

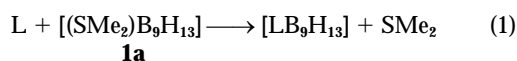
Polyhedral azaborane chemistry. The establishment of members of the *hypho*-type family [(RH₂N)B₈H₁₁NHR], where groups R are now other than ethyl

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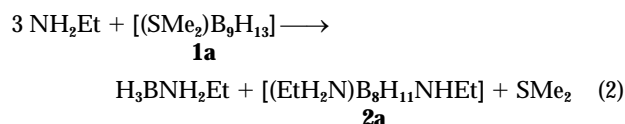
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The reaction of [B₉H₁₃(SMe₂)] with primary amines NH₂R to give eight-boron cluster species [(RH₂N)B₈H₁₁NHR] is not limited to the case where R = ethyl. We find that the *n*-butyl, isopropyl and *tert*-butyl analogues are also readily formed. The structural 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 [B₉H₁₃(SMe₂)] to give [B₉H₁₃(NH₂R)], as confirmed by treatment of [B₉H₁₃(SMe₂)] with NH₂Bu^t to give [B₉H₁₃(NH₂Bu^t)] followed by treatment with Pr^tH₂N to give the mixed species [(Pr^tH₂N)B₈H₁₁NHBu^t], also confirmed by single-crystal X-ray work, and showing that the amine on the starting *arachno*-{B₉H₁₃} 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-LB₉H₁₃], 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 SMe₂ ligand from [4-(SMe₂)B₉H₁₃] (compound **1a**) by stronger ligands L [equation (1)]. In this manner compounds where L is PPh₃,

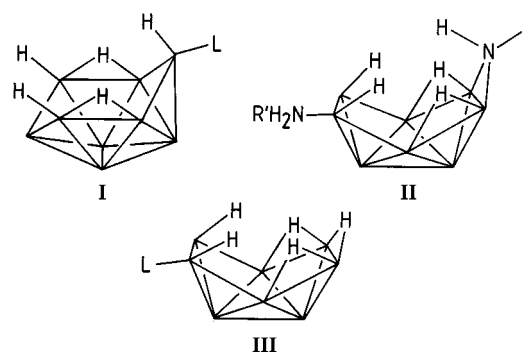


MeCN, a substituted pyridine, NEt₃, or NHEt₂, were made in yields of 60–80%.¹ Exceptionally, it was found that use of NH₂Et did not give [(EtH₂N)B₉H₁₃], but, instead, a 70% yield of a different type of product, compound **2a**, was obtained. This was initially formulated¹ as [NH₃Et]⁺[B₉H₁₂(NH₂Et)][−], but was subsequently shown² to be [(EtH₂N)B₈H₁₁NHET] (schematic cluster structure **II**) [equation (2)]. In this initial



work, compound **2a** was proposed to be an analogue of a hypothetical {B₈H₁₃}[−] anion of *arachno* eight-vertex constitution, with a two-electron three-centre BBN bridge joining the {NHET} moiety to the cluster.² Assigned ¹¹B NMR spectra, however, now show that it is not isospectral with ostensibly closer *arachno* analogues such as [B₈H₁₂(PMe₂Ph)], and suggest that the eight-boron unit is better regarded as formally analogous to that of a {B₈H₁₄}^{2−} anion, and therefore as of *hypho*-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 NH₂Et, although, where L is the [NCS][−] anion, a low yield of the eight-boron *arachno* type anionic species [B₈H₁₂(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 SMe₂ with equimolar quantities of the primary amines NH₂Buⁿ, NH₂Bu^t, NH₂(CH₂CMe₃) and NH₂(CHPh) have been reported⁵ to give the corresponding [4-(amine)B₉H₁₃] 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, {NR₂} and {NHR₂} is probably precluded on steric grounds.² However, sterically and electronically there seemed to us no reason that the primary amine NH₂Et 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 {EtNH₂}–{NHET} compound **2a** has shown initial promise, for example in the generation of seven-boron monometalla- and dimetalla-azaborane-species such as [(PhMe₂P)₂PtB₇H₁₁NHET] and [(C₅Me₅)₂-Rh₂B₇H₇NEt].^{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 NH₂Et are used. We report here on our investigations in this area.

