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Polyhedral azaborane chemistry. The establishment of members of the *hypho*-type family $[(RH_2N)B_8H_{11}NHR]$, where groups R are now other than ethyl

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The reaction of $[B_9H_{13}(SMe_2)]$ with primary amines NH_2R to give eight-boron cluster species $[(RH_2N)B_8H_{11}NHR]$ is not limited to the case where R = ethyl. We find that the *n*-butyl, isopropyl and *tert*-butyl analogues are also readily formed. The structural type is illustrated by a single-crystal X-ray diffraction analysis on the isopropyl member of the family. The reaction proceeds stepwise, *via* an initial ligand exchange on $[B_9H_{13}(SMe_2)]$ to give $[B_9H_{13}(NH_2R)]$, as confirmed by treatment of $[B_9H_{13}(SMe_2)]$ with NH_2Bu^t to give $[B_9H_{13}(NH_2Bu^t)]$ followed by treatment with Pr^iH_2N to give the mixed species $[(Pr^iH_2N)B_8H_{11}NHBu^t]$, also confirmed by single-crystal X-ray work, and showing that the amine on the starting *arachno*-$\{B_9H_{13}\}$ residue is the one that finishes in the more intimately bound bridging position.

In the initial exploratory work in the investigation of the preparation and chemistry of *arachno* nonaborane species $[4\text{-}LB_9H_{13}]$, where L is a two-electron donor ligand (compounds **1**, schematic structure **I**), it was found that a convenient route to many of these was by displacement of the SMe_2 ligand from $[4\text{-}(SMe_2)B_9H_{13}]$ (compound **1a**) by stronger ligands L [equation (1)]. In this manner compounds where L is PPh_3,

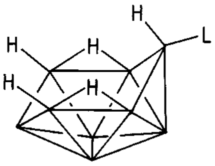
$$L + \underset{\textbf{1a}}{[(SMe_2)B_9H_{13}]} \longrightarrow [LB_9H_{13}] + SMe_2 \qquad (1)$$

MeCN, a substituted pyridine, NEt_3, or $NHEt_2$, were made in yields of 60–80%.[1] Exceptionally, it was found that use of NH_2Et did not give $[(EtH_2N)B_9H_{13}]$, but, instead, a 70% yield of a different type of product, compound **2a**, was obtained. This was initially formulated[1] as $[NH_3Et]^+[B_9H_{12}(NH_2Et)]^-$, but was subsequently shown[2] to be $[(EtH_2N)B_8H_{11}NHEt]$ (schematic cluster structure **II**) [equation (2)]. In this initial

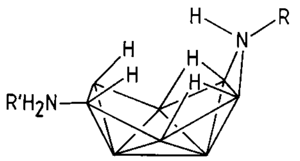
$$3\ NH_2Et + \underset{\textbf{1a}}{[(SMe_2)B_9H_{13}]} \longrightarrow H_3BNH_2Et + \underset{\textbf{2a}}{[(EtH_2N)B_8H_{11}NHEt]} + SMe_2 \qquad (2)$$

work, compound **2a** was proposed to be an analogue of a hypothetical $\{B_8H_{13}\}^-$ anion of *arachno* eight-vertex constitution, with a two-electron three-centre BBN bridge joining the {NHEt} moiety to the cluster.[2] Assigned ^{11}B NMR spectra, however, now show that it is not isospectral with ostensibly closer *arachno* analogues such as $[B_8H_{12}(PMe_2Ph)]$, and suggest that the eight-boron unit is better regarded as formally analogous to that of a $\{B_8H_{14}\}^{2-}$ anion, and therefore as of *hypo*-type eight-vertex character,[3] perhaps implying two two-electron bonds between the {NHEt} moiety and the cluster.

