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Synthesis of N-substituted derivatives of the *hypho*-(amine)(amino)B_8H_{11} system

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It is a pleasure for the authors to be able to dedicate this paper to Professor Sheldon G. Shore on the occasion of his 70th birthday, in recognition to his achievements and influence in inorganic chemistry.

Abstract

The chemistry of the *hypho*-(amine)(amino)B_8H_{11} system is developed by the synthesis of several derivatives by three routes. $[(Et_2HN)B_8H_{11}NEt_2]$ (**4**), characterised by single-crystal X-ray work, is prepared from the reaction between $B_9H_{13}(SMe_2)$ and Et_2NH. Methylation of $[(EtH_2N)B_8H_{11}NHEt]$ (**1**) using NaH and MeI gives, successively, $[(EtMeHN)B_8H_{11}NHEt]$ (**5**), $[(EtMe_2N)B_8H_{11}NHEt]$ (**6**) and $[(EtMe_2N)B_8H_{11}NMeEt]$ (**7**). Alternatively, a displacement reaction with $NHEt_2$ on (**1**) or on $[(MeH_2N)B_8H_{11}NHMe]$ (**2**) yields $[(Et_2HN)B_8H_{11}NHEt]$ (**8**) or $[(Et_2HN)B_8H_{11}NHMe]$ (**9**), and a displacement on (**1**) with pyridine yields $[(C_5H_5N)B_8H_{11}NHEt]$ (**10**). Phosphine-containing derivatives $[(Ph_3P)B_8H_{11}NHEt]$ (**11**) and $[(PhMe_2P)B_8H_{11}NHEt]$ (**12**) can be isolated from interaction of (**1**) with PPh_3, $[RhCl(PPh_3)_3]$ or $[PtCl_2(PMe_2Ph)_2]$.

Keywords: Boranes; *Hypho* cluster; Azaborane; N ligands; NMR spectroscopy; Crystal structure

1. Introduction

Polyhedral boron-containing cage chemistry based on eight boron atoms is relatively sparsely developed because suitable eight-boron starting materials are generally only available via multistep reactions from commercially available decaborane(14). The eight-boron species $[(EtH_2N)B_8H_{11}NHEt]$ (**1**), available in high yield in two simple steps from *nido*-$B_{10}H_{14}$, has been shown to constitute a good entry into azacarbaborane [1] and azametallaborane chemistry [2]. Its structure is based on a cluster of *hypho*-type eight-vertex character that bears two amine-derived residues, viz. one amine ligand in an *exo* terminal position and one amino group in a bridging position (Fig. 1). Compound **1**, first synthesized from $[B_9H_{13}(SMe_2)]$ and $NHEt_2$ in 1962 [3], and thence structurally identified in 1963 [4], was initially regarded as a unique compound. However, in 1997 it was reported that this route to the *hypho*-type $[(RH_2N)B_8H_{11}NHR]$ structural motif is not limited to the ethylamine system, but that other primary amine derivatives, specifically *n*-butyl, isopropyl and *tert*-butyl, could also readily be formed [5]. The synthesis was, however, limited to primary amines only. In order further to develop the area of azametallaborane chemistry containing seven or eight boron atoms we have become interested in the synthesis of additional members of this eight-boron family as starting substrates.

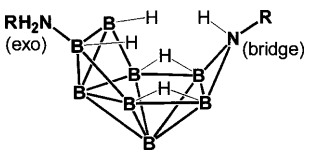

Fig. 1. Schematic structure of compounds of the *hypho*-type family $[(RH_2N)B_8H_{11}NHR]$.

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We therefore report here the syntheses of nine further species derived from the *hypho*-type (amine)-(amino)B_8H_{11} system. These were obtained by three different approaches: (a) by the direct reaction of secondary amines with $[B_9H_{13}(SMe_2)]$; (b) by the N-deprotonation and subsequent N-methylation of $[(EtH_2N)B_8H_{11}NHEt]$ (**1**); and (c) by ligand exchange on compound (**1**) and also on $[(MeH_2N)B_8H_{11}NHMe]$ (**2**) in which the *exo*-(NH_2R) group is replaced by other donor ligands.

