhere.29,57-59 Chemical shifts  $\delta$  are given in ppm relative to  $\Xi = 100$  MHz for  $\delta({}^{1}\text{H})$ (±0.05 ppm) (nominally TMS) and  $\Xi$  = 32.083972 MHz for  $\delta$ <sup>(1)</sup>B)  $(\pm 0.5 \text{ ppm})$  (nominally [F<sub>3</sub>BOEt<sub>2</sub>] in CDCl<sub>3</sub>).<sup>29</sup>  $\Xi$  is as defined by McFarlane.60

Formation of  $[5-(SMe_2)-nido-B_{10}H_{12}]$  (compound 2) and [1-(6' $nido-B_{10}H_{13}$ )-6,9-(SMe<sub>2</sub>)<sub>2</sub>-arachno-B<sub>10</sub>H<sub>11</sub>] (compound 3). A sample of  $[(SMe_2)_2B_{10}H_{12}]$  (compound 1; 100 mg; 410 µmol) was dissolved in toluene (20 ml) and heated at reflux for 3 h. After cooling to room temperature, the more volatile components were removed under reduced pressure, the solid residue redissolved in  $CH_2Cl_2$  (ca. 5 ml) and the products separated and purified by repeated preparative TLC, development using 30 : 70 hexane- $CH_2Cl_2$  as the liquid phase giving crude [7-( $SMe_2$ )-*nido*- $B_{10}H_{12}$ ] (compound 2) as a white solid ( $R_{\rm F}$  0.81). After recrystallisation by diffusion of hexane into a solution in CH<sub>2</sub>Cl<sub>2</sub> at room temperature, pure compound 2 was isolated in 30% yield (23 mg, 122 µmol). By using a mixture of cyclohexane (10 ml) and benzene (8 ml) as solvent for compound 1 (100 mg; 410 µmol), and heating at reflux for 6 h, two compounds were obtained. Both were separated and purified by repeated preparative TLC, final development with hexane- $CH_2Cl_2$  (3 : 7) giving [5-(SMe<sub>2</sub>)-nido- $B_{10}H_{12}$ ] (compound **2**;  $R_{\rm F}$  0.81; 8 mg, 11%) as a white solid, and [1-(6'-*nido*-B<sub>10</sub>H<sub>13</sub>)- $6,9-(SMe_2)_2$ -arachno- $B_{10}H_{11}$ ] (compound 3;  $R_F 0.50$ ; 15 mg, 20%) as a yellow solid. Measured NMR data for compound 2 (CDCl<sub>3</sub>, 294–297 K), ordered as  $\delta(^{11}B) [\delta(^{1}H) \text{ of directly bound H}]$ , are: B(1) +5.5 [+2.64], B(2) -27.5 [+0.62], B(3), -3.1 [+3.03], B(4) -41.7 [+0.41], B(5) -5.1 [+3.03], B(6) +21.9 [+4.22], B(7) +0.5  $({}^{1}J({}^{11}B, {}^{11}B) 110 \text{ Hz})$  [no H], B(8) -10.5 [+2.22], B(9) -5.1 [+2.93] and B(10) -11.0 [+3.30]; additionally  $\delta({}^{1}H){\mu-H(5,6)}$  -4.09,  $\{\mu$ -H(8.9) $\}$  -2.65,  $\{\mu$ -H(9,10) $\}$  -2.63 and  $\delta$ (<sup>1</sup>H) (SMe<sub>2</sub>) +2.68. Calculated  $\delta$  (<sup>11</sup>B) values (DFT/GIAO) for the minimum energy rotamer (schematic configuration VI above) as follows: B(1) + 7.6, B(2) - 28.0, B(3) - 2.7, B(4) - 41.8, B(5) + 0.4, B(6) + 17.2, B(7)-5.2, B(8) +5.2, B(9) -7.4 and B(10) -10.3. Measured NMR data for compound 3 (CDCl<sub>3</sub>, 294–297 K), ordered as  $\delta$ <sup>(1)</sup>B)  $[\delta(^{1}H) \text{ of directly bound H}]$ , are: B(1) -40.2 (no H), B(2',4') -37.9 [+0.45, +0.38], B(3) -32.3 [+0.67], B(6,9) -23.1 [-0.20], B(7,8) -19.1 [+1.63], B(5,10) -17.9 [+1.66], B(2,4) -2.8 [+2.23], B(5',7') -0.4 [+3.10], B(8',10') +0.3 [+3.00], B(9') +7.7 [+3.69], B(1',3') +11.4 [+3.56], B(6') +32.5 [1 (conjuncto position, no terminal H)]; additionally  $\delta({}^{1}H) \{\mu - H(5,10)\} - 4.42, \{\mu - H(7,8)\} - 4.53, \{\mu - 4.53, \{\mu$  $H(5',6' \text{ and } 6',7') - 1.36, \{\mu-H(8',9' \text{ and } 9',10')\} - 2.24 \text{ and } \delta(^{1}H)$  $(SMe_2) + 2.44.$ 

