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The First Example of a Direct *closo* to *arachno* Cluster-expansion Reaction in Boron Cluster Chemistry

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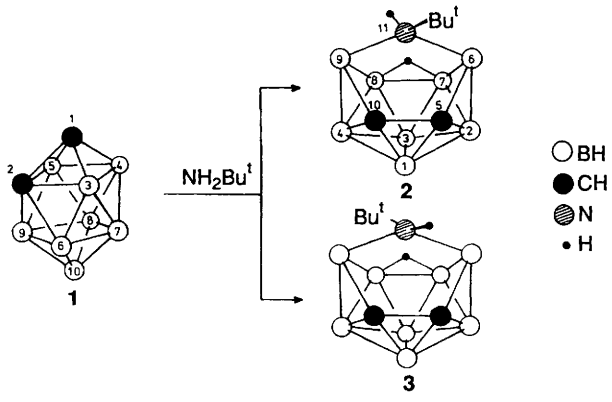
The reaction between *closo*-1,2-$C_2B_8H_{10}$ and NH_2Bu^t resulted in a straightforward cluster expansion to give the 11-vertex azadicarbaborane *anti*-11-Bu^t-*arachno*-5,10,11-$C_2NB_8H_{12}$, characterized by NMR and mass spectroscopy, together with the accompanying *syn* isomer.

We have for a long time been interested in the chemistry of cluster azaboranes,[1-3] diazaboranes,[4] azacarbaboranes[5] and azadicarbaboranes[6,7] and have contributed to this type of chemistry by isolating for the first time a series of essential representatives of these classes of compounds, such as *arachno*-4-NB_8H_{13},[1] *nido*-NB_9H_{12},[2,3] *arachno*-6,9-$N_2B_8H_{12}$,[4] *arachno*-6,9-CNB_8H_{13}[5] and *arachno*-$C_2NB_8H_{13}$.[6] All these compounds are available from simple boron degradation/nitrogen insertion reactions of various boron-cluster substrates with $NaNO_2$. This reagent has proved to be so far the most effective agent for the incorporation of a nitrogen centre into a boron cluster. Now we report an unprecedented reaction between NH_2Bu^t and *closo*-1,2-$C_2B_8H_{10}$ in which the amine acts as an excellent reagent for direct insertion of a nitrogen centre into the cluster without substantial degradation of the carbaborane substrate.

Treatment of *closo*-1,2-$C_2B_8H_{10}$ (**1** in Scheme 1)[3,4] with NH_2Bu^t in tetrahydrofuran (thf) for 8 h at ambient temperature* resulted in the isolation of a white sublimable compound which was identified as *anti*-11-Bu^t-*arachno*-5,10,11-$C_2NB_8H_{12}$ (**2** in Scheme 1). The mother-liquors from the crystallization of **2** from hexane were enriched in the structurally similar species, *syn*-11-Bu^t-*arachno*-5,10,11-$C_2NB_8H_{12}$ (**3** in Scheme 1). The reaction is accompanied by partial cage degradation, as documented by the isolation of 4,6-$C_2B_7H_{13}$ and $NH_2Bu^t{\cdot}BH_3$ in low yields (8 and 7%, respectively).

Compounds **2** and **3** were identified and structurally characterized by NMR, IR and mass spectroscopy,† the data for **3** being obtained by subtracting those for **2** from those of a *ca.* 2:1 mixture of **3** and **2**. Application of two-dimensional [^{11}B–^{11}B][9] and [^{1}H–^{1}H][10] NMR correlation spectroscopy, combined with ^{1}H-{^{11}B(selective)} NMR measurements,[11] led to complete assignments of all ^{1}H and ^{11}B resonances to individual {BH} cluster units. The data are clearly compatible with the C_2 symmetry and the *arachno* eleven-vertex cluster configuration. An interesting feature is the presence of one bridging hydrogen atom between the BH(7) and BH(8) sites along with one {Bu^tNH} unit interconnecting the B(6) and B(9) cluster positions and two identical {CH(5,10)} cluster vertices, the



Scheme 1 Formation and proposed cluster constitution of two isomeric *anti*-(**2**) and *syn*-(**3**) 11-Bu^t-*arachno*-5,10,11-$C_2NB_8H_{12}$. The isomers differ in the disposition of the Bu^t group and the μ(7, 8) bridging hydrogen

* *tert*-Butylamine (1 cm^3) was added dropwise to a solution of *closo*-1,2-$C_2B_8H_{12}$ (1.2 g, 100 mmol) in thf (15 cm^3) and the mixture left to stand for 10 h at ambient temperature. The thf was removed *in vacuo*, the solid residue dissolved in dichloromethane and the solvent was then removed after addition of silica gel (*ca.* 10 g). The solids were placed onto a silica gel column (*ca.* 30 × 2.5 cm) and elution with 100% hexane gave two fractions from which solid components were isolated after evaporation of the hexane and sublimation of the residue at 50–90 °C (oil-pump vacuum). The first fraction (R_f 0.15) afforded 4,6-$C_2B_7H_{13}$ (0.1 g, 8%) identified by NMR spectroscopy.[8] The second fraction (R_f 0.10), consisting of compound **2** contaminated by *ca.* 5% of the isomer **3** (as assessed by GC), was recrystallized from boiling hexane to give pure **2** (1.3 g, 68%; m.p. 162 °C). A six-fold recrystallization of the residue obtained from the hexane mother-liquors, followed by sublimation at 90 °C, yielded a 1:2 mixture of **2** and **3**, as assessed by NMR spectroscopy. Further elution of the column by dichloromethane led to the isolation of a white solid identified as $NH_2Bu^t{\cdot}BH_3$ by ^{11}B NMR spectroscopy.

