NMR ASSIGNMENTS OF [6-R-*nido*-5,6-$C_2B_8H_{10}$]$^-$ ANIONS (WHERE R = H, Me, AND n-C_6H_{13}). AN IRREVERSIBLE 5 → 6 ALKYL MIGRATION *via* A B9 VERTEX-SWING MECHANISM

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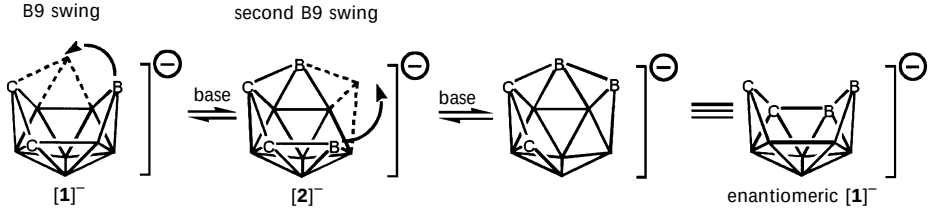
Dedicated to Dr Stanislav Heřmánek on the occasion of his 70th birthday for his merits in the systemization and in the practical uses of boron-cluster compounds, and in the applications of NMR spectroscopy to their study.

Deprotonation by "proton sponge" (PS = 1,8-dimethylaminonaphthalene) of the parent dicarbaborane *nido*-5,6-$C_2B_8H_{12}$ (**1**) and its 6-R-substituted derivatives (where R = Me and n-C_6H_{13}) leads to the anions [*nido*-5,6-$C_2B_8H_{11}$]$^-$ [**1**]$^-$ and [6-R-*nido*-5,6-$C_2B_8H_{10}$]$^-$ [6-R-**1**]$^-$, respectively. In contrast, the deprotonation of the 5-substituted isomers, 5-R-*nido*-5,6-$C_2B_8H_{11}$ (5-R-**1**), results in irreversible conversion into the 6-substituted anions [6-R-**1**]$^-$, from which the neutral compounds 6-R-**1** can be obtained *via* reprotonation. This 5 → 6 alkyl migration can be explained by the B9 vertex-swing mechanism previously proposed for the interenantiomeric fluxionality of [**1**]$^-$, but now with the product dictated by the higher thermodynamic stabilities of the 6-substituted derivatives. The work has also resulted in complete assignments of ^{11}B and ^{1}H NMR spectra of the [*nido*-5,6-$C_2B_8H_{11}$]$^-$ anion and of ^{11}B NMR spectra of the [6-R-*nido*-5,6-$C_2B_8H_{10}$]$^-$ anions.

Key words: Boranes; Boron clusters; Carboranes; Dicarbaboranes; 5,6-Dicarba-*nido*-decaborane(12); NMR spectroscopy.

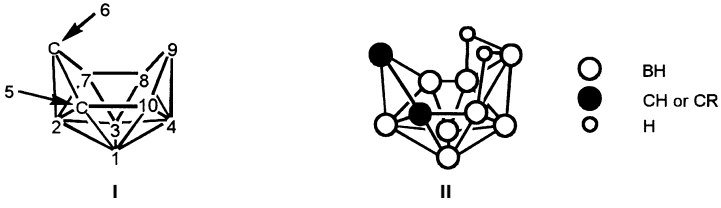
The parent ten-vertex dicarbaborane *nido*-5,6-$C_2B_8H_{12}$ (**1**) can be regarded as one of the most essential reagents of dicarbaborane chemistry (see reviews in refs[1–4]). For instance, it has been employed as a starting material for the preparation of a number of key dicarbaboranes, such as neutral *closo*-1,2-$C_2B_8H_{10}$, *closo*-1,6-$C_2B_8H_{10}$, *closo*-1,10-$C_2B_8H_{10}$, *arachno*-4,6-$C_2B_7H_{13}$

(ref.[5]) and *arachno*-6,9-$C_2B_8H_{14}$ (refs[6–8]), anions [*nido*-6,9-$C_2B_8H_{10}$]$^{2-}$ and [*arachno*-4,5-$C_2B_6H_{11}$]$^-$ (ref.[9]), and also of larger species such as derivatives of fourteen-vertex *arachno*-$C_4B_8H_{14}$ (refs[10,11]) and the fourteen-vertex methylazatricarbaboranes[12]. Very recently, 5,6-$C_2B_8H_{12}$ has also become an effective source for tricarbollides, the first representatives of the eleven-vertex family of tricarbaboranes[13–15], which are the objects of current interest and activity. Relevant to the results now presented here, we noted some time ago, in connection with the isolation of the laevorotatory enantiomer of carborane **1**, that the carborane **1** in fact underwent a facile base-induced racemisation[16]. This interesting process was explained by fluxionality of the [*nido*-5,6-$C_2B_8H_{11}$]$^-$ anion [**1**]$^-$ between its enantiomers in solution, and was rationalised in terms of a reversible double B9 vertex-swing mechanism[3] (see simplified Scheme 1; for clarity, all hydrogen positions are omitted, unmarked or B vertices denote BH cluster units, and the C vertices stand for CH units). The process involves a transient symmetrical intermediate anion, [*nido*-5,10-$C_2B_8H_{11}$]$^-$ [**2**]$^-$. A similar mechanism has already been applied to explain rearrangements in other reactions involving open-cage ten-vertex boron cluster substrates[17].