(compound 4),  $[6,9-(SMe_2)_2$ -arachno- $B_{10}H_{10}-1,3-(6'-nido-B_{10}H_{13})_2]$ (compound 5) and  $[1,6'-(nido-B_{10}H_{13})_2$  (compound 6). In a slightly modified repetition of the above procedure, a solution of [6,9- $(SMe_2)_2$ -arachno-B<sub>10</sub>H<sub>12</sub>] (compound 1; 107 mg, 440 µmol) in

benzene (10 ml) was heated under reflux for 6 h. The products were then subjected to separation by TLC, using 30: 70 hexane-CH<sub>2</sub>Cl<sub>2</sub> as liquid medium. Just behind the most mobile band at  $R_{\rm F}$  0.8 {identified as  $[5-(SMe_2)-nido-B_{10}H_{12}]$  (compound 2)} was a faint yellow band, which was subjected to further separation by HPLC (57 : 43 hexane-CH<sub>2</sub>Cl<sub>2</sub>, 20 ml min<sup>-1</sup>). Three components of interest were obtained: A,  $R_T$  9.6, B  $R_T$  11.3 and C  $R_T$  12.1 min. Multi-element NMR spectroscopy indicated that A contained a o-linked arachno-nido cluster species. It has eluded further characterisation. NMR analysis of B together with DFT/GAIO <sup>11</sup>B chemical shift calculations enabled us reasonably to identify the compound as [6,9-(SMe<sub>2</sub>)<sub>2</sub>-arachno-B<sub>10</sub>H<sub>10</sub>-1,3-(6'-nido- $B_{10}H_{13}$ ] (compound 5; 1 mg, 0.5%). NMR data for compound 5 (CDCl<sub>3</sub>, 294–297 K), ordered as measured value of  $\delta$ <sup>(1)</sup>B) {calculated  $\delta(^{11}B)$  value by DFT/GIAO} [ $\delta(^{1}H)$  of directly bound H], are as follows:  $B(1,3) - 38.5 \{-37.0\}$  [conjuncto site, no H],  $B(4',4'') - 37.4 \{-38.7\} [+0.35], B(2',2'') - 32.4 \{-32.1\} [+0.17],$  $B(6,9) - 23.0 \{-24.8\} [-0.13], B(5,7,8,10) - 16.9 \{-14.8\} [+1.62],$  $B(2,4) - 2.0 \{5.0\} [+2.31], B(8',10',8'',10'') - 0.3 \{-3.4\} [+2.87],$  $B(5',7',5'',7'') + 0.0 \{+1.1\} [+2.94], B(9',9'') + 8.3 \{+3.9\} [+3.66],$  $B(1',3',1'',3'') + 11.4 \{+10.2\} [+3.47] \text{ and } B(6',6'') + 32.1 \{+29.9\}$ [conjuncto site, no H]; additionally  $\delta({}^{1}\text{H}) \{\mu\text{-H}(5,10;7,8)\} - 4.33$ ,  $\delta({}^{1}\text{H}) \{\mu - \text{H}(5', 6' \text{ and } 6', 7'; 5'', 6'' \text{ and } 6'', 7'')\} - 1.41, \delta({}^{1}\text{H}) \{\mu - 1.41, \delta({}^{1}\text{H})\}$  $H(8',9' \text{ and } 9',10'; 8'',9'' \text{ and } 9'',10'') -1.41 \text{ and } \delta(^{1}H) (SMe_2)$ +2.66. Unfortunately, the compound was not amenable to mass spectrometric analysis. Peak C was identified as [6,9-(SMe<sub>2</sub>)<sub>2</sub>arachno- $B_{10}H_{10}$ -1,5-(6'-nido- $B_{10}H_{13}$ )<sub>2</sub>] (compound 4). Diffusion of hexane into a CDCl<sub>3</sub> solution of compound 4 yielded small yellow crystals which required a synchrotron-generated X-ray radiation source to obtain sufficient diffraction intensity for a crystallographic analysis. Selected geometrical data for 4 are listed in Table 1 above. Measured NMR data for compound 4 (CDCl<sub>3</sub>, 294–297 K), ordered as  $\delta^{(1)}$ B) [ $\delta^{(1)}$ H) of directly bound H], are: B(1) -40.5 [conjuncto position, no terminal H], B(3, 4') -37.5 [+0.44, +0.31], B(4') -36.2 [+0.51], B(2'') -32.8 [-0.27], B(2') - 31.7 [+0.68], B(9) - 22.9 [+0.14], B(6,7) - 19.6 [+1.72],+1.58], B(7,8) -17.5 [+1.79], B(5) -14.1 [conjuncto position, no terminal H], B(2) -3.2 [+2.30], B(1") -2.1 [+2.22], B(5',5", 10') -1.1 [+3.00{2H} and +2.87], B(8',8",10') +0.5 [+3.04], B(9',9")  $+8.4 [+3.77], B(1',3',1'',3'') +11.6 [+3.61{2H} and +3.52{2H}],$ B(6' or 6'') + 26.8 [conjuncto position, no terminal H], B(6'' or6') +32.2 [conjuncto position, no terminal H]; additionally  $\delta$ (<sup>1</sup>H)  $\{\mu$ -H(5,10) $\}$  -4.17,  $\{\mu$ -H(7,8) $\}$  -4.26,  $\{\mu$ -H(5',6' and 6',7'; 5'',6'' and 6",7")} -1.29, -1.52(2H), -1.62, {µ-H(8',9' and 9',10'; 8",9" and  $9^{"}, 10^{"}$  = 2.15, -2.24, -2.31(2H) and  $\delta(^{1}H)$  (SMe<sub>2</sub>) +2.46.