† NMR spectra [parameters for **2** and **3**, ordered as δ(^{11}B) ± 0.5 (reference $F_3B{\cdot}OEt_2$, Ξ 32.083 971 MHz), $^1J(^{11}B-^1H)$ ± 8 Hz, assignment, δ(^{1}H) ± 0.05 (reference $SiMe_4$)]: **2**, +5.5, 147, BH(7,8), +3.54; −4.6, 153, BH(2,4), +2.08; −11.0, 170, BH(1), +2.76; −17.5, 143, BH(6,9), + 2.01; −46.2, 149, BH(3), +0.05; CH(5,10), *ca.* +1.30; μ-H(7,8), −4.04; CH_3 (of Bu^t), +1.34 (intensity 9); **3**, −1.7, 143, BH(7,8), +3.28; −2.3, 153, BH(2,4), +2.18; −17.8. *ca.* 125, BH(1), +2.01; −18.5, *ca.* 150, BH(6,9) +1.93; −43.7, 149, BH(3), *ca.* 0.5; CH(5,10), *ca.* + 1.30; μ-H(7,8), −3.88; CH_3 (of Bu^t), +1.35 (intensity 9). IR (KBr disc, tentative assignments): **2**, 3240s [ν(NH)], 3128w [$\delta(CH_{cage})$], 3068s, 2600s, 2564s, 2524s [ν(BH)], 1388s, 1370s [ν(Bu^t)], 1256m and 1242m cm^{-1} [γ(Bu^t)]. Mass spectra [70 eV (*ca.* 1.12 × 10^{-17} J), electron impact]: **2**, high-mass cut-off at *m/z* 195 (M^+), corresponding to ($^{12}C_6{}^1H_{21}{}^{11}B_8{}^{14}N]^+$; other significant fragmentation patterns at *m/z* 138 ([$^{12}C_2{}^1H_{12}{}^{11}B_8{}^{14}N]^+$) and 57 ([$^{12}C_4{}^1H_9]^+$); **3** (isolated by GC), high-mass cut-off at *m/z* 195 (M^+ peak), corresponding to [$^{12}C_6{}^1H_{21}{}^1B_8{}^{14}N]^+$; other significant fragmentation patterns at *m/z* 139 ([$^{12}C_2{}^1H_{13}{}^{11}B_8{}^{14}N]^+$), 125 ([$^{12}C_2{}^1H_{13}{}^{11}B_8]^+$) and 57 ([$^{12}C_4{}^1H_9]^+$).

sterically more hindered *syn* disposition of the Bu^t group around the nitrogen atom (see Scheme 1) being assigned to the less-abundant isomer **3**. In agreement with Williams' rules,[12,13] all heteroatom centres occupy low-connectivity positions within the cage, as shown in Scheme 1. In cluster terms, both **2** and **3** are cage isomers of *arachno*-$NC_2B_8H_{13}$ reported earlier[6] and can be alternatively formulated as two conformers of μ-6,9-(NHBu^t)-*arachno*-5,10-$C_2B_8H_{11}$. Of different character is the *endo* $\{CH_2NMe_2\}$ bridging unit in μ-$(Me_2NCH_2)B_5H_8$ and its 1-Et and 1-Br derivatives.[14]

The overall reaction exhibits a simple stoichiometry [see equation (1)] which is consistent with an unprecedented direct cluster expansion of the 22-electron ($2n + 2$) *closo* cage of **1** leading to the formation of the 28-electron ($2n + 6$) *arachno* eleven-vertex system. As far as we are aware, the reaction

$$C_2B_8H_{10} + NH_2Bu^t \longrightarrow Bu^tNHC_2B_8H_{11} \quad (1)$$

represents the first known example of a straightforward *closo* to *arachno* cluster-expansion reaction resulting in substantial cluster opening associated with the addition of one more heteroatom vertex to the cage. Mechanistically, the formation of compounds **2** and **3** is consistent with nucleophilic attack by the NH_2Bu^t nitrogen at the most positive {B(3)} vertex with concomitant inclusion of the {Bu^{t}NH} unit between the B(3) and B(6) vertices in **1** and cluster opening in the area identified by the C(1), C(2), B(3), B(6), B(7) and B(10) atoms in the cage.

Studies aimed at extending the concept of cluster opening by amines and developing the chemistry of the eleven-vertex *arachno* azadicarbaborane class of compounds are in progress.

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