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Triple linking of the decaboranyl cluster. Structure of $[(SMe_2)_2B_{10}H_{10}(B_{10}H_{13})_2]$ as determined by synchrotron X-ray diffraction analysis†

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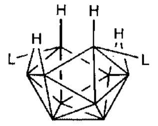
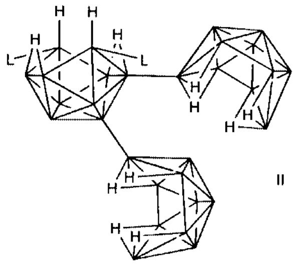
In an attempt to find generic routes to multiple inter-cluster σ-linking, mild thermolysis of [6,9-$(SMe_2)_2$-*arachno*-$B_{10}H_{12}$] 1 in inert hydrocarbon solution gives the tridecaboranyl species [6,9-$(SMe_2)_2$-*arachno*-$B_{10}H_{10}$-1,5-(6′-*nido*-$B_{10}H_{13})_2$] 3 (23%).

There is current activity in the linking together of boron-containing clusters to generate (a) chains, rods and rings of σ-linked clusters,[1] (b) strings and other assemblies in which clusters join with a common metal atom,[2] and (c) macropolyhedral assemblies of clusters fused with two or more atoms in common.[3] In this context, we have interest in the possibility of multiple σ-linking of several boron clusters to a central boron core for possible precursors to globular 'megaloboranes', of which structures would be based on central boron cluster cores of which, in turn, the peripheral valencies are σ-linked to outer boron–hydride cluster units which are themselves mutually σ-linked to form a boron–hydride skin around the central borons-only nucleus.[4] Here, we thought it useful to examine for activity of the $\{B_{10}H_{12}(SMe_2)\}$ fragment, as it has both 'reactive' and 'unreactive' forms: both forms will electrophilically add to olefins and acetylenes,[5] and thence might add to electrophilically susceptible sites of boron clusters in first steps of a possible synthetic approach involving initial assembly of boron hydride units around a central core. A 'reactive' form of $\{B_{10}H_{12}(SMe_2)\}$, of unestablished constitution, is proposed as a key intermediate in the formation of $\{C_2B_{10}\}$ dicarbaboranes from $[B_{10}H_{12}(SMe_2)_2]$ **1**.[5] A 'stable' form, [5-(SMe_2)-*nido*-$B_{10}H_{12}$] **2** is well established and is generated in yields of 40–60% by heating $[B_{10}H_{12}(SMe_2)_2]$ in the absence of other reagents, other products being unidentified.[6,7] We surmised that these other products might arise from electrophilic attack by the $\{B_{10}H_{12}(SMe_2)\}$ fragments, either 'stable' or 'unstable', on other decaboranyl residues in quasi-auto-fusion processes to generate multidecaboranyl assemblies. We here report preliminary results that are consistent with this idea.

Specifically, a solution of $[(SMe_2)_2B_{10}H_{12}]$ **1** (schematic structure **I**; 107 mg; 440 μmol) in benzene (10 mL) was heated at reflux for 6 h. TLC separation (silica G, hexane–CH_2Cl_2, 3:7) gave known [5-(SMe_2)-*nido*-$B_{10}H_{12}$] **2**[6] (R_F 0.8, 8 mg; 43 μmol, 9%). Closely following **2** on the TLC plate was a faint yellow band (R_F *ca.* 0.7) which was purified by HPLC (Lichrosorb SI 60, 25 cm × 2 cm, hexane–CH_2Cl_2 57:43, 20 mL min^{-1}). The fraction with R_T 1.3 min was the tridecaboranyl species [6,9-$(SMe_2)_2$-*arachno*-$B_{10}H_{10}$-1,5-(6′-*nido*-$B_{10}H_{13})_2$] **3**, (schematic structure **II**; 16 mg, 33 μmol, 23%), characterized by single-crystal X-ray diffraction analysis (Fig. 1)‡ and NMR spectroscopy.‡§ We hope to be able to describe other, lower-yield, by-products in due course.



