Short communication

Polyhedral nonaborane chemistry: an unsuspected new isomeric type in the nine-vertex *arachno*-$B_9H_{13}L$ system

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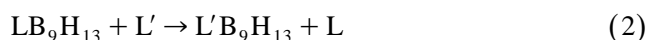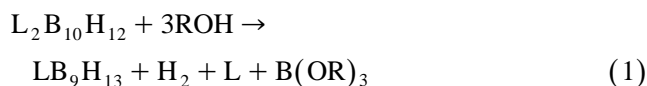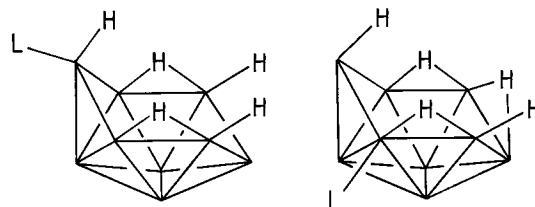*The School of Chemistry of the University of Leeds, Leeds LS2 9JT, England*

Abstract

NMR spectroscopy reveals that the preparation of conventionally-structured 4-(ligand)-*arachno*-B_9H_{13} species **1** by ligand exchange on 4-(SMe_2)-*arachno*-B_9H_{13} **1a** is often accompanied by the formation of their hitherto unsuspected and unreported 5-(ligand)-*arachno*-B_9H_{13} isomers **2**, which can be isolated by chromatography. 5-($4'$-PhC_5H_4N)-*arachno*-B_9H_{13} **2c** is characterised by a single-crystal X-ray diffraction analysis that also reveals an interesting stacking of the organic aromatic residues in the solid state. © 1998 Elsevier Science S.A.

Keywords: NMR spectroscopy; *Arachno*-$B_9H_{13}L$; X-ray diffraction; Borane cluster

It is a pleasure for us to dedicate this paper to Ken Wade. [1] Ken Wade's Rules have great predictive and rationalisation power in polyhedral borane, carborane and heteroborane chemistry, extending into organometallic assemblies and metal cluster species [1,2]. They are based initially on the recognition of empirical structural patterns [3]. Within series of compounds that obey Wade's Rules, a variety of isomeric structural configurations may exist, and it is important to recognize the associated patterns of cluster-substituent and cluster-constituent behaviour so that other useful empirical rules may ultimately emerge. Here, for example, empirical 'rules' governing the stabilities of the absolute and relative positioning of carbon atoms in mono-, di- and polycarborane clusters are well-established [4–7]. In this context it may be noted that many of the perceived configurational stereotypes in polyhedral boron-containing cluster chemistry derive from initial pioneering preparations, separations, and struc-

tural characterisations using techniques that may not have revealed certain species, or that may have involved preparative conditions that may have destroyed them. The example that is relevant to the work presented here consists of the series of well-known *arachno* nine-vertex compounds LB_9H_{13}, where L is a two-electron donor such as triorganophosphine, diorganosulphide, amine, etc. [8]. These are readily prepared in high yield from ten-vertex *arachno*-6,9-$L_2B_{10}H_{12}$ by alcoholysis (Eq. (1)) [9], or by ligand exchange on a preformed LB_9H_{13} species (Eq. (2)) [10–12]. They are generally held to have the configuration **I** in which the ligand is in the 4-position in the open face.

$$L_2B_{10}H_{12} + 3ROH \rightarrow$$
$$LB_9H_{13} + H_2 + L + B(OR)_3 \tag{1}$$
$$LB_9H_{13} + L' \rightarrow L'B_9H_{13} + L \tag{2}$$

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[1] We have pleasure in expressing our best wishes to Ken Wade on the occasion of his 65th birthday, and are pleased to dedicate this paper to him in recognition of his outstanding contributions and astute insights into organometallic, inorganic and boron cluster chemistry.