Other eight-boron azaboranes are rare, and are limited to those in the nine-vertex *nido* and *arachno* $\{NB_8\}$ systems [6–10], and the ten-vertex *arachno* $\{N_2B_8\}$, $\{CNB_8\}$ and $\{SNB_8\}$ systems [11–13]. Useful wider accounts of azaborane chemistry are in Refs. [14,15]. Boron-containing cluster compounds in the *hypho* category are not nearly as well represented as the better-known *closo*, *nido* and *arachno* cluster species. In this regard, and in view of the theme of this volume, it is particularly apposite to note that the first *hypho* boron hydride species, the $[B_5H_{12}]^-$ anion, and the Lewis-base adducts $L_2B_5H_9$, where L is a two-electron donor, were discovered by Sheldon Shore over a quarter of a century ago [16–18].

2. Results and discussion

2.1. Preparative results

2.1.1. Direct synthesis

The eight-boron cluster family $[(RH_2N)B_8H_{11}NHR]$, where R=Et (**1**) [3], Me (**2**) and ^{iso}Pr (**3**) [5] can be prepared from the reaction in refluxing benzene of $[B_9H_{13}(SMe_2)]$ with the primary amines NH_2Et, NH_2Me and $NH_2^{iso}Pr$, respectively. The reaction proceeds stepwise. First, the SMe_2 ligand is replaced by amine to give $[B_9H_{13}(NH_2R)]$ (Eq. (1)), and then reaction of additional amine with the $[B_9H_{13}(NH_2R)]$ affords the $\{B_8H_{11}\}$ cluster product by amine addition and elimination of one boron vertex (Eq. (2)). The resulting azaboranes can then be purified in reasonable overall yields by recrystallization from ethanol–water.

$$B_9H_{13}(SMe_2) + NH_2R \rightarrow B_9H_{13}(NH_2R) + SMe_2 \quad (1)$$

$$B_9H_{13}(NH_2R) + 2NH_2R \rightarrow (RH_2N)B_8H_{11}NHR + BH_3(NH_2R) \quad (2)$$

Under the same conditions no reaction was found with secondary amines. However, we have now found that use of a large, eightfold, excess of $NHEt_2$ with $[B_9H_{13}(SMe_2)]$ at a higher temperature, viz. + 100°C in toluene for 24 h can give the secondary amine analogue. $[(Et_2HN)B_8H_{11}NEt_2]$ ((**4**), 14% yield). Use of other secondary amines, however, has so far exclusively yielded only the amine-nonaborane species as in (Eq. (1)).

2.1.2. Alkylation of the nitrogen atoms

The low yield of the dialkylamine compound (**4**) by direct synthesis from $[B_9H_{13}(SMe_2)]$ prompted us to seek alternative routes for the generation of N-substituted derivatives. One approach is the replacement of the N-bound hydrogen atoms on the NH_2R group and/or on the bridging {NHR} group by alkyl substitutents. We have been able to demonstrate this using $[(EtH_2N)B_8H_{11}NHEt]$ (**1**) as starting substrate. Thus, at − 78°C, treatment a solution of (**1**) in THF with a slight excess of NaH, followed by reaction with MeI, yields $[(EtMeHN)B_8H_{11}NHEt]$ ((**5**), 37% yield) (Eq. (3)), in which a monomethylation of the *exo*-NH_2Et group to give *exo*-NHMeEt has occurred.

$$(EtNH_2)\underset{1}{B_8}H_{11}NHEt + NaH + MeI \rightarrow (EtMeNH)\underset{5}{B_8}H_{11}NHEt + H_2 + NaI \quad (3)$$

