# Two New Ten-vertex *arachno* Mixed-atom Diheteroboranes, 6,9-$CNB_8H_{13}$ and 6,9-$CSB_8H_{12}$

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Treatment of the monocarbaborane *arachno*-4-$CB_8H_{14}$ with either sodium nitrite or elemental sulphur in the presence of triethylamine results in the isolation of two representatives of the ten-vertex *arachno* family of cluster carbaheteroboranes, 6,9-$CNB_8H_{13}$ and 6,9-$CSB_8H_{12}$, the constitution of which has been established on the basis of $^1H$, $^{11}B$, [$^{11}B$–$^{11}B$]-COSY, and [$^1H$–$^1H$]-COSY NMR data and mass spectroscopic measurements.

The *arachno*-ten-vertex family of boranes, carbaboranes and heteroboranes form an important class of polyhedral boron compounds because of their key roles as substrates in systematic cluster *aufbau* and degradation sequences[1,2] and as substrates in metallaheteroborane syntheses. The family is based on the [*arachno*-$B_{10}H_{14}$]$^{2-}$ parent motif,[3] from which the structures of the family members can notionally be derived by replacement of one or two of the formal $\{BH_2\}^-$ cluster vertices of low cluster connectivity by isoelectrolobal[4] units such as $\{CH_2\}$, $\{NH\}$, or $\{S\}$. Although the anionic monoheteroatom species [6-$CB_9H_{14}$]$^-$,[5,6] [6-$NB_9H_{13}$]$^-$,[7–9] and [6-$SB_9H_{12}$]$^-$,[7,10–12] along with two netural diheteroatom compounds 6,9-$C_2B_8H_{14}$[13] and 6,9-$N_2B_8H_{12}$,[14] have been reported, routes to the potentially very interesting subcategory of mixed diheteroboranes have not been available. As part of our longer-term interest in the general development of this area,[5,12–15] we now report our preliminary findings on systematic synthetic approaches leading to the direct assimilation of an additional electron-rich ($\{NH\}$ or $\{S\}$) centre by the nine-vertex *arachno*-4-$CB_8H_{14}$ structure to generate the first monocarbaazaborane, *arachno*-6,9-$CNB_8H_{13}$, and the first representative of the ten-vertex family of carbathiaboranes, *arachno*-6,9-$CSB_8H_{12}$.

Treatment of the monocarbaborane *arachno*-4-$CB_8H_{14}$[15] **1** with a threefold excess of aqueous sodium nitrite in benzene (1.75 mmol scale, room temp., 7 days), followed by acidification of the reaction mixture [$H_2O$–conc. HCl (3 : 1, v/v)] and then column chromatography on silica gel in benzene, gave a colourless main fraction with $R_F$(anal.) 0.15. Vacuum sublimation of the solid residue from this fraction yielded a white species **2** [m.p. 193 °C (decomp.); yield 15% (unoptimised)]. This was identified by NMR† and mass spectroscopy‡ as *arachno*-6,9-$CNB_8H_{13}$ **2**.

Reaction between the carbaborane **1** and an excess of sulphur (1.75 mmol scale, room temp., 12 h) in the presence of triethylamine in chloroform (violent reaction, cooling to room temp.), followed by column chromatography (silica gel, hexane) gave a colourless main fraction with $R_F$(anal.) 0.45 from which a white compound **3** [m.p. 179–181 °C; yield 48% (unoptimised)] was isolated by sublimation at *ca.* 50 °C. This was identified as *arachno*-6,9-$CSB_8H_{12}$ **3** *via* NMR† and mass‡ spectroscopy.

The assigned $^{11}B$ and $^1H$ NMR spectra† of compounds **2** and **3** were entirely consistent with the proposed structures (see Fig. 1), noteworthy points being the resonances assigned to the $CH_2$ *exo* and *endo* protons for both **2** and **3**, and to the NH proton for **3**, and the overall shielding similarities with the structurally related *arachno*-compounds 6,9-$C_2B_8H_{14}$[13] and 6,9-$N_2B_8H_{12}$.[14] The structures have mirror-plane symmetry with the two heteroatomic $\{CH_2\}$ and $\{NH\}$/$\{S\}$ cage vertices