Experimental

Preparation of [(Pr^tH₂N)B₈H₁₁NHPr^t] **2b**, [(Bu^tH₂N)B₈H₁₁NHBu^t] **2c** and [(BuⁿH₂N)B₈H₁₁NHBuⁿ] **2d**

These compounds were all prepared similarly. A solution of [B₉H₁₃(SMe₂)] (compound **1a**, prepared as in ref. 1; 100 mg, 580 μmol) in dry benzene (10 cm³) was heated with a four-fold stoichiometry (2.32 mmol) of the appropriate amine (NH₂Pr^t, NH₂Bu^t or NH₂Buⁿ) at reflux temperature under N₂. After 3 h, the reaction mixture was cooled and the resulting crystalline precipitate filtered off. Recrystallization from ethanol–water (1 : 1, *ca.* 4 cm³) 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^dH₂N)B₈H₁₁NHPr^d] **2b**, [(Bu^dH₂N)B₈H₁₁NHBu^d] **2c**, [(Bu^hH₂N)B₈H₁₁NHBu^h] **2d** and [(Pr^dH₂N)-B₈H₁₁NHBu^d] **2e**

	2b		2c		2d		2e	
Position	δ(¹¹ B)	δ(¹ H)	δ(¹¹ B)	δ(¹ H)	δ(¹¹ B)	δ(¹ H)	δ(¹¹ B)	δ(¹ H)
(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)		-1.65 ^e		-1.43 ^f		-1.37 ^g		-1.40 ^h
NH								

^a {Pr^dH₂N} substituent site: (NH₂) at +3.97 (δ_H); (CH) at +52.2 (δ_C), +3.43 (δ_H); (CH₃) at +21.2 and +21.1 (δ_C), +1.05 (mean) (δ_H).
^b {Bu^dH₂N} substituent site: (NH₂) at +4.12 (δ_H), Quaternary C at +55.8 (δ_C); (CH₃) at +28.4 (δ_C), +1.47 (δ_H). ^c {Bu^hH₂N} substituent site: (NH₂) at +4.08 and +4.17 (δ_H); (CH₂) at +50.1 (δ_C), +3.11 (mean) (δ_H); (CH₂) at +30.8 (δ_C), +1.70 (mean) (δ_H); (CH₂) at +19.7 (δ_C), +1.42 (mean) (δ_H); (CH₃) at +13.5 (δ_C), +0.98 (δ_H). ^d {Pr^dH₂N} substituent site: (NH₂) at +4.12 (δ_H); (CH) at 52.2 (δ_C), +3.45 (δ_H); (CH₃) at +22.0 and +21.9 (δ_C), +1.41 (mean) (δ_H). ^e (CH) at +52.8 (δ_C), +2.53 (δ_H); (CH₃) at +21.2 and +21.1 (δ_C), +1.05 (mean) (δ_H). ^f Quaternary C at +53.2 (δ_C); (CH₃) +27.3 (δ_C), +1.06 (δ_H). ^g (CH₂) +51.4 (δ_C), +2.58 (mean) (δ_H); (CH₂) +30.1 (δ_C), +1.41 (mean) (δ_H); (CH₂) +19.7 (δ_C), +1.20 (mean) (δ_H); (CH₃) +13.6 (δ_C), +0.88 (δ_H). ^h Quaternary C at +53.2 (δ_C); (CH₃) +27.3 (δ_C), +1.06 (δ_H).