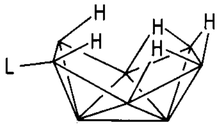
This one-boron dismantling process to give the eight-boron *hypho* product **2** has, so far, been believed to be unique to the reaction with the aliphatic primary amine NH_2Et, although, where L is the $[NCS]^-$ anion, a low yield of the eight-boron *arachno* type anionic species $[B_8H_{12}(NCS)]^-$ (species **3**, schematic **III**) is recorded.[4] In the initial work on these systems the reactions with other primary amines were not examined.[1] Much more recently, displacement of SMe_2 with equimolar quantities of the primary amines NH_2Bu^n, NH_2Bu^t, $NH_2(CH_2CMe_3)$ and $NH_2(CHPh)$ have been reported[5] to give the corresponding [4-(amine)B_9H_{13}] species of structure type **I** exclusively [equation (1)]. It has been proposed that an eight-boron structure of type **II** which involves two *secondary* amine residues, $\{NR_2\}$ and $\{NHR_2\}$ is probably precluded on steric grounds.[2] However, sterically and electronically there seemed to us no reason that the primary amine NH_2Et should be exceptional, and therefore that other *primary* amines should also give eight-boron species of type **II** according to equation (2). We have an interest in developing new substrates for entry into azametallaborane chemistry, for which the eight-boron $\{EtNH_2\}$–{NHEt} compound **2a** has shown initial promise, for example in the generation of seven-boron monometalla- and dimetalla-azaborane-species such as $[(PhMe_2P)_2PtB_7H_{11}NHEt]$ and $[(C_5Me_5)_2Rh_2B_7H_7NEt]$.[6,7] As part of the background work on this we have now found that compounds of structure type **II** can in fact be obtained when primary amines other than NH_2Et are used. We report here on our investigations in this area.



I



II



III

Experimental

Preparation of $[(Pr^iH_2N)B_8H_{11}NHPr^i]$ 2b, $[(Bu^tH_2N)B_8H_{11}NHBu^t]$ 2c and $[(Bu^nH_2N)B_8H_{11}NHBu^n]$ 2d

These compounds were all prepared similarly. A solution of $[B_9H_{13}(SMe_2)]$ (compound **1a**, prepared as in ref. 1; 100 mg, 580 μmol) in dry benzene (10 cm^3) was heated with a four-fold stoichiometry (2.32 mmol) of the appropriate amine (NH_2Pr^i, NH_2Bu^t or NH_2Bu^n) at reflux temperature under N_2. After 3 h, the reaction mixture was cooled and the resulting crystalline precipitate filtered off. Recrystallization from ethanol–water (1 : 1, *ca.* 4 cm^3) yielded the pure azaboranes **2** as white crystalline solids, yields 57% for **2b**, (m.p. 150); 49% for **2c** (168 °C);

Table 1 Selected NMR parameters for $[(Pr^iH_2N)B_8H_{11}NHPr^i]$ **2b**, $[(Bu^tH_2N)B_8H_{11}NHBu^t]$ **2c**, $[(Bu^nH_2N)B_8H_{11}NHBu^n]$ **2d** and $[(Pr^iH_2N)B_8H_{11}NHBu^t]$ **2e**

	2b		**2c**		**2d**		**2e**	
Position	$\delta(^{11}B)$	$\delta(^1H)$	$\delta(^{11}B)$	$\delta(^1H)$	$\delta(^{11}B)$	$\delta(^1H)$	$\delta(^{11}B)$	$\delta(^1H)$
(1)	+2.0	+2.52	+1.8	+2.59	+2.2	+2.58	+2.3	+2.59
(2)	−55.3	−0.65	−55.5	−0.68	−54.9	−0.64	−55.6	−0.68
(3)	−21.3	+1.18[a]	−23.2	+1.29[b]	−20.3	+1.20[c]	−21.3	+1.26[d]
(4)	−31.6	+0.76	−30.7	+0.65	−31.9	+0.76	−31.4	+0.80
(5)	−10.3	+2.38	−12.5	+2.56	−10.3	+2.40	−11.9	+2.56
(6)	−11.0	+2.50	−12.5	+2.59	−10.6	+2.50	−11.9	+2.59
(7)	−33.1	+0.76	−33.0	+0.65	−33.2	+0.76	−33.0	+0.80
(8)	−30.6	+0.50 −0.63	−29.5	+0.51 −0.47	−31.8	+0.76 −0.64	−30.7	+0.52 −0.54
(6,7)		−2.50		−2.25		−1.99		−2.20
(4,5)		−2.18		−2.25		−2.15		−2.31
(5,6) NH		−1.65[e]		−1.43[f]		−1.37[g]		−1.40[h]