Under these conditions no other products were observed, and only one hydrogen atom was replaced, specifically one of those on the NH_2Et site. At room temperature (r.t.), by contrast, the same reaction afforded the dimethylated species $[(EtMe_2N)B_8H_{11}NHEt]$ (**6**), in a low yield. The starting material (**1**) was largely recovered, and there was no evidence of formation of the monomethylated compound (**5**). The yield of dimethylated compound (**6**) was thence logically increased by the use of two equivalents of NaH followed by addition of two equivalents of MeI in the r.t. reaction (Eq. (4)). This resulted in the isolation of compound (**6**) in 45% yield. No nitrogen methylation at the bridging {NHEt} residue was observed; presumably steric crowding in the open face of the cluster [5] inhibits any initial hydride attack at this site, and reaction at the more accessible *exo*-NH_2R unit is therefore exclusively preferred. However, the use of three equivalents of NaH and MeI in the r.t. reaction does result in the replacement of all three N-bound hydrogen atoms by methyl, to give $[(EtMe_2N)B_8H_{11}NMeEt]$ ((**7**), 57% yield) (Eq. (5)). Under the same conditions, an attempt to replace all of the N-bound hydrogen atoms in $[(^{iso}PrH_2N)B_8H_{11}NH^{iso}Pr]$ (**3**) failed, presumably because of inhibitory steric effects of the bulkier isopropyl groups; use of an excess of NaH followed by MeI resulted only in cluster decomposition.

$$(EtH_2N)\underset{1}{B_8}H_{11}NHEt + 2NaH + 2MeI \rightarrow (EtMe_2N)\underset{6}{B_8}H_{11}NHEt + 2H_2 + 2NaI \quad (4)$$

$$(EtNH_2)\underset{1}{B_8}H_{11}NHEt + 3NaH + 3MeI \rightarrow (EtMe_2N)\underset{7}{B_8}H_{11}NMeEt + 3H_2 + 3NaI \quad (5)$$

2.1.3. Substitution of the exo-NH_2R moiety by another ligand

We have found that the exchange of the *exo* amine ligand by another amine is an equally convenient route

to new N-substituted derivatives of the *hypho*-(amine)(amino)B_8H_{11} system. For example, compound (**1**) reacts with $NHEt_2$ in refluxing benzene over 3 h to give $[(Et_2HN)B_8H_{11}NHEt]$ (**8**) in 31% yield (Eq. (6)). Under the same reaction conditions, the use of $[(MeH_2N)B_8H_{11}NHMe]$ (**2**) in place of compound (**1**) leads to the formation of $[(Et_2HN)B_8H_{11}NHMe]$ (**9**) in the higher yield of 61%. The *exo*-NH_2Me group therefore appears to be a better leaving group than NH_2Et, although in this case a significant amount of $[H_3B(NHMe_2)]$ (identified by NMR spectroscopy) was also isolated. When compound (**1**) was treated under the same conditions with the tertiary amines Et_3N and NPh_3, no exchange reaction was observed. Only unreacted starting compound (**1**) was recovered, even after prolonged heating. Presumably steric effects hinder the substitution of the NH_2Et unit by these more bulky amines.

$$(EtH_2N)\overset{1}{B_8}H_{11}NHEt + NHEt_2 \rightarrow (Et_2NH)\underset{8}{B_8}H_{11}NHEt + NH_2Et \quad (6)$$

Other bases, such as pyridines and phosphines, similarly react with compound (**1**). Thus pyridine replaces the *exo*-NH_2Et unit to give $[(C_5H_5N)B_8H_{11}NHEt]$ (**10**, 61% yield), and PPh_3 analogously gives the phosphine-substituted species $[(Ph_3P)B_8H_{11}NHEt]$ (**11**, 40% yield). It is not certain whether this last exchange happens because the trivalent phosphine is kinetically a better nucleophile than the amine, or whether it is more basic to this particular boron site than the amines, even though phosphines are more generally regarded as being less basic, for example in protic systems. In a direct comparison with NPh_3, which does not react, the small nitrogen atom radius will increase the steric demands of NPh_3 compared to PPh_3, and, in addition, the nitrogen lone pair will be more significantly delocalized into the aromatic rings. In attempts to generate metallated derivatives of compound (**1**), we have found that phosphine-containing metal halide complexes can function as another source of phosphine. Thus, in the reactions of both $[RhCl(PPh_3)_3]$ and $[PtCl_2(PMe_2Ph)_2]$ with (**1**), exchange of the *exo*-ligand occurs, and, respectively, $[(Ph_3P)B_8H_{11}NHEt]$ (**11**) and $[(PhMe_2P)B_8H_{11}NHEt]$ (**12**) can be isolated in good yields. The formation of the latter contrasts to the formation of $[(PMe_2Ph)_2PtB_7H_{10}(NHEt)]$ from the same reagents in the presence of NaH in CH_2Cl_2 solution 2(c).