I



II

Obtainable crystals under our conditions were of *ca.* 0.02 × 0.08 mm cross section, and needed synchrotron-generated X-ray radiation for sufficient diffraction intensity for structural analysis.[8] This revealed the *arachno* $\{(SMe_2)_2B_{10}\}$ configura-

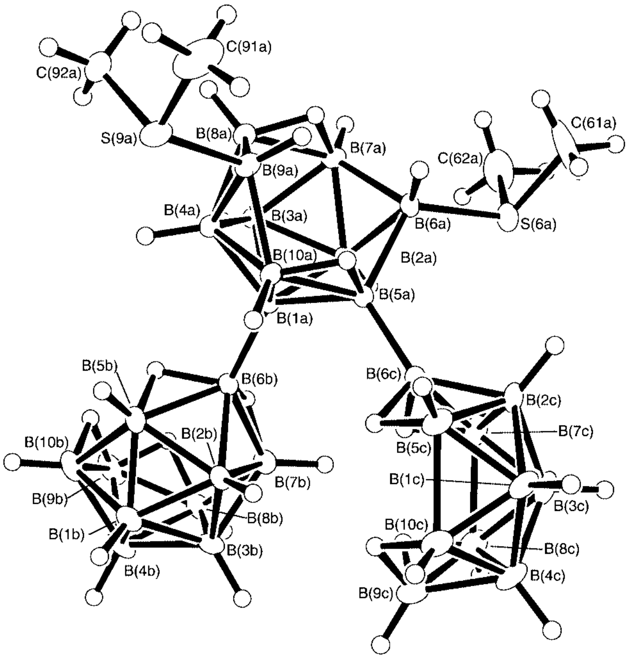


Fig. 1 Crystallographically determined molecular structure of [6,9-$(SMe_2)_2$-*arachno*-$B_{10}H_{10}$-1,5-(6′-*nido*-$B_{10}H_{13})_2$] **3**, drawn with 40% probability ellipsoids for non-hydrogen atoms, and with a small arbitrary radius for hydrogen atoms. The crystal structure had two molecules per unit cell, of which one was disordered over two positions. The undisordered molecule is drawn here. Selected interatomic distances (Å) for the undisordered molecule are as follows: B(6)–S(6) 1.924(3), B(9)–S(9) 1.927(3), B(1)–B(6′) 1.688(5), B(5)–B(6″) 1.676(5), B(5)–B(10) 1.874(5), B(7)–B(8) 1.861(5), B(5′)–B(10′) 1.969(5), B(7′)–B(8′) 1.993(5), B(5″)–B(10″) 1.980(6) and B(7″)–B(8″) 1.979(6).

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† Specifically 6,9-bis(dimethylsulfide)-1,5-bis(6′-*nido*-decaboranyl)-*arachno*-decaborane (IUPAC nomenclature).

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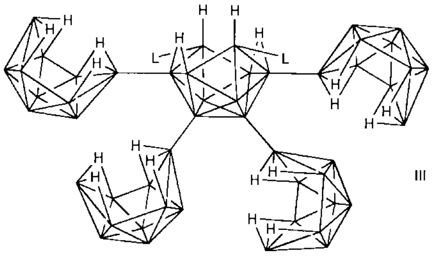
tion as in compound **1**, but now with two pendant open decaboranyl groups, on the B(1) and B(5) positions. These are established as $\{$*nido*-$B_{10}H_{13}\}$ moieties by their bridging hydrogen-atom positions, general *nido*-decaboranyl molecular dimensions, and NMR characteristics.‡ Compound **3** is the first tridecaboranyl specifically identified. Although bidecaboranyls are well recognized,[9] as far as we are aware this tridecaboranyl $\{B_{30}\}$ framework constitutes the biggest molecular all-boron skeletal assembly yet unequivocally characterized. Although $B_{30}H_{38}$, bis(*nido*-decaboranyl)-*nido*-decaborane, $[B_{10}H_{12}(B_{10}H_{13})_2]$, is formed in the thermolysis of *nido*-$B_{10}H_{14}$ in refluxing toluene with 0.03 mol% $[6,9\text{-}(SC_4H_8)_2$-*arachno*-$B_{10}H_{12}]$ (a close relative of compound **1**) as catalyst, this product is in low yield (0.2%), and is an unspecifiable mixture of isomers, of which 546 are possible.[10]

The reaction stoicheiometry and product constitution of compound **3** suggest initial dissociation of compound **1** to give $\{B_{10}H_{12}(SMe_2)\}$, followed by addition into B–H sites by $\{B_{10}H_{12}(SMe_2)\}$ to give B–$B_{10}H_{13}$ units with the elimination of SMe_2 [eqn. (1)].

$$[(SMe_2)_2B_{10}H_{12}]\ \mathbf{1} + 2\ \{B_{10}H_{12}(SMe_2)\} \rightarrow [(SMe_2)_2B_{10}H_{10}(B_{10}H_{13})_2]\ \mathbf{3} + 2\ SMe_2 \qquad (1)$$