[a] $\{Pr^iH_2N\}$ substituent site: (NH_2) at +3.97 (δ_H); (CH) at +52.2 (δ_C), +3.43 (δ_H); (CH_3) at +21.2 and +21.1 (δ_C), +1.05 (mean) (δ_H). [b] $\{Bu^tH_2N\}$ substituent site: (NH_2) at +4.12 (δ_H), Quaternary C at +55.8 (δ_C); (CH_3) at +28.4 (δ_C), +1.47 (δ_H). [c] $\{Bu^nH_2N\}$ substituent site: (NH_2) at +4.08 and +4.17 (δ_H); (CH_2) at +50.1 (δ_C), +3.11 (mean) (δ_H); (CH_2) at +30.8 (δ_C), +1.70 (mean) (δ_H); (CH_2) at +19.7 (δ_C), +1.42 (mean) (δ_H); (CH_3) at +13.5 (δ_C), +0.98 (δ_H). [d] $\{Pr^iH_2N\}$ substituent site: (NH_2) at +4.12 (δ_H); (CH) at 52.2 (δ_C), +3.45 (δ_H); (CH_3) at +22.0 and +21.9 (δ_C), +1.41 (mean) (δ_H). [e] (CH) at +52.8 (δ_C), +2.53 (δ_H); (CH_3) at +21.2 and +21.1 (δ_C), +1.05 (mean) (δ_H). [f] Quaternary C at +53.2 (δ_C); (CH_3) +27.3 (δ_C), +1.06 (δ_H). [g] (CH_2) +51.4 (δ_C), +2.58 (mean) (δ_H); (CH_2) +30.1 (δ_C), +1.41 (mean) (δ_H); (CH_2) +19.7 (δ_C), +1.20 (mean) (δ_H); (CH_3) +13.6 (δ_C), +0.88 (δ_H). [h] Quaternary C at +53.2 (δ_C); (CH_3) +27.3 (δ_C), +1.06 (δ_H).

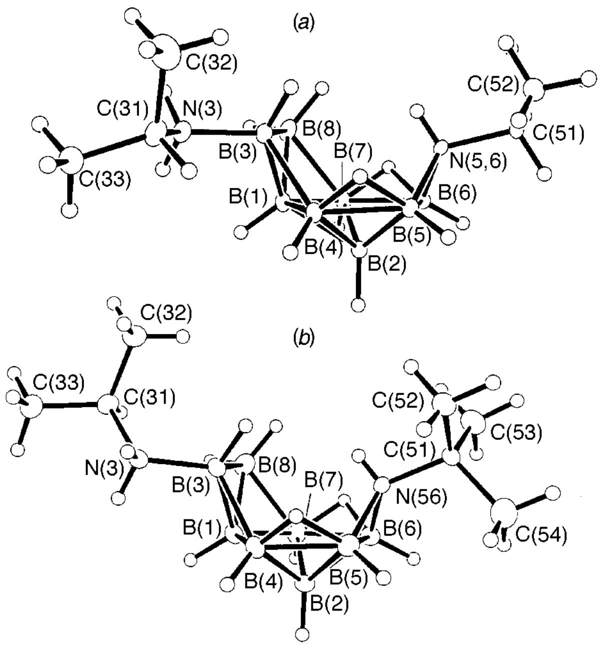


Fig. 1 ORTEP-type[8] drawings of the crystallographically determined molecular structures of $[(Pr^iH_2N)B_8H_{11}NHPr^i]$ **2b** (*a*) and $[(Pr^iH_2N)B_8H_{11}NHBu^t]$ **2e** (*b*). There is probable asymmetry of bonding to the bridging hydrogen atoms at the B(4)B(5) and B(6)B(7) positions, with boron–hydrogen distances from the B(4) and B(7) 'hinge' positions at 1.19(3)–1.22(2) Å being possibly shorter than those from the more exposed B(5) and B(6) positions at 1.32(2)–1.35(3) Å. This is consistent with the apparently differential couplings $^1J(^{11}B\text{-}^1H)$ observed in $^1H\text{-}\{^{11}B\}$ selective NMR experiments associated both with this work and that in ref. 3