2.2. NMR spectroscopic results

NMR data for compound (**2**), and for compounds **4**–**12**, are given in Table 1. Assignments are readily made by comparison with data reported previously, for example for compounds (**1**) [19] and (**3**) [5]. The 'primary amine' azaboranes of the type $[(RH_2N)B_8H_{11}NHR]$ are easily identified by NMR spectroscopy, as their ^{11}B NMR spectra present a characteristic shielding pattern over the quite large range of ca. −55 to +5 ppm, showing only minor differences in their overall ^{11}B cluster shielding patterns. A change of the ligands to a secondary amine residue, or to pyridine or to a phosphine, however, shows significant substituent effects at the substituted B(3) and bridged B(5) and B(6) sites, although the shieldings at other sites remain largely very similar to the primary amine models. Thus, when the H atoms of the *exo*-NH_2R group in compound (**1**) are successively replaced by methyl groups, $\delta(^{11}B)$ for B(3) is shifted progressively to lower shielding, from −20.0 ppm in (**1**) to −15.5 ppm in (**5**) and thence to −11.3 ppm in (**6**). Likewise, in compounds (**4**) and (**7**) the resonances of the boron atoms B(5) and B(6) are shifted by ca. 7 ppm to low field relative to (**1**) when the hydrogen atom of the {NHR} bridge is substituted by an alkyl group. Interestingly in this context, replacement of the *exo*-amine ligand by pyridine, in compound (**10**), has an effect on the B(3) chemical shift similar to a secondary aliphatic amine: this atom gives a signal at −15.4 ppm, comparable to that in compounds (**4**), (**5**), (**8**) and (**9**). The phosphine substituents at B(3) in (**11**) and (**12**) cause a shift to high-field of ca. 18 ppm, which is within the range of established substituent effects for phosphine-for-amine substitution [20]. In the ^1H NMR spectra, the N-bound H atoms of the *exo*-NH_2R group diagnostically resonate at ca. +4.0 ppm and those of the bridging {NHR} group at ca. −1.4 ppm. Some small deviations in these positions are observed in compounds **4**–**12**, as expected (Fig. 2).

2.3. Structural study of compound (4)

A single crystal of compound (**4**) was analysed by X-ray diffraction analysis in order to establish whether the cluster structure suffers any gross structural effects as a result of the presence of the additional ethyl groups. In particular, we were interested in any structural consequences from the introduction of the more sterically demanding ethyl substituent *endo* on the bridging nitrogen atom. An *endo* ethyl group might disruptively impinge upon the cluster face, which, with its concave nature and five bridging and *endo* hydrogen atoms, could be regarded as crowded [5]. The molecular structure derived from this study (Fig. 1) thence confirms that **4** is architecturally a direct analogue of compounds (**1**) and (**3**), for which crystallographically determined structures have been previously reported [4,5]. Selected geometric parameters for (**4**) are presented in Table 2, along with those of (**1**) and (**3**) for comparison. Interboron distances in all three species are essentially identical within experimental error, and the additional N-bound ethyl groups, both *exo*, and, more particularly, *endo*, do not therefore significantly