Calculated  $\delta$ <sup>(11</sup>B) values (DFT/GIAO) are shown in Table 2 and a comparison diagram of the measured and calculated  $\delta(^{11}B)$  values is shown in Fig. 7. Mass spectrometry showed an isotopomer envelope centred at m/z 484 corresponding to that calculated for  $\{C_4H_{48}B_{30}S_2\}^+$ . Repeat reactions were carried out similarly but with two equivalents of nido-B<sub>10</sub>H<sub>14</sub> present. Yields varied with each reaction but the following is a typical procedure: [6,9- $(SMe_2)_2$ -arachno-B<sub>10</sub>H<sub>12</sub>] (compound 1; 129 mg, 0.53 mmol) and  $nido-B_{10}H_{14}$  (0.138 g, 1.1 mmol) in benzene (20 ml) were heated under reflux for 3 h. The solvent was then removed using a rotary evaporator (water-bath, ca. 30 °C) and the decaborane removed by overnight ambient temperature vacuum sublimation (ca. 0.01 mm Hg). Preparative TLC (70 : 30 CH<sub>2</sub>Cl<sub>2</sub>-hexane) of the residue showed a characteristic pattern of three main bands: **B** ( $R_{\rm F}$  0.5, yellow), **C** ( $R_{\rm F}$  0.4, yellow, compound 3, 27.5 mg, 14%) and **D** ( $R_{\rm F}$  0.2, colourless, detected under UV irradiation, compound 1, 10 mg). Further TLC separation of B using 50 : 50 CH<sub>2</sub>Cl<sub>2</sub>-hexane as liquid medium revealed the presence of a faint UV-active band above the main yellow band. The yellow band was identified as [6,9-(SMe<sub>2</sub>)<sub>2</sub>-arachno-B<sub>10</sub>H<sub>10</sub>-1,5-(6'-nido-B<sub>10</sub>H<sub>13</sub>)<sub>2</sub>] (compound 4; 33 mg, 0.68 mmol, 13%). Further HPLC separation (30 : 70 CH<sub>2</sub>Cl<sub>2</sub>:hexane, 20 ml min<sup>-1</sup>) of the UVactive band gave three components, **E**, **F** and **G**, with  $R_{\rm T}$  5.5, 7.4 and 8.4 min, respectively. The first two components, E and **F**, appeared to be isomeric  $[(B_{10}H_{13})_2]$  species but there was insufficient material for further characterisation. Vacuum sublimation of component G (sealed glass tube with one end placed on a warm surface) gave colourless crystals that enabled its characterisation by single-crystal X-ray diffraction analysis as [1,6'-(nido-B<sub>10</sub>H<sub>13</sub>)<sub>2</sub>] (Compound 6, 2.5 mg, 10 µmol 0.5%). Selected geometrical data for 6 are listed in Table 1 above.