and 42% for **2d** (oil), identified by NMR spectroscopy (Table 1) and mass spectrometry, and, for compound **2b**, by a single-crystal X-ray diffraction analysis [Fig. 1(*a*) and Table 2].

Preparation of $[(Pr^iH_2N)B_8H_{11}NHBu^t]$ 2e

To a solution of $[B_9H_{13}(NH_2Bu^t)]$ (compound **1b**, prepared as in ref. 5; 300 mg, 1.63 mmol) in benzene (10 cm^3) was added NH_2Pr^i (0.202 g, 3.4 mmol) at room temperature. The solution was then heated at reflux for 3 h. Examination of the product mixture by integrated NMR spectroscopy revealed a *ca.* 20:80 mol % mixture of the bis(isopropyl) compound **2b** (19%), and the mixed isopropyl–*tert*-butyl species $[(Pr^iH_2N)B_8H_{11}NHBu^t]$ (compound **2e**) (81%). Recrystallisation from ethanol–water (1:1, *ca.* 6 cm^3) thence gave pure **2e** (m.p. 162 °C; 172 mg, 46%), characterized by NMR spectroscopy (Table 1), mass spectrometry, and a single-crystal X-ray diffraction analysis [Table 2 and Fig. 1(*b*)].

Table 2 Selected interatomic distances (Å) for $[(EtH_2N)B_8H_{11}NHEt]$ **2a** (data from ref. 2), $[(Pr^iH_2N)B_8H_{11}NHPr^i]$ **2b** and $[(Pr^iH_2N)B_8H_{11}NHBu^t]$ **2e**

	2a	**2b**	**2e**
B(1)–B(2)	1.813(9)	1.819(2)	1.823(4)
B(1)–B(3)	1.709(10)	1.707(2)	1.705(4)
B(1)–B(4)	1.769(8)	1.762(2)	1.747(4)
B(1)–B(7)	1.741(8)	1.743(2)	1.754(3)
B(1)–B(8)	1.726(9)	1.718(2)	1.714(4)
B(2)–B(4)	1.812(9)	1.800(2)	1.809(4)
B(2)–B(5)	1.810(10)	1.767(2)	1.775(4)
B(2)–B(6)	1.793(7)	1.771(2)	1.773(4)
B(2)–B(7)	1.791(9)	1.803(2)	1.804(4)
B(3)–B(4)	1.919(9)	1.896(2)	1.882(4)
B(3)–B(8)	1.918(9)	1.914(2)	1.906(4)
B(4)–B(5)	1.841(9)	1.819(2)	1.813(4)
B(5)–B(6)	1.989(9)	1.963(2)	1.962(4)
B(6)–B(7)	1.825(8)	1.815(2)	1.819(4)
B(7)–B(8)	1.902(9)	1.913(2)	1.900(4)
B(3)–N(3)	1.578(7)	1.592(2)	1.584(3)
B(5)–N(5,6)	1.573(9)	1.557(2)	1.566(3)
B(6)–B(5,6)	1.572(9)	1.560(2)	1.552(3)
N(3)–C(31)	1.500(8)	1.510(2)	1.509(3)
N(5,6)–C(51)	1.490(7)	1.497(2)	1.509(3)

Nuclear magnetic resonance spectroscopy

The NMR spectroscopy was performed at *ca.* 5.9 and 9.4 T (fields corresponding to 250 and 400 MHz ^1H frequencies respectively) using commercially available instrumentation and using techniques and procedures as described elsewhere.[3,9,10] Chemical shifts δ are given in ppm relative to $\Xi = 100$ MHz for $\delta(^1H)$ (±0.05 ppm) (nominally $SiMe_4$), $\Xi = 32.083\,972$ MHz for $\delta(^{11}B)$ (±0.5 ppm) (nominally $[F_3B\cdot OEt_2]$ in $CDCl_3$),[11,12] and $\Xi = 25.145\,004$ MHz for $\delta(^{13}C)$ (±0.5 ppm) (nominally $SiMe_4$); Ξ is as defined in ref. 13.

