Tricarbollides—Compounds of the Eleven-vertex Series of Tricarbaboranes

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Alternative syntheses of the zwitterionic compounds 7-L-*nido*-7,8,9-$C_3B_8H_{10}$ (where L = H_2N^-, Me_3N, and Bu^tNH_2) are reported from reactions involving the [*nido*-5,6-$C_2B_8H_{11}$]$^-$ anion, the CN^- anion and/or alkyl isocyanides RNC (for R = Bu^t); deamination of the Me_3N derivative leads to the first unsubstituted eleven-vertex tricarbaboranes *nido*-7,8,9-$C_3B_8H_{12}$ and [*nido*-7,8,9-$C_3B_8H_{11}$]$^-$.

The cyanide anion[1] and isonitriles[2] have been previously shown to be susceptible to nucleophilic attack by polyhedral boron hydrides in the *endo*-substitution manner, resulting in the insertion of the carbon atom into the cluster area. A high-yield monocarbon-insertion reaction has been observed more recently between the [*arachno*-4,6-$C_2B_7H_{12}$]$^-$ anion and acetonitrile[3,4] or polarized alkynes[4] by Sneddon's group. These reactions yielded a large number of *C*-alkylated compounds of the nine- and ten-vertex tricarbaborane series[3–5] and thus greatly enriched the largely unexplored class of tricarbaborane and metallatricarbaborane clusters.[6–9] The only parent (unsubstituted) tricarbaboranes so far reported have been the uniquely structured compounds *closo*-$C_3B_5H_7$[10] and *hypho*-$C_3B_4H_{12}$.[11] Here we report our preliminary results on the reactions involving the [*nido*-5,6-$C_2B_8H_{11}$]$^-$ anion,[12] cyanide anion and/or alkyl isocyanides that lead to a number of the long expected compounds of the eleven-vertex *nido* tricarbollide series, zwitterionic derivatives 7-L-*nido*-7,8,9-$C_3B_8H_{10}$ (where L = amines) and to the parent tricarbaboranes 7,8,9-$C_3B_8H_{12}$ and [7,8,9-$C_3B_8H_{11}$]$^-$.

Reaction between the [*nido*-5,6-$C_2B_8H_{11}$]$^-$ anion **1**,[12] generated *in situ* by treatment of the hexane solution of the neutral 5,6-$C_2B_8H_{12}$ (reaction scale 10 mmol) with 2 equiv. aqueous NaCN at ambient temperature for 24 h, followed by precipitation with aqueous NMe_4Cl, has led to the isolation of NMe_4^+[7-H_2N-*nido*-7,8,9-$C_3B_8H_{10}$]$^-$ [compound **2a** of general structure **2** in Scheme 1, paths *a* and *b*, R = free electron pair] in 30% yield [see also eqn. (1)]. Alternatively, treatment of the

$$\underset{\mathbf{1}}{[C_2B\ _8H_{11}]^-} + CN^- + H_2O \rightarrow \underset{\mathbf{2a}}{[H_2N\text{-}C_3B_8H_{10}]^-} + OH^- \tag{1}$$

aqueous layer by Me_2SO_4 in alkaline medium, followed by filtration of the precipitate and its purification by preparative TLC, using 5% MeCN–CH_2Cl_2 as the mobile phase [R_f(prep.) 0.30], has led to the isolation of 7-Me_3N-*nido*-7,8,9-$C_3B_8H_{10}$ **2b** (yield 27%, based on carbaborane **1** used).