Isolation of [5-(SMe<sub>2</sub>)-4-(2'-*nido*-B<sub>10</sub>H<sub>13</sub>)-*nido*-B<sub>10</sub>H<sub>11</sub>] (compound 7). A solution of  $[1,5'-(nido-B_{10}H_{13})_2]$  (98.7 mg, 0.41 mmol) in SMe<sub>2</sub> (5 ml) was heated at reflux for 5 h, after which time the SMe<sub>2</sub> was removed using a rotary-film evaporator (waterbath *ca.* 30 °C). The resulting solid was redissolved in CH<sub>2</sub>Cl<sub>2</sub>, precipitated with diethyl ether, and filtered off. The off-white precipitate thus obtained was identified by <sup>11</sup>B NMR spectroscopy as  $[6,9-(SMe_2)-arachno-B_{10}H_{12}]$  (compound 1; 62 mg, 30%). The filtrate was reduced in volume, applied to a preparative TLC plate and developed using 100% CH<sub>2</sub>Cl<sub>2</sub> as liquid medium. Four bands between  $R_F$  0.6 and  $R_F$  0.4 were identified under UV and

Position	Central <i>arachno</i> sub-cluster	<i>nido</i> -Decaboranyl sub-cluster attached at 1'	<i>nido</i> -Decaboranyl sub-cluster attached at 5'	
1	-36.80	+10.23	+10.16	
2	-2.65	-33.31	-32.33	
3	-37.18	+10.00	+9.91	
4	+0.29	-37.90	-36.54	
5	-13.30	-1.21	-1.89	
6	-17.90	+28.43	+23.19	
7	-18.18	-1.95	-1.74	
8	-16.61	+0.25	-0.31	
9	-20.35	+5.65	+7.41	
10	-17.30	+0.94	-0.68	

$B_{10}H_{11}(mido-B_{10}H_{13})$ ] 7. Note: Dat	a for compound 4 are previous	sly reported (ref. 25) but are incl	luded here for convenience of reference		
Compound no.	2	3	4	9	7
CCDC deposition no.	280344	280345	162053	280346	280347
Empirical formula	$\mathbf{C}_{2}\mathbf{H}_{18}\mathbf{B}_{10}\mathbf{S}$	$\mathrm{C_4H_{36}B_{20}S_2}$	$C_4H_{48} B_{30}S_2$	$\mathrm{B}_{20}\mathrm{H}_{26}$	$C_2 H_{30} B_{20} S$
$M_r$	182.32	364.65	484.84	242.41	302.52
$T/\mathbf{K}$	160(2)	223(2)	150(2)	150(2)	100(2)
Source, $\lambda/\AA$	Cu-Ka, 1.54184	Mo-Ka, 0.71073	Synchrotron, 0.6895	Mo-Ka, 0.71073	Mo-Ka, 0.71073
Crystal system	Orthorhombic	Monoclinic	Triclinic	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$	$P\overline{1}$	Pbca	$P2_1/n$
$a/ m \AA$	5.7777(4)	7.0367(1)	13.693(2)	11.3252(3)	6.9622(2)
$b/ m \AA$	12.9809(8)	32.4271(4)	13.823(2)	14.0450(4)	6.4999(6)
$c/ m \AA$	15.0483(6)	10.5289(1)	17.961(3)	20.8013(7)	10.6444(3)
$a/^{\circ}$		06	90.469(3)	06	90
$\beta/^{\circ}$	90	96.089(1)	105.008(3)	90	96.6540(10)
y /°	90	60	104.249(3)	90	90
$V/ m \AA^3$	1128.62(11)	2388.93(5)	2550.55(6)	3308.71(17)	1950.64(9)
Ζ	4	4	4	8	4
$D_{ m c}/{ m Mgm^{-3}}$	1.073	1.014	1.015	0.973	1.03
$\mu/\mathrm{mm}^{-1}$	1.976	0.212	0.169	0.036	0.145
Crystal size/mm	$0.38 \times 0.30 \times 0.23$	0.28  imes 0.08  imes 0.02	$0.18\times0.08\times0.02$	0.20  imes 0.14  imes 0.05	0.43  imes 0.07  imes 0.05
F(000)	384	768	1016	1008	632
$\theta$ Range/°	4.50 - 64.45	1.26-25.00	1.8–26	2.51–26	2.46–26
Index ranges, hkl	-6 to 6, 0 to 15, 0 to 17	-8 to 8, -0 to 40, 0 to 12	-17 to $17$ , $-17$ to $17$ , $-22$ to $22$	-13 to 13, -17 to 17, -25 to 25	-8 to 8, -30 to 32, -13 to 13
Indep. refl. $(R_{int})$	1785 (0.000)	4212 (0.014)	13451 (0.0432)	3237 (0.0927)	3820 (0.0828)
Max., min. transmission	0.659, 0.520		0.9966, 0.9703	9982, 0.9929	0.9928, 0.9404
Data/restraints/parameters	1785/0/168	3237/0/331	13451/0/947	3237/0/286	3820/0/947
Goodness-of-fit on $F^2$	1.048	1.081	1.058	1.073	1.049
Final R indices $[I > 2\sigma(I)] R_1$	0.0298	0.0711	0.785	0.053	0.0455
$wR_2(F^2)$	0.0773	0.1405	0.2099	0.1309	0.1220
Largest diff. peak, hole/e Å <sup>-3</sup> Absolute structure parameter	0.170, -0.175 0.00(2)	0.241, -0.281	0.995, -0.524	0.239, -0.178	0.427, -0.373