Table 3 Crystal data and details of refinement for compounds **2b** and **2e**

	2b	**2e**
Empirical formula	$C_6H_{28}B_8N_2$	$C_7H_{30}B_8N_2$
M	214.79	228.81
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$Pbca$
a/Å	15.2254(7)	10.8180(10)
b/Å	6.0820(3)	11.1465(13)
c/Å	16.1216(7)	25.451(2)
β/°	101.716(4)	—
U/Å^3	1461.77(11)	3069.0(5)
Z	4	8
D_c/Mg m^{-3}	0.976	0.990
μ/mm^{-1}	0.338	0.346
F(000)	472	1008
Crystal size/mm	0.56 × 0.36 × 0.22	0.66 × 0.30 × 0.12
θ_{min}, θ_{max}/°	3.64, 64.09	3.47, 64.37
hkl Ranges	−17 to 17, −6 to 6, −18 to 18	0–12, 0–12, 0–29
Reflections collected	4238	2480
Independent reflections, p	2287	2480
R_{int} [a]	0.023	—
Reflections with $F_o^2 > 2\sigma F_o^2$	2142	1897
Weighting scheme parameters a, b [b]	0.0513, 0.7548	0.0523, 2.3503
Extinction coefficient, x [c]	0.0062(6)	—
Data, parameters (n)	2286, 194	2472, 207
Goodness of fit on F^2, S [d]	1.037	1.025
$R1$ [e]	0.0416	0.0527
$wR2$ [f]	0.1104	0.1557
Largest difference map peak and hole/e Å^{-3}	0.251 and −0.176	0.398 and −0.322

[a] $R_{int} = \Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma F_o^2$. [b] $w = [\sigma^2(F_o^2) + aP^2 + bP)]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$. [c] F_c has been multiplied by $k[1 + 0.001xF_c^2\lambda^3/\sin(2\theta)]^{\frac{1}{4}}$ where k is the overall scale factor. [d] $[\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{\frac{1}{2}}$. [e] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [f] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(F_o^2)^2]^{\frac{1}{2}}$.

Single-crystal X-ray diffraction analysis

Crystals of $[(Pr^iH_2N)B_8H_{11}NHPr^i]$ **2b** and of $[(Pr^iH_2N)B_8H_{11}NHBu^t]$ **2e** suitable for the single-crystal X-ray work were both grown from ethanol–water (1:1). All crystallographic measurements were carried out at 120 K using a Stoe STADI4 diffractometer operating in the ω–θ scan mode using Cu-Kα radiation (λ = 1.541 85 Å). Crystal data and refinement parameters for both structures are listed in Table 3. Cell dimensions were refined from the values of 40 selected reflections (together with their Freidel opposites) measured at ±2θ in order to minimize systematic errors.

Both structures were solved by direct methods using SHELXS 86[14] and were refined by full-matrix least squares (against all the unique F^2 data) using SHELXL 93.[15] Refinement was the same for both structures. All non-hydrogen atoms were refined with anisotropic displacement parameters. Amine-associated hydrogen atoms were constrained to idealized positions with a riding model including free rotation of methyl groups, whilst the cluster-associated hydrogen atoms were located on Fourier-difference syntheses and were freely refined isotropically.

Atomic coordinates, thermal parameters, and interatomic distances and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions to Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quite the full literature citation and the reference number 186/566.

