

## Macropolyhedral Boron-containing Cluster Chemistry. The Eighteen-vertex Monocarbaborane [(Me<sub>3</sub>CNH<sub>2</sub>)CB<sub>17</sub>H<sub>18</sub>(CN)]<sup>†</sup>

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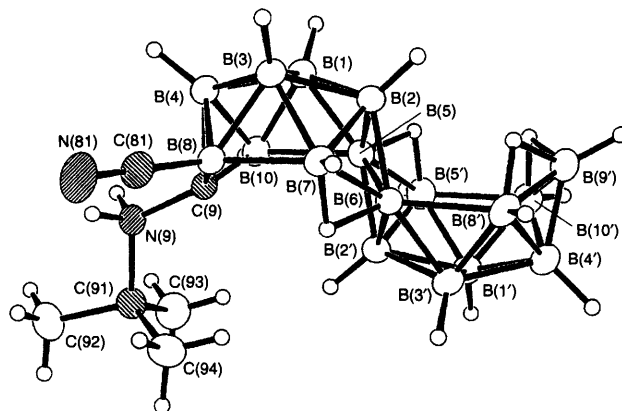
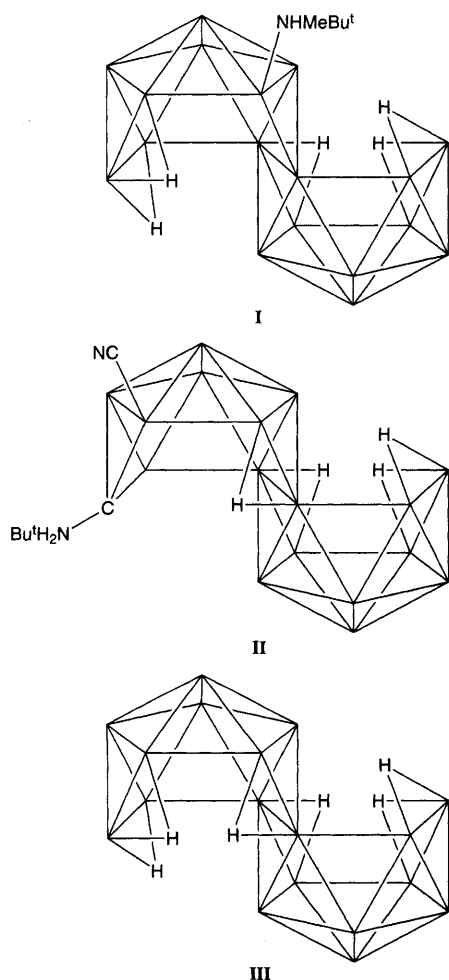
The first definitively characterised macropolyhedral carbaborane species, neutral [(Bu<sup>t</sup>NH<sub>2</sub>)CB<sub>17</sub>H<sub>18</sub>(CN)], is isolated from the products of the reaction between [*anti*-B<sub>18</sub>H<sub>22</sub>] and Bu<sup>t</sup>NC in CH<sub>2</sub>Cl<sub>2</sub>; the structure is based on the [*anti*-B<sub>18</sub>H<sub>22</sub>] type of macropolyhedral cluster, with an amine-substituted carbon atom occupying the 9-position in one subcluster.

The basic chemistry of the polyhedral boron-containing cluster compounds is extended considerably by the recognition that extended 'macropolyhedral' structures can be generated by the fusion, with common edges or faces, of the smaller cluster building blocks. Of the basic single-cluster building blocks, the carbaboranes, particularly dicarbaboranes, are very well examined,<sup>1</sup> and their known chemistry extensively exceeds that of the boranes themselves. Surprisingly, however, although macropolyhedral heteroboranes are known in which the heteroatom is sulfur,<sup>2</sup> nitrogen,<sup>3</sup> or even oxygen<sup>4</sup> or a transition element,<sup>5</sup> no unequivocally characterised macropolyhedral carbaboranes have yet been established. Some time ago<sup>6</sup> the pioneering macropolyhedral heteroborane work of Sneath and Todd tentatively identified a compound, from the reaction of [*syn*-B<sub>18</sub>H<sub>22</sub>] with *cyclo*-C<sub>6</sub>H<sub>12</sub>NC, as nineteen-vertex [(*cyclo*-C<sub>6</sub>H<sub>12</sub>NH<sub>2</sub>)CB<sub>18</sub>H<sub>20</sub>]. However, a comparison of the <sup>11</sup>B spectrum of this<sup>6</sup> with that<sup>7</sup> of the [*syn*-B<sub>18</sub>H<sub>21</sub>]<sup>-</sup> monoanion now suggests that the product actually observed was a salt of [*syn*-B<sub>18</sub>H<sub>21</sub>]<sup>-</sup>, or was a neutral species [*syn*-B<sub>18</sub>H<sub>20</sub>L] in which