We now report preliminary results that show that the formation of these 4-substituted species **1** by the exchange route of Eq. (2) above is in fact often accompanied by the hitherto unsuspected formation of their 5-substituted isomers **2** of configuration **II** in proportions of up to ca. 90%. The five open-face bridging and terminal hydrogen atoms of these new 5-isomers **2** mutually rapidly exchange sites at ambient temperatures. Moderate heating converts the 5-isomers **2** to the conventional 4-isomers **1**.

Thus, in the product mixture from the treatment of $B_9H_{13}(SMe_2)$ (**1a**, of structure type **I**) with $^{sec}BuNH_2$ (Eq. (2)) (60°C, benzene solution, 2 h, reaction scale 900 μmol), integrated NMR spectroscopy [2] showed that the 4-substituted species $4-(NH_2^{sec}Bu)$-*arachno*-B_9H_{13} **1b** was accompanied by an approximately equimolar proportion of the 5-substituted species $5-(NH_2^{sec}Bu)$-*arachno*-B_9H_{13} **2b**. A reaction at lower temperature between **1a** and $4-Ph-C_5H_4N$ (room temperature, toluene solution, 16 h, 600 μmol scale) showed an excess of $5-(4'-Ph-C_5H_4N)$-*arachno*-B_9H_{13} **2c** over the 4-substituted species $4-(4'-Ph-C_5H_4N)$-*arachno*-B_9H_{13} **1c** in ca. 9:1 proportion. In the former case ca. 10% of the starting material $B_9H_{13}(SMe_2)$ **1a** was unreacted.

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[2] NMR parameters, measured at B_0 ca. 5.875 T, CDCl$_3$ solution, 298 K, ordered for BH groups as tentative assignment $\delta(^{11}B)$/ppm relative to BF$_3$OEt$_2$ [$\delta(^1H)(exo)$/ppm relative to TMS] as follows: for **2b** BH(1) and BH(2) $+2.4$ and $+2.8$ [$+3.06$ and $+2.98$], BH(8) -8.3 [$+2.85$], BH(7) and BH(9) -8.3 and -7.3 [$+2.35$ and $+2.25$], BH(5) -24.6 [ligand position, no $^1H(exo)$], BH(4) and BH(6) both ca. -21.7 [both ca. $+1.55$], BH(3) -50.5 [-0.41], additionally, $\delta(^1H)$ -0.91 (broad, 5H, *endo* and bridging), $+4.24$, $+4.02$ (broad, $2\times1H$, NH$_2$), $+1.91$, $+1.70$ (multiplets, $2\times1H$, CH$_2$), $+3.35$ (multiplet, 1H, CH), $+1.45$ (doublet, 3H, CH$_3$), and $+1.03$ (triplet, 3H, CH$_3$) (note the chiral nature of the ^{sec}Bu group gives asymmetry to the {B$_9$} cluster); for **2c** BH(1,2) $+2.3$ [$+3.12$], BH(8) ca. -7.3 [$+2.96$], BH(7) and BH(9) ca. -7.3 [$+2.56$], B(5) -18.8 [ligand position, no $^1H(exo)$], B(4) and BH(6) -22.0 [$+1.81$], B(3) -50.0 [-0.21], additionally $\delta(^1H)$ -0.52 [broader, 5H, mutually exchanging bridging and *endo*)], $+7.37$ to $+7.87$ (multiplets, 7H, C$_6$H$_5$ and C$_5$H$_4$N), $+9.06$ (d, 2H, $^3J(^1H-^1H)$ ca. 6Hz, C$_5$H$_4$N); for **1a** BH(7) $+18.1$ [$+4.07$], BH(1) $+4.4$ [$+3.04$], BH(5,9) -17.7 [$+1.81$], BH$_2$(6,8) -21.5 [$+1.96(exo)$, $-0.01(endo)$], BH(4) -23.3 [$+0.39(endo)$], BH(2,3) -39.2 [$+0.44$] and $\delta(^1H)\{\mu H(5,9;6,8)\}$ -3.53, $\delta(^1H)(SMe_2)$ $+2.54$; for **1b** BH(7) $+15.6$ [$+4.00$], BH(1) $+4.2$ [$+2.88$], BH(5,9) -17.7 [$+1.78$], BH(6,8) -20.8 [$+1.93$ (exo) and -0.18 ($endo$)], BH(4) -20.9 [$+0.60(endo)$], BH(2,3) -39.8 [$+0.39$] and $\delta(^1H)\{\mu H(5,9;6,8)\}$ -3.53; additionally, $\delta(^1H)$ $+4.04$ (broad, 2H, NH$_2$), $+1.83$, $+1.71$ (multiplets, $2\times1H$, CH$_2$), $+3.25$ (multiplet, 1H, CH), $+1.42$ (doublet, 3H, CH$_3$), and $+0.99$ (triplet, 3H, CH$_3$) (note that, in contrast to **2b** above, any asymmetry in the {B$_9$} cluster arising from the chiral ^{sec}Bu group is not apparent at the polarizing field strength used in these NMR experiments); for **1c** BH(7) $+16.7$ [$+4.14$], BH(1) $+4.8$ [$+3.24$], BH(5,9) ca. -15.5 [$+1.95$], BH(4) ca. -15.5 [$+1.54$ ($endo$)], BH(6,8) -20.3 [$+2.10$ (exo) and $+0.00$ ($endo$)], BH(2,3) -38.9 [$+0.57$] and $\delta(^1H)\{\mu H(5,9;6,8)\}$ -3.18; additionally, $\delta(^1H)$ $+7.60$ to $+7.95$ (multiplets, 7H, C$_6$H$_5$ and C$_5$H$_4$N) and $+8.88$ (doublet, 2H, $^3J(^1H-^1H)$ ca. 6 Hz, C$_5$H$_4$N).