Results and Discussion

It is apparent from the results that the primary amines NH_2Pr^i, NH_2Bu^t or NH_2Bu^n react with nine-boron *arachno*-$[(SMe_2)B_9H_{13}]$ **1a** to give the corresponding eight-boron *hypho* species $[(RH_2N)B_8H_{11}NHR]$ (where R is Pr^i **2b**, Bu^t **2c** or Bu^n **2d**) according to equation (1) in reasonable yield. In this regard they therefore mimic the ethyl analogue NH_2Et in the original report,[1] and so this reaction and the resulting *hypho* structural type are not limited just to the ethylamine species **2a**. In accord with this, structurally the single-crystal X-ray study of the isopropylamine compound **2b** (Table 2 and Fig. 1) clearly shows it to be a direct analogue of the initially reported ethylamine derivative **2a**. In the original structural work on compound **2a**,[2] it was noted that there was steric crowding associated with the open face, so that, for example, a second organic group would be very sterically compromised in this position, which presumably inhibited the formation of compounds of type **2** with other ligand types. The van der Waals radius plot in Fig. 2 shows that this is indeed the case, and that moieties much bulkier than a one-atom unit would on this basis not seem to be accommodated in the position occupied by this nitrogen-bound hydrogen atom. Although this nitrogen-bound hydrogen atom, the two *endo* and the two bridging hydrogen atoms fill the open face, it is apparent from Fig. 2 that the organic groups on the amines are distal from this open face, and therefore the more demanding isopropyl

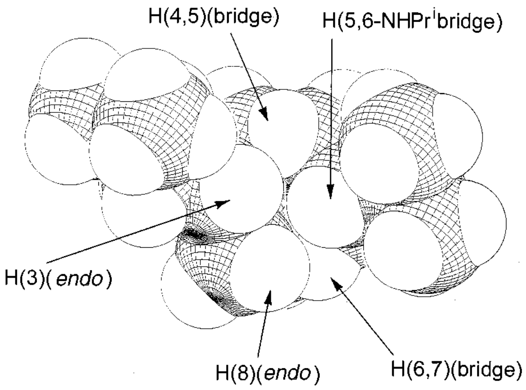


Fig. 2 A van der Waals radius drawing of the molecular structure of $[(Pr^iH_2N)B_8H_{11}NHPr^i]$ **2b**, showing the pocket of steric crowding arising from the close juxtapositioning of the bridging and *endo* borane hydrogen atoms and the *endo* amine hydrogen atom about the open face. The view chosen is the enantiomer of that in Fig. 1

groups do not influence the basic cluster structure (Table 2) or NMR spectroscopic parameters (Table 1). Thermodynamically the {NPr^i} molecule **2b** is therefore not significantly destabilised relative to the original {NEt} species **2a** and, in view of the ready syntheses, there is obviously also no significantly different kinetic steric barrier. This must also apply to the {NBu^t} derivative **2c**. The X-ray-derived structural data for **2a** and **2b** (Table 2) show very similar structures, with interboron distances essentially identical within experimental error. The NMR spectroscopic data among all the family members **2a**–**2e** are also very similar (Table 1), although there are some minor variations in proton shielding as the organoamine group changes, which can be diagnostic (see below in the characterisation of compound **2e**).