Another source of the zwitterionic compounds of type **2** is provided by the synthesis involving anion **1** (Na^+ salt, generated *in situ* by treatment of carbaborane **1** with NaH, reaction scale 4 mmol) and Bu^tNC in glyme (1,2-dimethoxyethane) [room temp., 2 d, see eqn. (2) for R = Bu^t], followed by evaporation

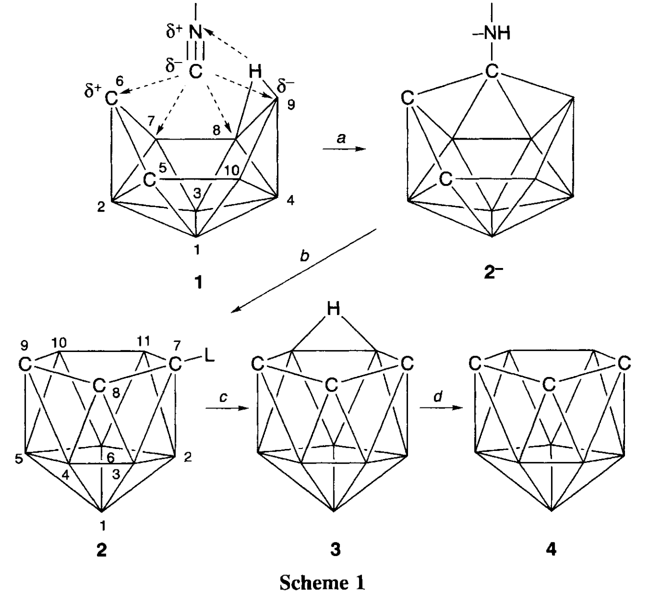
$$\underset{\mathbf{1}}{[C_2B_8H_{11}]^-} + RNC \rightarrow \underset{\mathbf{2c^-}}{[RNH\text{-}C_3B_8H_{10}]^-} \xrightarrow{H^+} \underset{\mathbf{2c}}{RNH_2\text{-}C_3B_8H_{10}} \tag{2}$$

of the solvent, addition of equal amounts of CH_2Cl_2 and water, and acidification with diluted hydrochloric acid [path *b*]. This resulted in the isolation of 7-Bu^tNH_2-*nido*-7,8,9-$C_3B_8H_{10}$ **2c** from the dichloromethane extracts [yield 53% upon purification by preparative TLC in 100% CH_2Cl_2, R_f(prep.) 0.1]. Methylation of compound **2c** (reaction scale 1.5 mmol) with excess MeI (4 equiv.) in the presence of *ca.* 4 equiv. NaH in glyme (reflux for 2 h), followed by evaporation of the solvent, addition of water and repeated extraction with 50% MeCN–CH_2Cl_2, led to the isolation of the trimethylamine derivative **2b** as the main product. This was isolated in 37% yield by preparative TLC [5% MeCN–CH_2Cl_2, R_f(prep.) 0.30] from the organic layer. Other chromatographic fractions yielded 7-Bu^tNHMe-7,8,9-$C_3B_8H_{10}$ and methylated derivatives of **3**, which will be characterized in more detail in a full paper.

The Me_3N functionality in **2b** was removed by treatment with 2 equiv. sodium metal (reaction scale 10 mmol) in THF (room temp., 24 h) in the presence of naphthalene. The anticipated Na_2[7,8,9-$C_3B_8H_{10}$] intermediate thus formed was then decomposed with a slight excess of water and the THF evaporated. Addition of hexane and CF_3CO_2H (*ca.* 3 equiv.), followed by evaporation of the hexane, TLC chromatography [100% hexane, R_f(prep.) 0.20], and sublimation of the solid residue *in vacuo* at *ca.* 60 °C, yielded the neutral tricarbaborane *nido*-7,8,9-$C_3B_8H_{12}$ **3** [path *c*] in 60% yield (based on **2b**). Deprotonation of **3** in the NMR tube in CD_3CN with a threefold excess of proton sponge [PS, 1,8-$(Me_2N)_2C_{10}H_6$] led to complete removal of the μH(10,11) bridging hydrogen and to quantitative formation of the parent 'tricarbollide' anion [*nido*-7,8,9-$C_3B_8H_{11}$]$^-$ **4** [path *d*]. The crystalline salt $[PSH]^+$ [*nido*-7,8,9-$C_3B_8H_{11}$]$^-$ can be obtained by the addition of 1 equiv. PS to a CH_2Cl_2 solution of compound **3** that was overlaid by a twofold amount of hexane.