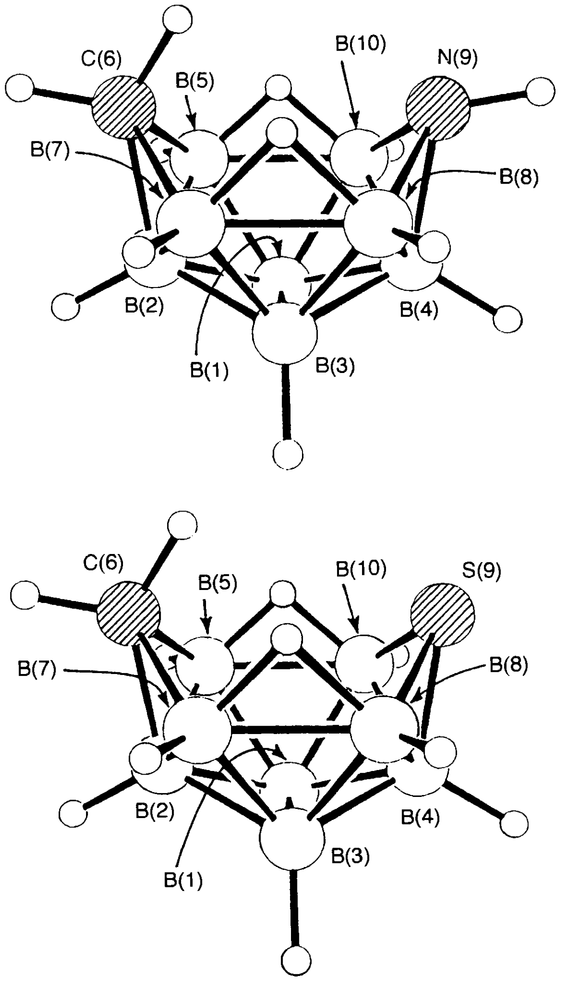

**Fig. 1** Proposed molecular structures for the [*arachno*-6,9-$CEB_8H_{12}$] compounds (**2**, E = NH and **3**, E = S). The position of the *exo*-type nitrogen-bound hydrogen atom on N(9) for compound **2** (compare ref. 14, for example) implies stereochemically active lone pairs in the *endo* positions on N(9) and S(9), which in turn has implications for further chemistry.

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† *NMR spectra*: parameters for compounds **2** and **3**, ordered as assignment, $\delta(^{11}B)$ ±0.5 (in ppm w.r.t. $F_3B\cdot OEt_2$, $\Xi$ 32.083971 MHz) $\{^1J(^{11}B–^1H)$ ±8 (in Hz)$\}$ [$\delta(^1H)$ ±0.05 (in ppm w.r.t. $SiMe_4$)]; compound **2**: BH(2) +5.4 {166} [+3.31], BH(4) +1.5 {177} [+3.13], BH(8,10) −15.7 {150/29} [+2.68], BH(5,7) −28.3 {154/61} [+1.72], BH(1,3) −41.6 {150} [+0.60], CH(6)-*exo* [+0.88], CH(6)-*endo* [+0.67], NH(9) [+2.86], μH(5,10/7,8) [−0.75]; compound **3**: BH(2) +10.7 {162} [+3.30], BH(4) +6.1 {177} [+3.37], BH(8,10) −12.6 {156/47} [+2.56], BH(5,7) −21.6 {155/56} [+1.99], BH(1,3) −34.1 {151} [+1.29], CH(6)-*exo* [+1.11], CH(6)-*endo* [+0.26], μH(5,10/7,8) −1.14; $CDCl_3$ solutions at 294–297 K; assignments based on [$^{11}B$–$^{11}B$]-COSY, [$^1H$–$^1H$]-COSY and $^1H\{^{11}B$(selective)$\}$ experiments.

‡ *Mass spectra* of compounds **2** and **3** (70 eV, electron impact ionisation); compound **2**: high-mass cut-off at *m/z* 127 ($M^+$ peak), corresponding to [$^{12}C^{14}N^{11}B_8{}^1H_{13}$]$^+$, most intense peaks at *m/z* 123; compound **3**: cut-off at *m/z* 144 ($M^+$ peak), most intense peak at *m/z* 140.

in the plane defined by the B(2), B(4), C(6) and N(9)/S(9) atoms, the last positions being of lowest connectivity.[16]

The formation of the two new heteroboranes **2** and **3** in synthetic terms constitutes a straightforward insertion of nitrogen or sulphur into the area capping the open B(9)–B(7)–B(8) triangle in the *arachno*-nine-vertex $\{4\text{-CB}_8\}$ basic structural skeleton. B(9), B(7) and B(8) become B(8), B(4) and B(10), respectively in compounds **2** and **3** (see Fig. 1).

As such this application of the two synthetic methods to produce mixed polyheteroboranes now establishes a useful principle of designed synthesis for multiheteroatom incorporation for the development of general cluster heteroborane and polyheteroborane chemistry, an area that is largely undeveloped. Further research aimed at the preparation of further heteroboranes with diverse combinations of electron-rich main group elements, at the development of synthetic routes to incorporate other main-group centres, and at developing the metallaheteroborane chemistry of this class of compounds, is in progress.

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