SCHEME 1

We now report another apparent manifestation of the same mechanism. Here it can be used to account for an irreversible isomerisation, rather than a reversible one, specifically the conversion of representative 5-alkyl substituted isomers of **1** to give the 6-isomers. Reported are, as a necessary part of this work, the assignments of the individual resonances in the ^{11}B NMR spectra of the parent anion [*nido*-5,6-$C_2B_8H_{11}$]$^-$ together with those for the



substituted anions [6-R-*nido*-5,6-$C_2B_8H_{10}$]$^-$ (where R = Me and n-C_6H_{13}). The numbering scheme for the ten-vertex *nido* compounds discussed in this work is in the general structure **I** and the neutral species 6-R-**1** and 5-R-**1** have an open-face disposition of their two bridging hydrogen atoms as in structure **II.**

EXPERIMENTAL

General

All reactions were carried out with use of standard vacuum or inert-atmosphere techniques as described by Shriver[18]. The starting *nido* dicarboranes 5,6-$C_2B_8H_{12}$, 5-R-5,6-$C_2B_8H_{11}$ and 6-R-5,6-$C_2B_8H_{11}$ (where R = Me and n-C_6H_{13}) were prepared according to literature[19,20]. Hexane and CH_2Cl_2 were dried over CaH_2, and freshly distilled before use. The purity of individual compounds was checked by analytical TLC on Silufol (Kavalier, silica gel on aluminium foil; detection by UV 254 or iodine vapour, followed by spraying with 2% aqueous $AgNO_3$). ^1H and ^{11}B NMR spectroscopy was performed at 11.75 Tesla on a Varian XL-500 instrument. The [^{11}B-^{11}B]-COSY (ref.[21]) and ^1H-{^{11}B(selective)} (ref.[22]) NMR experiments were essentially as described in other related papers from our laboratories[23]. Chemical shifts are given in ppm to high frequency (low field) of Ξ = 32.083971 MHz (nominally $F_3B{\cdot}OEt_2$ in $CDCl_3$) for ^{11}B (±0.5 ppm) and Ξ = 100 MHz ($SiMe_4$) for ^1H (±0.05 ppm), Ξ being defined as in ref.[24]. Solvent resonances were used as internal secondary standards. Coupling constants $^1J(^{11}B\text{-}^1H)$ are taken from resolution-enhanced ^{11}B spectra with digital resolution ±8 Hz and are given in Hz.

Conversion of the 5-R-5,6-$C_2B_8H_{11}$ Derivatives (5-R-**1**) (R = Me and n-C_6H_{13}) into 6-R-5,6-$C_2B_8H_{11}$ (6-R-**1**) Isomers

A solution of 5-CH_3-**1** (or a mixture of 5-(n-C_6H_{13})-**1** and 6-(n-C_6H_{13})-**1**) (1 mmol) in dichloromethane (10 ml) was treated with PS (214 mg, 1 mmol) and the mixture was stirred at ambient temperature for 30 min. The mixture was then shaken with 5% aqueous HCl (10 ml), and the dichloromethane layer was separated and dried with $MgSO_4$. Evaporation of the solvent at room temperature, followed by microdistillation of the residuum at 50–100 °C (bath), gave pure compounds 6-R-**1** identified by ^{11}B NMR spectroscopy in accord with data reported previously[19,20] in yields in the region of 80%. In another experiment, a solution of 6-R-**1** (1 mmol) in dichloromethane (10 ml) was treated with PS (214 mg, 1 mmol) and the mixture was stirred at ambient temperature for 30 min. The mixture was then shaken with 5% aqueous HCl (10 ml), and the dichloromethane layer was separated and dried with $MgSO_4$. Evaporation of the solvent at room temperature, followed by microdistillation of the residuum at 50–100 °C (bath), resulted in the recovery of the unchanged pure compounds 6-R-**1** (where R = Me and n-C_6H_{13}) in yields ranging from 75 to 80%.