Table 1
Selected NMR parameters [a] for [(MeH_2N)B_8H_{11}NHMe] (**2**), [(Et_2HN)$B_8H_{11}NEt_2$] (**4**), [(EtMeHN)B_8H_{11}NHEt] (**5**), [($EtMe_2N$)B_8H_{11}NHEt] (**6**), [($EtMe_2N$)B_8H_{11}NMeEt] (**7**), [(Et_2HN)B_8H_{11}NHEt] (**8**) [(Et_2HN)B_8H_{11}NHMe] (**9**), [(C_5H_5N)B_8H_{11}NHEt] (**10**), [(Ph_3P)B_8H_{11}NHEt] (**11**), and [($PhMe_2P$)B_8H_{11}NHEt] (**12**)

	B1	B2	B3	B4	B5,6	B7	B8	μH(4,5) μH(6,7)	NH NH_2
	$\delta(^{11}B)$ [$\delta(^1H)$]	$\delta(^{11}B)$ [$\delta(^1H)$]	$\delta(^{11}B)$ [$\delta(^1H)$]	$\delta(^{11}B)$ [$\delta(^1H)$]	$\delta(^{11}B)$ [$\delta(^1H)$]	$\delta(^{11}B)$ [$\delta(^1H)$]	$\delta(^{11}B)$ [$\delta(^1H)$]	[$\delta(^1H)$]	[$\delta(^1H)$]
2	−1.2 [+2.60]	−55.4 [−0.80]	−19.6 [+1.15] [b]	−33.2 [+0.65]	−11.3/−10.4 [+2.42] [+2.30]	−34.4 [+0.65]	−31.4 [+0.65] [−0.48]	[−2.02] [−2.26]	[−0.80] [c] [+5.57]
4	+5.5 [+2.95]	−55.7 [−0.49]	−15.7 [+1.63] [d]	−29.5 [+0.79]	−3.6 [+2.71] [+2.80]	−29.5 [+0.77]	−29.5 [+0.59] [+0.55]	[−2.62] [–2.87]	[e] [+1.38]
5	+1.7 [+2.62]	−54.8 [−0.64]	−15.5 [+1.21] [f]	−32.7 [+0.71]	−10.6 [+2.46] [+2.39]	−34.0 [+0.73] [–0.68]	−31.2 [+0.57]	[−1.96] [–2.19]	[−1.40] [g] [+3.50]
6	−0.4 [+2.95]	−55.0 [−0.62]	−11.3 [+1.01] [h]	−32.9 [+0.69]	−11.3 [+2.42]	−34.2 [+0.69]	−31.4 [+0.52] [−0.43]	[−1.98] [−2.17]	[−1.40] [i]
7	+2.9 [+3.25]	–56.1 [−0.52]	–11.2 [+1.73] [j)]	–29.8 [+0.75]	–3.5 [+2.83] [+2.81]	–29.8 [+0.75]	–29.8 [+0.75] [+0.59]	[−2.57] [–2.74]	[k]
8	+1.4 [+2.59]	−55.0 [−0.66]	−16.7 [+1.26] [l]	−32.8 [+0.69]	−10.8 [+2.45] [+2.39]	−34.1 [+0.69]	−31.3 [+0.54] [−0.66]	[−1.97] [−2.18]	[−1.40] [m] [+3.52]
9	+1.4 [+2.59]	−55.0 [−0.67]	−16.6 [+1.27] [n]	−32.9 [+0.69]	−10.1 [+2.43] [+2.36]	−34.4 [+0.69]	−31.3 [+0.55] [−0.67]	[−1.94] [−2.12]	[−1.30] [o] [+3.55]
10	+2.0 [+2.94]	−54.7 [−0.52]	−15.4 [+2.12] [p]	−29.2 [+0.92]	−11.2 [+2.43] [+2.51]	−32.3 [+0.92]	−29.2 [+0.77] [−0.24]	[−1.72] [−1.72]	[−1.15] [q]
11	+2.2 [+2.49]	−54.3 [−0.71]	−37.9 [−0.23] [r] [+2.52]	−27.7 [+1.11]	−5.8/−10.3 [+2.62] [+0.50]	−27.7 [+0.80] [−1.70]	−27.7 [+1.11]	[−1.60]	[−0.73] [s]
12	+1.4 [+2.62]	−54.6 [−0.63]	−38.7 [−0.21] [t] [+2.40]	−28.7 [+1.08]	−6.0/−10.6 [+2.62] [+0.27]	−28.6 [+0.74] [−1.87]	−28.6 [+1.16]	[−1.67]	[−0.96] [u]