As shown in Scheme 1, the formation of compounds of type **2** is consistent with the hydrogenation of the highly polarized isonitrile/cyanide N≡C triple bond by the bridging proton of anion **1** under concomitant attack of the nucleophilic isonitrile/cyanide carbon at the electrophilic[3,4] C(6) centre of **1** and insertion of this carbon into the cluster area under the formation of anions **2**$^-$ (for R = free electron pair or Bu^t). Protonation of **2**$^-$ leads directly to either anion **2a** or the zwitterionic compound **2b**.

The constitution of the tricarbaborane compounds discussed above has so far been based on high-field multinuclear,



Scheme 1

selective, and [^{11}B–^{11}B] COSY NMR measurements.† These have confirmed unambiguously a cluster configuration with three {CH} cluster units in adjacent positions within the open pentagonal face of the eleven-vertex *nido* cage. As seen in Fig. 1, the ^{11}B NMR shifts for the neutral carbaborane **3** correlate only approximately with those for the isoelectronic, but not isostructural, anion [*nido*-7,8-$C_2B_9H_{12}$]$^-$ **5**,[13] evidently owing to the different character of the 'extra' hydrogen atom in both species. Unfortunately, the absence of the corresponding data for the *nido* 'dicarbollide'[14] dianion [7,8-$C_2B_9H_{11}$]$^{2-}$ does not permit straightforward comparison to the ^{11}B shielding patterns for the isostructural compounds of type **2** and for the parent anion **4**. Noticeable are the remarkable upfield shifts of the high-field ^{11}B(1) and ^{11}B(2,5) resonances ($\Delta\delta$ *ca.* 12 and 16 ppm, respectively) as a consequence of the removal of the bridging proton from compound **3**, whereupon the spectrum of the anion **4** re-adopts the original features characteristic for the isostructural compounds of type **2**. Mass spectra† of the zwitterionic compounds of type **2** and of the neutral tricarbaborane **3** exhibit, besides other fragmentation patterns, the expected high-mass molecular cut-off corresponding to the highest isotopomer of the proposed molecular ion.

The compounds described above are, as far as we are aware, the first representatives of the long expected eleven-vertex *nido* family of tricarbaboranes; species of type **2** and the parent anion **4** being isostructural analogues of the 'dicarbollide'[14] anion [7,8-$C_2B_9H_{11}$]$^{2-}$. The straightforward availability of these stable compounds from 5,6-$C_2B_8H_{12}$ makes them accessible for further investigations, such as isomerisation, boron degradation and, in particular, metal insertion reactions. Relevant researches into these new areas of carbaborane chemistry are in progress.

We thank the Spanish Government (Grant SAB94–0067 to B. Š.), the CIRIT (project QNF92-43B) and the Grant Agency of the Academy of Sciences of the Czech Republic (Grant No. 432402) for support (to B. Š. and J. H.) and Drs J. Fusek and Z. Plzák for partial NMR measurements and mass spectra.