Characterization of [*nido*-5,6-$C_2B_8H_{11}$]$^-$ [**1**]$^-$ and [6-R-*nido*-5,6-$C_2B_8H_{10}$]$^-$ Anions [6-R-**1**]$^-$ (R = Me and n-C_6H_{13})

Solutions of the PSH^+ salts of anions [**1**]$^-$ and [6-R-**1**]$^-$ (where R = CH_3 and n-C_6H_{13}) for NMR measurements were obtained by adding varying amounts of PS to 0.1 mmol quantities of

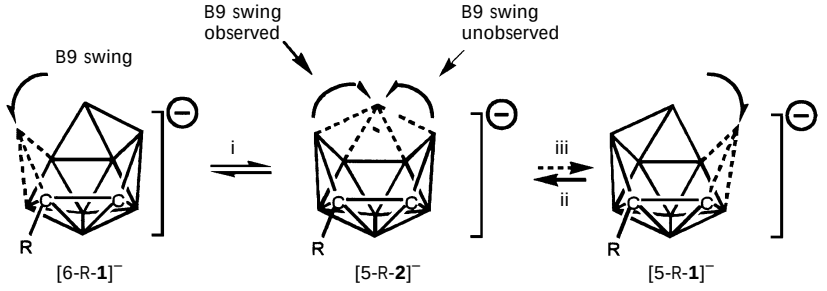
the neutral compounds **1**, 5-R-**1** and 6-R-**1**, in NMR tubes containing *ca* 0.5 ml of solvent. According to the ^{11}B NMR spectra, the addition of 0.1 mmol PS to a CD_3CN solution of **1** gave the anion [**1**]$^-$, but the addition of 0.1 mmol of PS to CD_3CN solutions of a mixture of 5-(n-C_6H_{13})-**1** and 6-(n-C_6H_{13})-**1** both generated exclusively anionic [6-(n-C_6H_{13})-**1**]$^-$ in each case. In $CDCl_3$ solution, the same procedure with either 5-CH_3-**1** and 6-CH_3-**1** in each case established a *ca* 1 : 1 equilibrium between neutral 6-CH_3-**1** and anionic [6-CH_3-**1**]$^-$. NMR data for (PSH)$^+$[**1**]$^-$ are as follows: $\delta(^{11}B)$ (CD_3CN) (assignment, multiplicity, and $^1J_{BH}$ in Hz, if applicable) +16.9 (B9, broad t, 119), +8.4 (B7, d, 139), –2.0 (B(1,8), d, ≈147), –13.8 (B3, d, ≈125), –14.7 (B10, d, $J(^{11}B\text{-}^{11}B)$ ≈ 50), –28.3 (B4, d, 137), –30.7 (B2, d, 162), all the [^{11}B-^{11}B]-COSY cross-peaks for adjacent sites were observed; selected observed [^{1}H-^{1}H]-COSY cross-peaks are: H6-H2, H5-H10, μ-H(8,9)-H9, μ-H(8,9)-H8, μ-H(8,9)-H4; $\delta(^1H)$ ($CDCl_3$) (assignments for individual cluster {BH} protons by ^{1}H-{^{11}B(selective)} measurements) +4.62 (H6), +3.77 (H9), +3.55 (H5), +1.89 (H3), +1.48 (H10), +0.98 (H(2), +0.43 (H4), –4.15 (μ-H(8,9)), the H(1,8) resonances overlap with those from the PS methyl groups in the range +3.2 to +2.5 ppm. NMR data for (PSH)$^+$[6-CH_3-**1**]$^-$ are: $\delta(^{11}B)$ ($CDCl_3$) +12.5 (B9, broad s, –), +5.2 (B7, d, –), –2.1 (B8, d, –), –3.7 (B1, d, 144), –14.9 (B(3,10), d, ≈177), –27.4 (B2, d, 160), –32.4 (B4, d, 138), all the [^{11}B-^{11}B]-COSY cross-peaks for adjacent sites were observed; $\delta(^1H)(CDCl_3)$ +3.77 (H9), +1.26 (CH_3), –3.75 (μ-H(8,9)), other resonances overlap with those of the PS methyl groups in the range +3.2 to +1.8 ppm. NMR data for (PSH)$^+$[6-(n-C_6H_{13})-**1**]$^-$ are: $\delta(^{11}B)$ (CD_3CN) +14.4 (B9, broad s, –), +5.8 (B7, d, 138), –1.7 (B8, d, 137), –3.2 (B1, d, 143), –14.6 (B(3,10), d, ≈125), –27.5 (B2, d, 162), –31.1 (B4, d, 131), all the [^{11}B-^{11}B]-COSY cross-peaks for adjacent sites were observed; $\delta(^1H)$ (CD_3CN) +3.55 (H9), +3.21 (H5), +1.76 (H10), +1.41 to +1.09 (C_6H_{13}), +0.98 (H2), +0.13 (H4), –4.07 (μ-H(8,9)); the H(1,3,8) resonances overlap with those of the PS methyl groups in the range +3.2 to +2.4 ppm.