Thin-layer chromatographic separation (silica gel G, CH$_2$Cl$_2$) of the ^{sec}BuNH$_2$ products **1b** and **2b** resulted in the isolation of each of these compounds in yields of ca. 45%, with ca. 10% of the SMe$_2$ starting compound **1a** recovered. In the $4-Ph-C_5H_4N$ system, the filtered CH$_2$Cl$_2$ extract of an evaporated reaction mixture containing **2c** and **1c** in proportion 2:1 was fractionally crystallized twice (CH$_2$Cl$_2$/hexane) to afford essentially pure **2c** (41%, unoptimised); and thence **1c** ($<$ ca. 5%) was recovered by repeated thin-layer chromatography (silica gel G, CH$_2$Cl$_2$-hexane mixtures) of the combined supernatants. Moderate heating (e.g., perdeuterotoluene solutions, 75°C, 15 h for **2b**, 100°C,
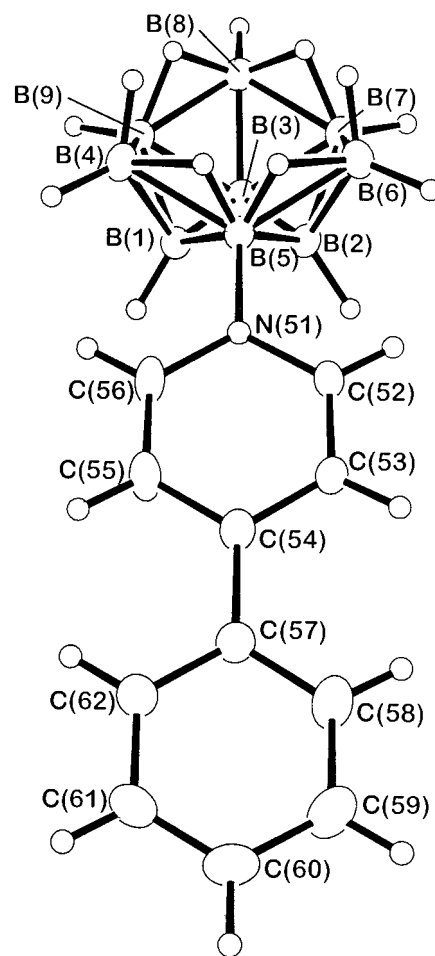