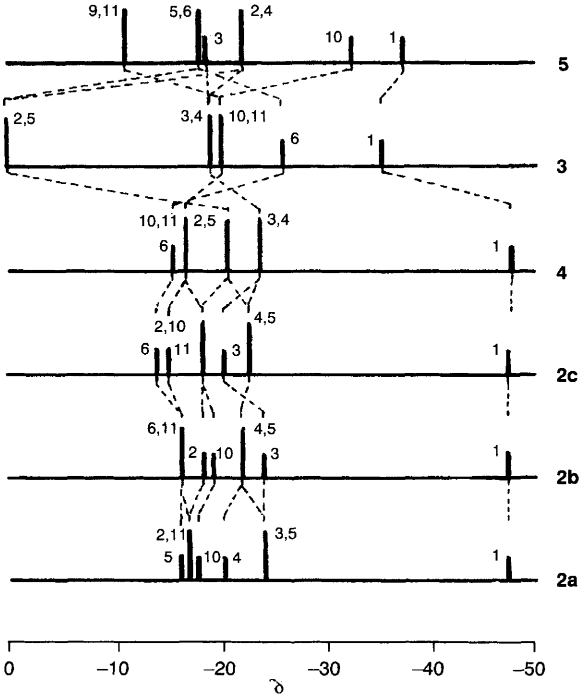


Fig. 1 Stick representations of the chemical shifts and relative intensities in the ^{11}B NMR spectra of the eleven-vertex nido compounds 7-L-7,8,9-$C_3B_8H_{10}$ [where L = H_2N^- **2a**, Me_3N **2b**, and Bu^tNH_2 **2c**], [7,8,9-$C_3B_8H_{11}$]$^-$ **4**, 7,8,9-$C_3B_8H_{12}$ **3**, and [7,8-$C_2B_9H_{12}$]$^-$ **5**. Hatched lines interconnect equivalent positions in all compounds under comparison.

Received, 17th January 1995; Com. 5/00295H

Footnote

† *Spectroscopic data*. NMR data for compounds of types **2**, **3**, and **4** {assignment, $\delta(^{11}B)$ [$\delta(^1H)$]} in CD_3CN solutions at 294–303 K: For **2a** (NMe_4^+ salt) BH(6), −16.1 [+0.98]; BH(2,11), −16.8 [+1.25, +1.11]; BH(10), −17.3 [+1.44]; BH(4), −19.8 [1.58]; BH(3,5), −24.1 [+1.49, +0.91]; BH(1), −47.0 [+0.08]; for **2b** BH(6,11), −16.2 [+1.32, +1.09]; BH(2), −18.0 [+1.72]; BH(10), −19.2 [+1.42]; BH(4,5), −21.9 [+1.9, +1.17]; BH(3), −23.7 [+1.60]; BH(1), −47.2 [+0.18]; for **2c** [$^2H_6$]acetone BH(6), −14.0 [+1.29]; BH(11), −14.9 [+1.49]; BH(2,10), −18.5 [+1.49, *ca*, +1.6]; BH(3), −20.2 [+1.66]; BH(4,5), −22.7 [+1.14, *ca.* +1.60]; BH(1), −47.1 [+0.18]; for **3** BH(2,5) +0.45 [+2.65]; BH(3,4), −19.0 [+1.85]; BH(10,11), −20.0 [+1.84]; BH(6), −25.9 [+0.91]; BH(1) −35.2 [+1.15]; for **4** BH(6), −15.5 [+0.97]; BH(10,11), −16.6 [+1.55]; BH(2,5), −20.6 [+1.09]; BH(3,4), −23.6 [+1.47]; BH(1), −47.4 [+0.05]; NMR assignments [tentative for compounds of type **2** owing to closely spaced resonances in the range of $\delta(^{11}B)$ *ca.* −14 to −24] by [^{11}B–^{11}B] COSY experiments and $^1H\{^{11}B(\text{selective})\}$ spectroscopy. Additional $\delta(^1H)$ data for: **2a** NMe_4^+ +3.50 (12 H), H_2N +3.07 (2 H), CH(9) +2.51, CH(8) +1.58; for **2b** NMe_3 +3.09 (9 H), CH(9) +2.70, CH(8) +1.79; for **2c** H_2N +7.57 (br, 2 H), CH(9) +2.82, Bu^t + 1.62, CH(8) +1.78; for **3** CH(8) +3.76, CH(7,9) +3.08, μH(10,11) −2.13; for **4** CH(7,9) +2.15, CH(8) +1.48. MS (70 eV EI ionisation): for **2b** m/z_{max} 193 (11%, M$^+$), 59 (32%, NMe_3^+); for **2c** m/z_{max} 207 (4%, M$^+$), 192 [50%, (M–Me)$^+$], 57 (28%, Bu^t); for **3** m/z_{max} 136 (3%, M$^+$).

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