RESULTS AND DISCUSSION

It is apparent from ^{11}B NMR spectroscopy that addition of one equivalent of PS to the neutral, 6-substituted compounds 6-R-5,6-$C_2B_8H_{11}$ (6-R-**1**) (R = Me and n-C_6H_{13})[19,20] led immediately to the formation of the corresponding [6-R-5,6-$C_2B_8H_{10}$]$^-$ anions [6-R-**1**]$^-$. This occurred in both CD_3CN and $CDCl_3$ solution. As shown by preparative-scale experiments in CH_2Cl_2 as solvent, these anionic species yield pure starting materials 6-R-**1** upon re-protonation, with no sign of the presence of the 5-substituted isomers. On the other hand, the deprotonation of their neutral 5-substituted isomers 5-R-5,6-$C_2B_8H_{11}$ (5-R-**1**) under the same conditions resulted in quantitative conversion into the corresponding 6-substituted neutral species 6-R-**1** upon re-protonation.

These observations can be explained as in Scheme 2 (extra hydrogen atoms omitted for clarity). This involves the B9 vertex-swing mechanism as previously proposed for unsubstituted [**1**]$^-$ (Scheme 1)[3,17]. Now, an analogous swing (path ii in Scheme 2) would generate the transient anion [5-R-5,10-$C_2B_8H_{10}$]$^-$ [5-R-**2**]$^-$ from the [5-R-**1**]$^-$ anion that would be formed from the initial deprotonation of neutral 5-R-**1**. From this point, the rever-

sal of this swing (path iii) to generate [5-R-**1**]$^-$ would appear to be inhibited, whereas the otherwise equivalent swing to generate [6-R-**1**]$^-$ (path i) is concomitantly favoured. Since the ready enantiomerisation of unsubstituted [**1**]$^-$ shows no high kinetic barriers in compounds of this type, and the steric effect of the methyl or n-hexyl groups is small, the preferential generation of [6-R-**1**]$^-$ and thence 6-R-**1** is presumably caused by higher thermodynamic stabilities of the 6-substituted derivatives[25].



SCHEME 2

Assignments in the NMR spectra of the species discussed here were straightforward, but the spectra of the anions [**1**]$^-$ and [6-R-**1**]$^-$ merit some comment. Of these, the ^{11}B spectra consist of one low-field ^{11}B9 signal (broad triplet for [**1**]$^-$ and broad singlets for [6-R-**1**]$^-$) and seven doublets of equal intensity. This broad shape, with incipient fine structure, of the low-field ^{11}B9 resonance, both in the straightforward ^{11}B spectrum and also in the ^{11}B-{^{1}H} spectra, we believe arises from a partially resolved coupling $^1J(^{11}B\text{-}^{11}B)$ between the B9 and B10 positions that is somewhat larger than typical intracluster interboron couplings of up to *ca* 15 Hz. In unpublished work we have observed a similarly large coupling for the equivalent unbridged B5–B6 connectivity in 5-(Me_2S)-*nido*-$B_{10}H_{12}$; in accord with this proposal, the ^{11}B10 resonances in anions [**1**]$^-$ and [6-R-**1**]$^-$ are also somewhat broad. Presumably, a strong localisation of bonding s-character in this type of the *nido* ten-vertex open-face unbridged interboron linkage might be general. Eight different singlets attributable to BH cluster units were found in the ^{1}H-{^{11}B(selective)} spectra of anions [**1**]$^-$ and [6-(n-C_6H_{13})-**1**]$^-$, together with two different singlets arising from the CH5 and CH6 units and one broad high-field singlet at *ca* –4 ppm. As shown by strong [^{1}H-^{1}H]-COSY cross-peaks, this latter ^{1}H resonance is associated with the BH9, BH8, and BH4 vertices, supporting the presence of a conventional localised μ-H(8,9) bridge. For these reasons, we prefer the structure pre-

sented in Fig. 1 for all the anions [**1**]$^-$ and [6-R-**1**]$^-$ in solution. Noticeable are also the shielding changes caused by the 6-R substituents at the antipodal[26] ^{11}B4 site ($\Delta\sigma_A(^{11}B)$ = +4.1 and +2.8 ppm for R = CH_3 and n-C_6H_{13}, respectively). This effect interchanges the ordering of the ^{11}B2 and ^{11}B4 resonances in the spectra of anions [6-R-**1**]$^-$, in comparison with that of the parent anion [**1**]$^-$.

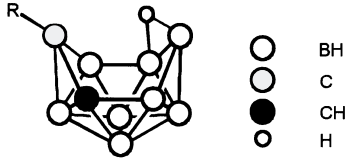


FIG. 1
Proposed structure for the [6-R-*nido*-5,6-$C_2B_8H_{10}$]$^-$ anions [**1**]$^-$ (R = H) and [6-R-**1**]$^-$ (R = CH_3 and n-C_6H_{13})

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