Table 3 Crystal data and structure refinement for [(SMe<sub>2</sub>)-nido-B<sub>10</sub>H<sub>12</sub>] 2, [(SMe<sub>2</sub>)<sub>2</sub>-arachno-B<sub>10</sub>H<sub>11</sub>-(nido-B<sub>10</sub>H<sub>13</sub>)] 3, [(SMe<sub>2</sub>)<sub>2</sub>-arachno-B<sub>10</sub>H<sub>10</sub> (nido-B<sub>10</sub>H<sub>13</sub>)<sub>2</sub>] 4, [(nido-B<sub>10</sub>H<sub>13</sub>)<sub>2</sub>] 6, and [(SMe<sub>2</sub>)-nido-

visible light, of which two yielded identifiable products. A very pale yellow band at  $R_{\rm F}$  ca. 0.5 was identified as [6,9-(SMe<sub>2</sub>)-arachno- $B_{10}H_{12}$ ] (compound 1; 19 mg, giving a total yield of 39%). A pale yellow band at  $R_{\rm F}$  ca. 0.55 was subject to further separation by preparative HPLC (43 : 57 CH<sub>2</sub>Cl<sub>2</sub>-hexane, 20 ml min<sup>-1</sup>), giving  $[1-(6'-nido-B_{10}H_{13})-6,9-(SMe_2)_2-arachno-B_{10}H_{11}]$  (compound 3;  $R_T$ 22.0 min; 16.0 mg, 10.5%) and [5-(SMe2)-4-(2'-nido-B10H13)-nido- $B_{10}H_{11}$  (compound 7;  $R_T$  28.6 min; 0.8 mg, 0.6%). NMR data for compound 7 (CDCl<sub>3</sub>, 294-297 K), ordered as measured value of  $\delta({}^{11}B)$  {calculated  $\delta({}^{11}B)$  value by DFT/GIAO} [ $\delta({}^{11}H)$  of directly bound H], are: B(4) -39.6 {-40.2} [conjuncto site, no H], B(4') -35.4 {-36.7} [+0.61], B(2') -30.5 {-31.4} [conjuncto site, no H], B(2)  $-27.2 \{-26.6\} [-0.61], B(10) -9.8 \{-12.2\}$ [+2.05], B(7 and 9) -4.2 {-2.4 and -6.0} [+2.96(2H)], B(3) -2.0  $\{-3.4\}$  [+2.56], B(5',7', 8',10') +1.4  $\{+0.71, +1.47, +1.81, +0.90\}$  $[+3.13(2H) \text{ and } +3.09(2H)], B(5) +1.4 \{+0.5\}$  [site of SMe<sub>2</sub> substituent, no H], B(8) +3.8 {+4.9} [+3.21], B(9') +7.1 {+6.7} [+2.98] and B(1)+8.5  $\{+7.3\}$  [+3.75], B(6')+10.9  $\{+8.6\}$  [+4.13], B(1', 3') +13.8 {+13.0 and +13.4} [+3.74 and 3.62], B(6) +20.2  $\{+19.1\}$  [+4.13]; additionally  $\delta({}^{1}\text{H})$  { $\mu$ -H(6,7)} -4.31,  $\delta({}^{1}\text{H})$  { $\mu$ -(5'6', 6'7') -1.85 (2H), { $\mu$ -H(8,9, 9'10')} -2.06 (2H), { $\mu$ -H(89, 910)  $\{-2.44 \ (2H) \text{ and } \delta(^{1}H) \ (SMe_{2}) + 2.66. \text{ Mass spectrometry} \}$ showed an isotopomer envelope centred at m/z 302 corresponding to that calculated for  $\{C_2H_{30}B_{20}S_1\}^+$ . <sup>11</sup>B NMR spectroscopy indicated that the remaining two bands also contained  $\sigma$ -linked arachno-nido cluster species but we have been unable to fully characterise them. Hexane diffusion into a CDCl<sub>3</sub> solution of 7 gave colourless needles suitable for the single-crystal X-ray diffraction analysis, from which selected geometrical data are listed in Table 1 above.