[a] In $CDCl_3$ at +20°C.
[b] *exo* N-group: [$\delta(^1H)$](CH_3) +2.63.
[c] Bridging N-group: [$\delta(^1H)$](CH_3) +2.39.
[d] *exo* N-group: [$\delta(^1H)$](CH_3CH_2) +3.35 and +3.10; [$\delta(^1H)$](CH_3CH_2) +1.40 and +1.31.
[e] Bridging N-group: [$\delta(^1H)$](CH_3CH_2) +2.70 and +1.40; [$\delta(^1H)$](CH_3CH_2) +1.08 and +0.79.
[f] *exo* N-group: [$\delta(^1H)$](CH_3CH_2) +2.99; [$\delta(^1H)$](CH_3CH_2) +1.34; [$\delta(^1H)$](CH_3) +2.83.
[g] Bridging N-group: [$\delta(^1H)$](CH_3CH_2) +2.62; [$\delta(^1H)$](CH_3CH_2) +1.05.
[h] *exo* N-group: [$\delta(^1H)$](CH_3CH_2) +3.21; [$\delta(^1H)$](CH_3CH_2) +1.37; [$\delta(^1H)$](CH_3) +2.78 and +2.75.
[i] Bridging N-group: [$\delta(^1H)$](CH_3CH_2) +2.66; [$\delta(^1H)$](CH_3CH_2) +1.06.
[j] *exo* N-group: [$\delta(^1H)$](CH_3CH_2) +3.21; [$\delta(^1H)$](CH_3CH_2) +1.35; [$\delta(^1H)$](CH_3) +2.77 and +2.73.
[k] Bridging N-group: [$\delta(^1H)$](CH_3CH_2) +2.68; [$\delta(^1H)$](CH_3CH_2) +1.16; [$\delta(^1H)$](CH_3) +1.49.
[l] *exo* N-group: [$\delta(^1H)$](CH_3CH_2) +3.32 and +3.17; [$\delta(^1H)$](CH_3CH_2) +1.37 and +1.33.
[m] Bridging N-group: [$\delta(^1H)$](CH_3CH_2) +2.61; [$\delta(^1H)$](CH_3CH_2) +1.06.
[n] *exo* N-group: [$\delta(^1H)$](CH_3CH_2) +3.35 and +3.15; [$\delta(^1H)$](CH_3CH_2) +1.35 and +1.32.
[o] Bridging N-group: [$\delta(^1H)$](CH_3) +2.41.
[p] Pyridine substituent site: [$\delta(^1H)$](NCHCHCH) +8.00; [$\delta(^1H)$](NCHCHCH) +7.54; [$\delta(^1H)$](NCHCHCH) +8.94.
[q] Bridging N-group: [$\delta(^1H)$](CH_3CH_2) +2.73; [$\delta(^1H)$](CH_3CH_2) +1.10.
[r] $^1J(^{31}P\text{-}^{11}B)$ ca. 110 Hz,{Ph_3P} substituent site: [$\delta(^1H)$](Ph) +7.20 to +7.80.
[s] Bridging N-group: [$\delta(^1H)$](CH_3CH_2) +2.71; [$\delta(^1H)$](CH_3CH_2) +1.27.
[t] $^1J(^{31}P\text{-}^{11}B)$ ca. 125 Hz, {PMe_2 Ph} substituent site: [$\delta(^1H)$](CH_3) +1.72 and +1.68, $^2J(^{31}P\text{–}^1H)$ ca. 10 Hz, [$\delta(^1H)$](Ph) +7.18 to +7.84; $\delta(^{31}P)$ = +2.0.
[u] Bridging N-group: [$\delta(^1H)$](CH_3CH_2) +2.68; [$\delta(^1H)$](CH_3CH_2) +1.07.

perturb the gross structure. There are, however, small but significant enlargements of the N(5,6)–B(6)–B(7) and N(5,6)–B(5)–B(4) angles, of 5.93 and 8.00°, respectively, at the bridging NEt_2 site of compound (**4**) relative to the corresponding parameters in (**3**), and similar effects are observed for the B(8)–B(7)–B(6) and B(3)–B(4)–B(5) angles, which could be associated with steric factors due to the additional ethyl groups on the nitrogen atoms in compound (**4**).