The result of one predominant isomer, from three clusters conjoined σ, in good yield for a thermolytic three-molecule conjoining reaction, has interesting auguries. Firstly, the ready attack of a $\{(SMe_2)B_{10}H_{12}\}$ moiety at nucleophilic sites on $[(SMe_2)_2B_{10}H_{12}]$ **1** suggests a more general use for compounds **1** and **2** in co-thermolysis reactions with other boranes 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 novel fused-cluster $[B_{22}H_{22}]^{2-}$ anion,[11] would be an attractive target here. Second, the high yield and site specificity for this predominant product suggest preferential activation by the first boron substituent to the addition of the second boron substituent at an adjacent site, which would augur well for the observation of further addition in this and related systems. Third, the observed multiple addition of borane residues to adjacent sites is of potential use in the synthesis of higher more condensed boranes, as mentioned above. Here, the nearness of the *nido*-decaboranyl residues on the central borane unit of compound **3** might imply that coupling reactions among them, with dihydrogen loss, may be readily effected. Thus, for example, establishment of conditions for multiple addition in this type of reaction system to generate species such as in **III**, followed by cross-linking among the pendant $B_{10}H_{13}$ moieties, could engender the type of 'megaloborane' globular species presaged by the structures of very condensed metallaboranes such as $[(PPh_3)_2(PPh_2)Pd_2B_{20}H_{16}Pd(PPh_3)]$.[4] Such big 'filled-ball' globular species with borons-only cores surrounded by boron hydride sheaths may well be those that ultimately typify much big borane chemistry.[3,4] Their 'filled-ball' constitution contrasts to the hollow-ball structures of the fullerenes.



III

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Notes and references

‡ *Crystal data*: $[6,9\text{-}(SMe_2)_2$-*arachno*-$B_{10}H_{10}$-1,5-(6′-*nido*-$B_{10}H_{13})_2]$ **3** (colourless, from C_6H_{14}–CH_2Cl_2 at 245 K, 0.18 × 0.08 × 0.02 mm), $C_4H_{48}B_{30}S_2$, $M = 484.84$, triclinic, space group $P\bar{1}$, $a = 13.693(2)$, $b = 13.823(2)$, $c = 17.961(3)$ Å, $\alpha = 90.469(3)$, $\beta = 105.008(3)$, $\gamma = 104.249(3)°$, $U = 3173.2(8)$ Å^3, $Z = 4$, synchrotron wiggler-generated radiation,[8] $\lambda = 0.6895$ Å, $\mu = 0.169$ mm^{-1}, $T = 150$ K, $R1 = 0.0785$ for 10613 reflections with $I > 2\sigma(I)$, $wR2 = 0.2099$ for all 13451 independent data. Methods and programs were standard and from the SHELX suite.[12]

CCDC reference number 162053.

See http://www.rsc.org/suppdata/cc/b1/b105551h/ for crystallographic data in CIF or other electronic format.

§ *NMR data* for compound **3** ($CDCl_3$, 294–297 K): $\delta(^{11}B)$ [$\delta(^1H)$ of directly bound H atom] as follows: B(1) −40.5 [*conjuncto* position, no terminal H], BH(3) and BH(4′) both at *ca.* −37.5 [+0.44 and +0.31], BH(4″) −36.2 [+0.51], BH(2″) −32.8 [−0.27], BH(2′) −31.7 [+0.68], BH(9) −22.9 [+0.14], BH(6) and BH(7) both at *ca* −19.6 [+1.72 and +1.58], BH(7) and BH(8) both at *ca.* −17.5 [both at *ca.* +1.79], B(5) −14.1 [*conjuncto* position, no terminal H], BH(2) −3.2 [+2.30], BH(1″) −2.1 [+2.22], BH(5′), BH(5″) and BH(10′) all three at *ca.* −1.1 [two at *ca.* +3.00 and one at +2.87], BH(8′), BH(8″) and BH(10′) all three at *ca.* +0.5 [all three at *ca.* +3.04], BH(9′) and BH(9″) both at *ca.* +8.4 [both at *ca.* +3.77], BH(1′), BH(3′), BH(1″) and BH(3″) all four at *ca.* +11.6 [two at *ca.* +3.61{2H} and two at *ca.* +3.52{2H}], B(6′) and *B*(6″) +26.8 and +32.2 [*conjuncto* positions, no terminal H atoms]; additionally $\delta(^1H)$ {μ-H(5,10)} −4.17, {μ-H(7,8)} −4.26, {μ-H(5′,6′},{μ-H(6′,7′), {μ-H(5″,6″) and {μ-H(6″,7″)} −1.29, two at *ca.* −1.52, and −1.62, {μ-H(8′,9′), {μ-H 9′,10′); {μ-H 8″,9″} and {μ-H 9″,10″)} −2.15, −2.24, and two at *ca.* −2.31(2H), and $\delta(^1H)(SMe_2)$ +2.46. Mass spectrometry showed an isotopomer envelope centred at *m*/*z* 484 corresponding to that calculated for $C_4H_{48}B_{30}S_2$.

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