the substituent chemical shift of the two-electron ligand L is essentially the same as that of the hydride ligand, H<sup>-</sup>. Furthermore, it is now known that the reaction of MeNC with [*anti*-B<sub>18</sub>H<sub>22</sub>] preferentially gives [*anti*-B<sub>18</sub>H<sub>20</sub>L], where L is {Me<sub>2</sub>(MeNH)HC<sub>3</sub>N<sub>2</sub>} resulting from reductive trimerisation of MeNC,<sup>8</sup> rather than undergoing cluster incorporation of the isocyanide carbon atom to generate a contiguous carbaborane.

We now report that, by use of the more sterically hindered isocyanide Bu<sup>t</sup>NC with [*anti*-B<sub>18</sub>H<sub>22</sub>], the reductive oligomerisation is suppressed, and that cluster carbon-atom insertion can now occur to give an entry into macropolyhedral carbaborane chemistry.

A solution of [*anti*-B<sub>18</sub>H<sub>22</sub>] (740 mg; 3.37 mmol) and Bu<sup>t</sup>NC (475 mg, 5.72 mmol) in benzene (50 cm<sup>3</sup>) was stirred at ambient temperature for 12 h, and then heated under reflux for 24 h. The benzene was evaporated and the viscous residue extracted with boiling hexane to remove unreacted [*anti*-B<sub>18</sub>H<sub>22</sub>] and Bu<sup>t</sup>NC. Two main fractions were isolated from column chromatography of the residue (silica gel, CH<sub>2</sub>Cl<sub>2</sub>-MeCN, 6 : 1, v/v) with *R<sub>F</sub>* 0.65 and 0.25 (analytical TLC on foil-backed silica gel). These were further purified by preparative TLC on silica, using CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>2</sub>Cl<sub>2</sub>-MeCN (10 : 1 v/v) respectively as liquid phases, respectively yielding [7-(Bu<sup>t</sup>MeHN)-(*anti*)-B<sub>18</sub>H<sub>20</sub>] (compound **1**; schematic structure **I**) (60 mg, 0.20 mmol, 6%) and [9-(Bu<sup>t</sup>NH<sub>2</sub>)-(*anti*)-9-CB<sub>17</sub>H<sub>19</sub>-8-(CN)] **2** (130 mg, 0.42 mmol, 12%). Compound **1** was reasonably characterised as such by mass spectrometry and NMR spectroscopy,<sup>‡</sup> and the more



**Fig. 1** ORTEP<sup>17</sup> drawing of the crystallographically determined molecular structure of [9-(Bu<sup>t</sup>NH<sub>2</sub>)-(*anti*)-9-CB<sub>17</sub>H<sub>18</sub>-8-(CN)] **2**. Ellipses are drawn at the 50% probability level. Selected interatomic dimensions are as follows: distances (in pm): B(7)-B(8) 188.9(2), B(5)-B(10) 193.7(2), B(6)-B(7) 179.5(2), B(6)-B(8') 196.1(2), B(5')-B(10') 197.5(3), B(4)-C(9) 168.3(2), B(8)-C(9) 154.2(2), B(8)-C(81) 155.7(2), B(10)-C(9) 152.0(2), C(9)-N(9) 149.3(2), and N(9)-C(91) 153.7(2); angles (in °): B(8)-C(9)-B(10) 118.10(12), B(4)-C(9)-N(9) 117.43(11), B(8)-C(9)-N(9) 118.68(12), B(10)-C(9)-N(9) 119.74(12), B(8)-C(81)-N(81) 179.6(2), and C(9)-N(9)-C(91) 119.38(11). The numbering scheme of the eighteen-atom {CB<sub>17</sub>} cluster of compound **2** is as also used for B<sub>18</sub>H<sub>22</sub> (schematic **III**) and compound **1** (schematic **I**). Schematic structures **I**, **II** and **III** are all drawn from the same perspective, which can be related to that in Fig. 1 in order to facilitate comparison. In particular, the Bu<sup>t</sup>MeHN substituent in compound **1** (schematic **I**) is seen to be in the 7-position.

novel compound **2** by NMR spectroscopy $\S$  and by single-crystal X-ray diffraction analysis. $\P$  Other fractions contained the anion [*anti*-B<sub>18</sub>H<sub>20</sub>]<sup>2-</sup> (identified by NMR spectroscopy),<sup>7</sup> together with additional macropolyhedral boron-containing cluster compounds that we are currently attempting to purify and identify; one has been tentatively identified as the diastereoisomer of compound **1**; another is probably the diastereoisomer of compound **2**.