Fig. 1. ORTEP [15] type drawing of the crystallographically determined molecular structure of $5-(4'-PhC_5H_4N)$-*arachno*-B_9H_{13} **2c**. Selected interatomic distances (Å) are: B(5)–N(51) 1.558(2), B(4)–B(5) 1.759(3), B(5)–B(6) 1.884(3), B(6)–B(7) 1.973(3), B(7)–B(8) 1.789(3), B(8)–B(9) 1.787(3) and B(9)–B(4) 1.970(3), with other interboron distances in the range 1.713(3)–1.801(3) Å. Note that there is crystallographic disorder with half-occupancies of the two $\mu(4,5)$ and $\mu(5,6)$ bridging hydrogen atom positions. These are shown with hatched connectivities. This disorder between the $\mu(4,5)$ and $\mu(5,6)$ bridging hydrogen atoms may obscure differential solid-state bridging versus *endo* character in the *endo* H(4) and *endo* H(6) positions, and thence differential *endo* versus bridging character in the $\mu H(7,8)$ and $\mu H(8,9)$ positions.
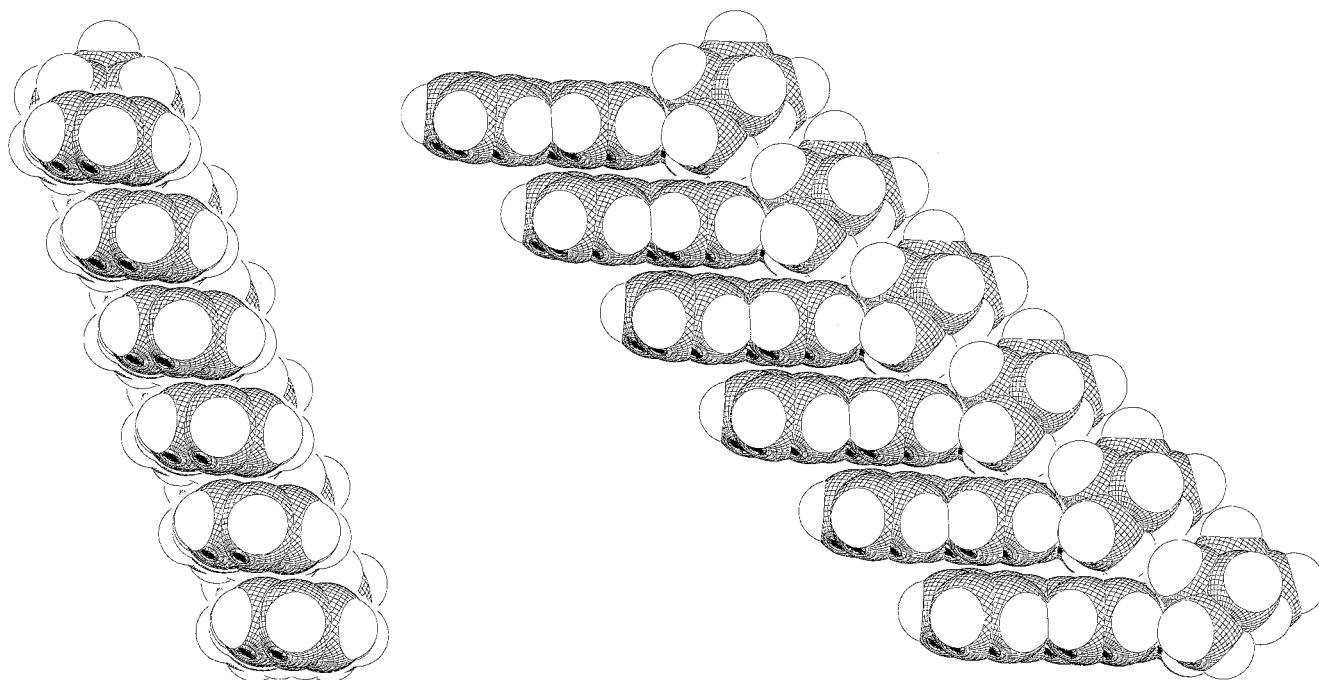
Fig. 2. Mutually perpendicular views of the molecular π-stacking that occurs among the PhC$_5$H$_4$N ligands along the crystallographic *a* direction in the crystal of 5-(4'-PhC$_5$H$_4$N)-*arachno*-B$_9$H$_{13}$ **2c**.