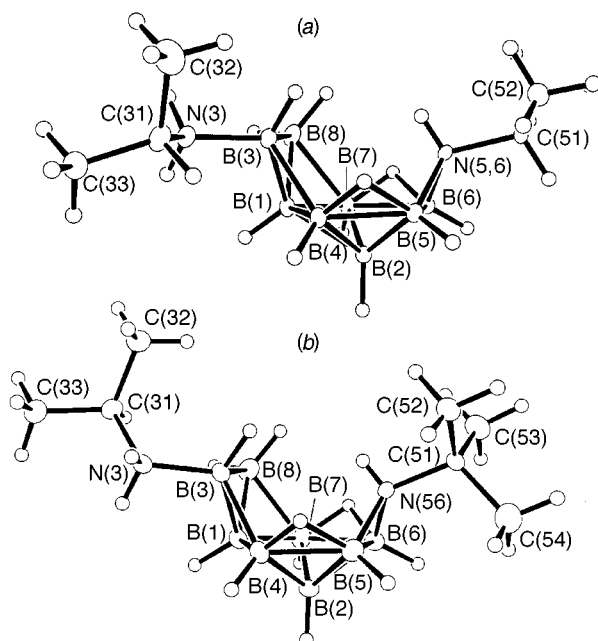


Fig. 1 ORTEP-type⁸ drawings of the crystallographically determined molecular structures of [(Pr^dH₂N)B₈H₁₁NHPr^d] **2b** (a) and [(Pr^dH₂N)B₈H₁₁NHBu^d] **2e** (b). There is probable asymmetry of bonding to the bridging hydrogen atoms at the B(4)B(5) and B(6)B(7) positions, with boron-hydrogen distances 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(¹¹B–¹H) observed in ¹H–{¹¹B} 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^dH₂N)B₈H₁₁NHBu^d] **2e**

To a solution of [B₉H₁₃(NH₂Bu)⁺] (compound **1b**, prepared as in ref. 5; 300 mg, 1.63 mmol) in benzene (10 cm³) was added NH₂Pr^d (0.202 g, 3.4 mmol) at room temperature. The solution

Table 2 Selected interatomic distances (Å) for [(EtH₂N)B₈H₁₁NHEt] **2a** (data from ref. 2), [(Pr^dH₂N)B₈H₁₁NHPr^d] **2b** and [(Pr^dH₂N)B₈H₁₁NHBu^d] **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)

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^dH₂N)B₈H₁₁NHBu^d] (compound **2e**) (81%). Recrystallisation from ethanol–water (1:1, ca. 6 cm³) 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)].

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 Ξ = 100 MHz for δ(¹H) (±0.05 ppm) (nominally SiMe₄), Ξ = 32.083 972 MHz for δ(¹¹B) (±0.5 ppm) (nominally [F₃B·OEt₂] in CDCl₃),^{11,12} and Ξ = 25.145 004 MHz for δ(¹³C) (±0.5 ppm) (nominally SiMe₄); 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 ₆ H ₂₈ B ₈ N ₂	C ₇ H ₃₀ B ₈ N ₂
<i>M</i>	214.79	228.81
Crystal system	Monoclinic	Orthorhombic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>Pbca</i>
<i>a</i> /Å	15.2254(7)	10.8180(10)
<i>b</i> /Å	6.0820(3)	11.1465(13)
<i>c</i> /Å	16.1216(7)	25.451(2)
β/°	101.716(4)	—
<i>U</i> /Å ³	1461.77(11)	3069.0(5)
<i>Z</i>	4	8
<i>D_c</i> /Mg m ^{−3}	0.976	0.990
μ/mm ^{−1}	0.338	0.346
<i>F</i> (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
<i>hkl</i> Ranges	−17 to 17, −6 to 6, −18 to 18	0–12, 0–12, 0–29
Reflections collected	4238	2480
Independent reflections, <i>p</i>	2287	2480
<i>R</i> _{int} ^a	0.023	—
Reflections with <i>F</i> _o ² > 2σ <i>F</i> _o ²	2142	1897
Weighting scheme parameters <i>a</i> , <i>b</i> ^b	0.0513, 0.7548	0.0523, 2.3503
Extinction coefficient, <i>x</i> ^c	0.0062(6)	—
Data, parameters (<i>n</i>)	2286, 194	2472, 207
Goodness of fit on <i>F</i> ² , <i>S</i> ^d	1.037	1.025
<i>R</i> 1 ^e	0.0416	0.0527
<i>wR</i> 2 ^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 $R_{\text{int}} = \sum |F_o^2 - F_o^2(\text{mean})| / \sum F_o^2$. ^b $w = [\sigma^2(F_o^2) + aF^2 + bP]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$. ^c F_c has been multiplied by $k[1 + 0.001xF_c^2\lambda^3/\sin(2\theta)]^4$ where k is the overall scale factor. ^d $\sum w(F_o^2 - F_c^2)^2 / (n - p)$. ^e $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^f $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum (F_o^2)^2]^{1/2}$.