The structure of [9-(Bu<sup>t</sup>NH<sub>2</sub>)-(anti)-9-CB<sub>17</sub>H<sub>18</sub>-8-(CN)] **2** (Fig. 1, schematic cluster structure **II**) is seen to be based on that of neutral [*anti*-B<sub>18</sub>H<sub>22</sub>] (schematic cluster structure **III**),<sup>9,10</sup> with, in one of the two ten-vertex subclusters, a carbon atom in the 9-position instead of a boron vertex. There is only one bridging hydrogen atom in this subcluster, rather than the three in the basic [*anti*-B<sub>18</sub>H<sub>22</sub>] structural model (see schematic cluster structure **III**), but the carbon vertex contributes one more electron than boron to the cluster bonding scheme, and the two-electron ligand Bu<sup>t</sup>NH<sub>2</sub> contributes one electron more than a terminal hydrogen, and so the two subclusters are isoelectronic and both have *nido* ten-vertex character. The non-carbon-containing subcluster is closely related to the *nido*-decaborane-like subcluster<sup>9,10</sup> of [*anti*-B<sub>18</sub>H<sub>22</sub>] itself, as judged by geometry, and by NMR properties. $\S$  The carbaborane subcluster is closely related to that of [6-(NMe<sub>3</sub>)-*nido*-6-CB<sub>9</sub>H<sub>11</sub>] **3**,<sup>11</sup> as judged by NMR similarities. $\S$  As such it has an interesting zwitterionic ligand structure on C(9), exhibiting a negative-charge stabilisation by the *nido* ten-vertex 'prow' position, as also occurs in the [*nido*-6,9-C<sub>2</sub>B<sub>8</sub>H<sub>10</sub>]<sup>2-</sup> anion.<sup>10</sup>

The effective boron displacement by carbon to transform the ten-vertex {B<sub>10</sub>} subcluster into a ten-vertex {CB<sub>9</sub>} subcluster merits comment: this contrasts with single-cluster chemistry, in which, for example, *nido*-decaboranes incorporate isocyanide<sup>13</sup> carbon atoms to generate eleven-vertex {CB<sub>10</sub>} clusters in Aufbau processes without B-vertex loss. The {CB<sub>17</sub>} cluster generation observed here parallels the formation of eighteen-vertex seventeen-boron {NB<sub>17</sub>}<sup>3</sup> and {RhB<sub>17</sub>}<sup>14</sup> species when attempts are made to incorporate {NH} and {(C<sub>5</sub>Me<sub>5</sub>)Rh} centres into [*anti*-B<sub>18</sub>H<sub>22</sub>]. These together suggest a driving force to retain this particular eighteen-vertex structure that is based on the (6,7:5,6) fusion of two *nido* ten-vertex units. This eighteen-vertex stability thereby dictates an effective vertex substitution rather than cluster Aufbau to generate a nineteen-vertex macropolyhedral cluster. In the reaction with the less sterically hindered MeNC the eighteen-vertex stability manifests itself instead in the retention of the eighteen-boron unit and reductive trimerization of the isocyanide entity.<sup>8</sup> The cleavage of the Bu<sup>t</sup> group from a Bu<sup>t</sup>NC moiety to generate a cyanide ligand bound to boron in compound **2** is also noteworthy, the observed reduction to Bu<sup>t</sup>NHMe in compound **1** perhaps being illustrative of a step along this path.

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## Footnotes

† A full IUPAC nomenclature would be *nido*-decaborano-[6',7':5,6]-9-*tert*-butyl-8-cyano-*nido*-9-carbadecaborane. The anion is enantiomeric, the other enantiomer being *nido*-decaborano-[5',6':6,7]-9-*tert*-butyl-10-cyano-*nido*-9-carbadecaborane. Note both enantiomers are contained in the unit cell of the crystals examined (space-group *I*<sub>4</sub>*1*/*a*). Note also that the compound has two chiral centres; the other diastereoisomer is believed to be one of the other reaction products.