#### **Computational methods**

For the IGLO calculations, structures were initially optimised with the 3-21G basis set and the final optimization was performed using the 6-31G\* basis set and the Gaussian 92 package.<sup>61</sup> The resultant geometry was used to predict the NMR chemical shifts using the IGLO package<sup>62-66</sup> and the DZ basis set incorporated therein. For the DFT calculations, both structures were initially optimised with the STO-3G and 6-31G\* basis sets using standard methods. The final optimizations, frequency analyses (to confirm true minima) and GIAO NMR predictions were performed using the 6-31G\* basis set and B3LYP methodology as incorporated in the Gaussian 98 package.<sup>67</sup> Gas-phase NMR predictions were calibrated *via* a prediction at the same level of theory on diborane, which is taken to have an NMR shift  $\delta$ (<sup>11</sup>B) of -16.6 ppm with respect to BF<sub>3</sub>OEt<sub>2</sub>.

#### X-Ray crystallography

Table 3 gives information for the structures of compounds 2, 3, 4, 6 and 7. Data for compound 4 were reported elsewhere,<sup>25</sup> but are included here for convenience of reference. Data for compound 2 were collected on a Stoe STADI 4 diffractometer with a conventional sealed-tube X-ray source for Cu-Ka radiation (1.541 84 Å). Data for compounds 3, 6 and 7 were collected on a pre-Bruker Nonius KappaCCD diffractometer with a conventional sealed-tube X-ray source for Mo-Ka radiation  $(\lambda = 0.71073 \text{ Å})$ ; data for compound 4 were measured with synchrotron radiation ( $\lambda = 0.6874$  Å), using a Bruker AXS SMART CCD diffractometer.<sup>25,26,68-70</sup> In each case, the crystal was cooled with a nitrogen gas stream. Absorption corrections were made by semi-empirical methods. The structures were solved by automatic direct methods and refined by least squares methods on all measured  $F^2$  values, with a weighting scheme  $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + (bP)$ , where  $P = (F_o^2 + 2 F_c^2)/3$ . Residuals were defined by  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ,  $wR_2 = \left[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\right]^{1/2}$ . Programs consisted of standard control software for the diffractometers, members of the SHELX family,71 and local programs. There were two molecules in the asymmetric unit of compound 4 and of these, one of the decaboranyl subclusters contained disorder due to a pseudoplane of symmetry through B(1)B(4)B(6). This was resolved in terms of the partial occupancy of the B(7)/B(5) positions. The crystallographically determined structures of all the compounds were consistent with their assigned 11B and 1H NMR spectra, confirming that in each case the crystals were representative of the bulk samples. Drawings of molecular structures are by the ORTEP-3 program,<sup>72</sup> and atoms are represented by 50% probability ellipsoids.

CCDC reference numbers 280344 (2), 280345 (3), 162053 (4), 280346 (6) and 280347 (7).

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b604295c

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