The reaction to incorporate two amine residues is obviously more than a single-step process. It was therefore of interest to confirm that the initial stage was the straightforward replacement, as established elsewhere for some amines,[1,5] and then to examine for the second step using a different amine. This would then in principle result in the generation of mixed amine compounds [(R′H$_2$N)B$_8$H$_{11}$NHR] of potential synthetic interest. Additionally, the knowledge of which of the two amine residues occupied the bridge and *exo*-terminal positions would then give initial information about possible mechanistic pathways, of interest in attempts to find ready routes to substrates with eight boron atoms and fewer. We examined for this by use of the *tert*-butylamine nine-boron *arachno* species [B$_9$H$_{13}$(NH$_2$Bu^t)] (compound **1b**) as starting substrate, one reason for this choice being that the high basicity of the *tert*-butylamine residue should minimize any tendency to exchange in further reaction with a less basic amine. Thus a straightforward 1:1 stoichiometric exchange reaction [equation (1)][5] between [B$_9$H$_{13}$(SMe$_2$)] (compound **1a**) with NH$_2$Bu^t gave [B$_9$H$_{13}$(NH$_2$Bu^t)] (compound **1b**), readily confirmed as such by NMR spectroscopy in comparison with literature values.[5] Treatment of this with a slight excess of NH$_2$Pr^i in refluxing benzene solution thence gave the eight-boron mixed species [(Pr^{i}H$_2$N)B$_8$H$_{11}$NHBu^t] (compound **2e**). NMR spectroscopy showed that this constituted *ca.* 80% of the product mixture, the remaining 20% being [(Pr^{i}H$_2$N)-B$_8$H$_{11}$NHPr^i] (compound **2b**), demonstrating some initial ligand exchange with the excess NH$_2$Pr^i under the reaction conditions. Pure **2e** was readily obtained by recrystallisation. Comparative NMR spectroscopy readily established the constitution of this mixed compound **2e**. In particular the high-field NH position in the ^{1}H NMR spectrum at $\delta(^1\text{H})$ -1.40 was analogous to that in the bis(*tert*-butyl) species **2c** at -1.43, rather than the bis(isopropyl) species **2b** at -1.65, thus demonstrating the siting of the {NHBu^t} residue in the bridging position, and the siting of the incoming {NH$_2$Pr^i} residue in the *exo*-terminal position. These relative dispositions of the isopropyl and *tert*-butyl groupings in compound **2e** were confirmed by the results of single-crystal X-ray diffraction analysis (Table 2 and Fig. 1). Mechanistically, therefore, in the formation of compounds of the general type **2** formulation [(R′H$_2$N)B$_8$H$_{11}$NHR], it is the amine residue in the [B$_9$H$_{13}$(NH$_2$R)] starting material **1** that becomes incorporated more intimately in the {NHR} bridge position, whereas the new incoming NH$_2$R′ residue is the one that appears in the pendant *exo* {NH$_2$R′} position [equation (3)]. There are no significant geometric differences in the common structural features of the isopropyl–isopropyl species **2b** and the mixed species **2e** (Table 2 and Fig. 1), and their NMR spectroscopic parameters (Table 1) are also very similar indeed, apart from the small diagnostic differences in the ^{1}H shieldings of the open-face hydrogen atoms as mentioned in the last paragraph.

$$2\,\mathrm{NH_2R'} + \underset{\mathbf{1}}{[(\mathrm{RH_2N})\mathrm{B_9H_{13}}]} \longrightarrow \underset{\mathbf{2}}{[(\mathrm{R'H_2N})\mathrm{B_8H_{11}NHR}]} + \mathrm{H_3BNH_2R'} \qquad (3)$$

No reaction of [B$_9$H$_{13}$(NH$_2$Bu^t)] (compound **1b**) was found to occur with the less basic aromatic primary amine NH$_2$Ph, or with the weakly basic SMe$_2$ under the same conditions (refluxing solution in benzene). With an excess of the more basic but sterically more challenged secondary amine NHEt$_2$ a slow reaction with the NH$_2$Bu^t compound **1b** did occur. However, the monitoring of the proceeding reaction mixture by NMR spectroscopy showed that progressive loss of compound **1b** occurred exclusively to give only H$_3$BNHR$_2$ [$\delta(^{11}\text{B})$ -16.1; compare H$_3$BNHEt$_2$ (lit.[12] -17.0)], implying that any initial polyborane species formed was unstable with respect to an immediate terminal degradative cascade process involving a complete cluster dismantling. There are therefore still problems associated with the extension of this system to include residues other than those of aliphatic primary amines, but the demonstration that a suite of these, rather than just the ethyl analogue, are easily synthesised in reasonable yield and thereby available for further chemistry, should assist the development of the chemistry of polyhedral boron-containing clusters involving seven or eight boron atoms, an area that is generally difficult to enter into.

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