‡ The cluster <sup>11</sup>B and <sup>1</sup>H NMR data for [7-(Bu<sup>t</sup>MeHN)-(anti)-B<sub>18</sub>H<sub>20</sub>] **1** are very similar to those for [7-{Me<sub>2</sub>(MeNH)HC<sub>3</sub>N<sub>2</sub>}-(*anti*)-B<sub>18</sub>H<sub>20</sub>],<sup>8</sup> except that δ (<sup>11</sup>B) BH(7) is +4.2 for **1**. Note that **1** has two chiral centres; the other diastereoisomer is believed to be one of the other reaction products.

$\S$  NMR data for [9-(Bu<sup>t</sup>NH<sub>2</sub>)-(anti)-9-CB<sub>17</sub>H<sub>18</sub>-8-(CN)] **2**: {ordered as assignment δ (<sup>11</sup>B) [δ (<sup>1</sup>H) in square brackets]} for CDCl<sub>3</sub> solution at 294–303 K: carbaborane subcluster (compare data for compound **3**,<sup>11</sup>): BH(1) –11.7 [+2.19], BH(2) –32.4 [+0.10], BH(3) +1.2 [+3.04], BH(4) –31.7 [+0.63], BH(7) –24.9 [+1.71], BH(8) –8.0 [CN ligand site], BH(10) +8.5 [+3.79]; borane subcluster: BH(1') +13.0 [+1.61], BH(2') –33.1 [+0.08], BH(3') –1.4 [+2.80], BH(4') –41.8 [+0.16], BH(5') –13.9 [+2.53], BH(8') +6.9 [+3.84], BH(9') +2.3 [+3.24], BH(10') –5.8 [+2.70]; common atoms: B(5/6') +2.3 [–], B(6/7') –0.4 [–]; bridging H atoms: μ-H(5',5/6') –1.64, μ-H(8',9') –0.27, μ-H(9',10') –2.54, μ-H(6/7',7) –1.85; δ (<sup>1</sup>H) (Bu<sup>t</sup>NH<sub>2</sub>) at +2.22 (9 H), +7.89 (1 H, br) and +6.91 (1 H, br). NMR assignments by [<sup>11</sup>B–<sup>1</sup>H]-COSY experiments and <sup>1</sup>H-<sup>11</sup>B (selective) spectroscopy. Note that, in the comparison between compounds **1** and **3**, the formal numbering of equivalent atom sites differs because of numbering conventions. In particular, the 6-position in compound **3** is equivalent to the 9-position in compound **1**.

$\P$  Crystallography: All measurements were made at 220 K on a Stoe STADI4 diffractometer operating in the ω–θ scan mode using graphite-monochromated Cu-Kα radiation (λ = 1.54184 Å). The structure was determined by direct methods using SHELXS-86<sup>15</sup> and was refined by full-matrix least squares (based on *F*<sup>2</sup>) using SHELXL-93.<sup>16</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters. The methyl hydrogen atoms were constrained to calculated positions (C–H = 0.98 Å) and refined with a fixed isotropic displacement parameter of 1.5U<sub>eq</sub> of the parent carbon atom; all other hydrogen atoms were located on a Fourier difference map and were freely refined. The weighting scheme *w* = [σ<sup>2</sup>(*F*<sub>o</sub><sup>2</sup>) + 0.0713(*P*)<sup>2</sup> + 2.682*P*]<sup>–1</sup> was used, where *P* = (*F*<sub>o</sub><sup>2</sup> + 2*F*<sub>c</sub><sup>2</sup>)/3.

Crystal data: C<sub>6</sub>H<sub>29</sub>B<sub>17</sub>N<sub>2</sub>, *M*<sub>r</sub> = 313.08, tetragonal, space group *I*<sub>4</sub>*1*/*a*, *a* = 25.274(5), *c* = 12.778(4) Å, *U* = 8.162(3) Å<sup>3</sup>, *Z* = 2, *D*<sub>c</sub> = 1.019 g cm<sup>–3</sup>, μ = 0.32 mm<sup>–1</sup>, *F*(000) = 2624. All 3346 unique data collected in the range 4.0 < 2θ < 130° were used in the refinement, which converged with *R*<sub>1</sub> {= Σ|*F*<sub>o</sub> – *F*<sub>c</sub>|/Σ|*F*<sub>o</sub>|} = 0.0423 and *wR*<sub>2</sub> {= (Σ[*w*(*F*<sub>o</sub><sup>2</sup> – *F*<sub>c</sub><sup>2</sup>)<sup>2</sup>]/Σ[*w*(*F*<sub>o</sub><sup>2</sup>)<sup>2</sup>])<sup>1/2</sup>} = 0.1206. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors Issue No. 1.

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