18 h for **2c**) resulted in quantitative conversions of the 5-isomers **2b** and **2c** to the conventional 4-isomers **1b** and **1c** respectively. The new 5-isomers **2** are thus reasonably robust, requiring several hours heating for complete conversion to isomers **1**. It is therefore perhaps remarkable that they have not previously been detected in the 36 years since the initial reports of the syntheses of the 4-isomers **1** via the reaction of Eq. (2).

Recrystallization of the 5-(4'-Ph-C$_5$H$_4$N) derivative **2c** from dichloromethane/hexane at $-30°$C yielded pale yellow air-stable crystals suitable for single-crystal X-ray diffraction work. [3] The molecular structure (Fig. 1) has the basic *arachno* nine-vertex shape, but is clearly shown to have the previously unreported 5-ligand configuration (schematic **II**), with a the distribution of

the five *endo* terminal and bridging hydrogen atoms about the open face being different from those in the conventionally-structured 4-LB$_9$H$_{13}$ species **1** (schematic **I**) [16–18]. The ^{1}H NMR results for each of compounds **2b** and **2c** show that the five *endo* terminal and bridging hydrogen atoms are rapidly interchanging positions with each other, in contrast to neutral 4-LB$_9$H$_{13}$ species which are generally static, but in a similar manner to anionic species [4-XB$_9$H$_{13}$]$^-$ (when X$^-$ [NCS]$^-$, [(NC)BH$_3$]$^-$) [19] and to the [B$_9$H$_{14}$]$^-$ anion [20] and its conjugate acid, neutral '*iso*'-B$_9$H$_{15}$ [21]. An interesting feature in the solid state structure of **2c** is the extended stacking (along the *a* axis) of the phenylpyridine ligands (Fig. 2). The stacking is 'step-like' in nature such that the phenyl group of one molecule stacks directly over the pyridyl group of the molecule beneath and so on. A similar phenomenon is recently noted in mutual polymorphs of 6,9-(C$_5$H$_5$N)$_2$-*arachno*-B$_{10}$H$_{12}$ [22]. This interesting supramolecular assembly behaviour has possible implications for crystal engineering in precursive work to nano-layered boron, boron–carbon, boron–nitrogen, etc. ceramic materials. We currently extend studies to other ligands L, to the quantitative measurement of the fluxionalities and of the **2** → **1** interconversions and thence to the factors that might stabilize the structure type **2**, to conditions that might further favour the formation of the new isomers **2** rather than isomers of type **1**, and to the further investigation of ligand stacking phenomena in these and other related boron systems.

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[3] Crystal data: C$_{11}$H$_{22}$B$_9$N, monoclinic, $a = 5.5868(6)$, $b = 19.804(3)$, $c = 14.428(2)$ Å, $\beta = 97.036(13)°$, $U = 1584.3(4)$ Å^3, $P2_1/n$, $Z = 4$. 2486 independent reflections collected ($\pm h$, $+k$, $+l$) for $3.81 \leq \theta \leq 64.39°$ [Stoe STADI4 diffractometer, 200(2) K, Cu K$_\alpha$, $\bar{\lambda}$ 1.54184 Å]. Empirical absorption correction (ψ scans) applied. Structure solved by direct methods [SHELXS-86] [13] and refined by full-matrix least-squares [SHELXL-93] [14]. Non-hydrogen atoms refined anisotropically; ligand hydrogen atoms constrained to ideal positions; borane-cluster hydrogen atoms located on a Fourier difference map and freely refined isotropically. The bridging/*endo* hydrogen atom associated with B(5) appeared to be disordered with half-occupancy over the two positions B(4)B(5) and B(5)B(6). 2477 data refined by full-matrix least-squares on F^2 (12 restraints, 242 parameters) to final residuals (all data) $R_1 = 0.0576$, $wR_2 = 0.1381$, G.o.F $= 1.097$.

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