Single-crystal X-ray diffraction analysis

Crystals of [(PrⁱH₂N)B₈H₁₁NHPrⁱ] **2b** and of [(PrⁱH₂N)B₈H₁₁NHBuⁱ] **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 Friedel opposites) measured at ±2θ in order to minimize systematic errors.

Both structures were solved by direct methods using SHELXS 86¹⁴ 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 quote the full literature citation and the reference number 186/566.

Results and Discussion

It is apparent from the results that the primary amines NH₂Prⁱ, NH₂Buⁱ or NH₂Buⁿ react with nine-boron *arachno*-[(SMe₂)B₉H₁₃] **1a** to give the corresponding eight-boron *hypho* species [(R₂H₂N)B₈H₁₁NHR] (where R is Prⁱ **2b**, Buⁱ **2c** or Buⁿ **2d**) according to equation (1) in reasonable yield. In this regard they therefore mimic the ethyl analogue NH₂Et in the original report,¹ and so this reaction and the resulting *hypho* structural type are not limited just to the ethylamine species

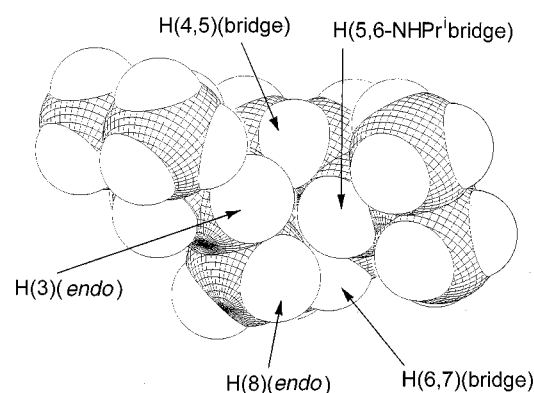


Fig. 2 A van der Waals radius drawing of the molecular structure of [(PrⁱH₂N)B₈H₁₁NHPrⁱ] **2b**, showing the pocket of steric crowding arising from the close juxtapositioning of the bridging and *endo* borane hydrogen atoms and the *endo* amine hydrogen atom about the open face. The view chosen is the enantiomer of that in Fig. 1

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

groups do not influence the basic cluster structure (Table 2) or NMR spectroscopic parameters (Table 1). Thermodynamically the {NPr⁴} 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 {NBu⁴} 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'H₂N)B₉H₁₃NHR] 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 [B₉H₁₃(NH₂Bu⁴)] (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 [B₉H₁₃(SMe₂)] (compound **1a**) with NH₂Bu⁴ gave [B₉H₁₃(NH₂Bu⁴)] (compound **1b**), readily confirmed as such by NMR spectroscopy in comparison with literature values.⁵ Treatment of this with a slight excess of NH₂Pr⁴ in refluxing benzene solution thence gave the eight-boron mixed species [(Pr'H₂N)B₈H₁₁NHBu⁴] (compound **2e**). NMR spectroscopy showed that this constituted *ca.* 80% of the product mixture, the remaining 20% being [(Pr'H₂N)-B₈H₁₁NHPr⁴] (compound **2b**), demonstrating some initial ligand exchange with the excess NH₂Pr⁴ 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 ¹H NMR spectrum at δ(¹H) –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 {NHBu⁴} residue in the bridging position, and the siting of the incoming {NH₂Pr⁴} 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'H₂N)B₈H₁₁NHR], it is the amine residue in the [B₉H₁₃(NH₂R)] starting material **1** that becomes incorporated more intimately in the {NHR} bridge position, whereas the new incoming NH₂R' residue is the one that appears in the pendant *exo* {NH₂R'} 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 ¹H shieldings of the open-face hydrogen atoms as mentioned in the last paragraph.

No reaction of [B₉H₁₃(NH₂Bu⁴)] (compound **1b**) was found to occur with the less basic aromatic primary amine NH₂Ph, or with the weakly basic SMe₂ under the same conditions (refluxing solution in benzene). With an excess of the more basic but sterically more challenged secondary amine NHET₂ a slow reaction with the NH₂Bu⁴ 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 H₃BNHR₂ [δ(¹¹B) –16.1; compare H₃BNHET₂ (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.

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft for a Fellowship to U. D., and the EPSRC for equipment grants.

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Received 19th March 1997; Paper 7/01930K