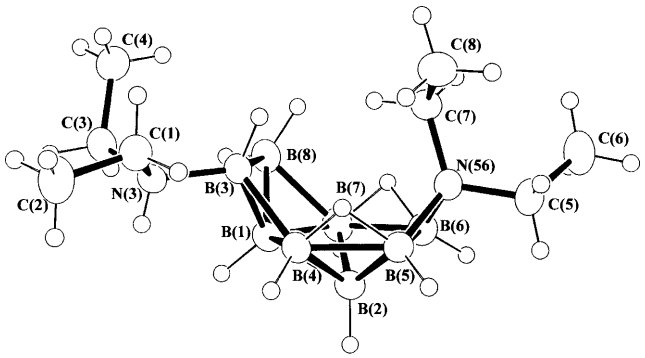

Fig. 2. An ORTEP [27] drawing of the crystallographically determined molecular structure of $[(Et_2HN)B_8H_{11}NEt_2]$ (**4**) with thermal ellipsoids shown at the 50% probability. In the interest of clarity hydrogen atoms are drawn as circles with an arbitrary small radius.

Table 2
Selected interatomic distances (Å) and angles (°) for $[(EtH_2N)B_8H_{11}NHEt]$ (**1**); data from reference [4], $[(^{iso}PrH_2N)B_8H_{11}NH^{iso}Pr]$ (**3**); data from reference [5] and $[(Et_2HN)B_8H_{11}NEt_2]$ (**4**); this work

	1	3	4
Bond interatomic distances			
B(1)–B(2)	1.826(9)	1.819(2)	1.807(3)
B(1)–B(3)	1.709(10)	1.707(2)	1.701(3)
B(1)–B(4)	1.769(8)	1.762(2)	1.762(2)
B(1)–B(7)	1.741(8)	1.743(2)	1.737(3)
B(1)–B(8)	1.726(9)	1.718(2)	1.727(3)
B(2)–B(4)	1.812(9)	1.800(2)	1.799(3)
B(2)–B(5)	1.810(10)	1.767(2)	1.764(3)
B(2)–B(6)	1.793(7)	1.771(2)	1.777(3)
B(2)–B(7)	1.791(9)	1.803(2)	1.798(3)
B(3)–B(4)	1.919(9)	1.896(2)	1.876(2)
B(3)–B(8)	1.918(9)	1.927(2)	1.923(3)
B(4)–B(5)	1.841(9)	1.819(2)	1.819(3)
B(5)–B(6)	1.989(9)	1.963(2)	1.987(3)
B(6)–B(7)	1.825(8)	1.815(2)	1.822(3)
B(7)–B(8)	1.902(9)	1.926(2)	1.919(3)
B(3)–N(3)	1.578(7)	1.590(2)	1.600(2)
B(5)–N(5,6)	1.573(9)	1.557(2)	1.571(2)
B(6)–N(5,6)	1.572(9)	1.560(2)	1.573(2)
Bond angles			
N(5,6)–B(6)–B(7)		118.86(10)	126.86(27)
N(5,6)–B(5)–B(4)		119.67(10)	125.60(26)
B(8)–B(7)–B(6)		116.64(11)	124.76(27)
B(3)–B(4)–B(5)		116.62(10)	124.93(12)

3. Experimental

Reactions were carried out in dry solvents under dry nitrogen but subsequent manipulatory and separatory procedures were carried out in air. Preparative thin-layer chromatography (TLC) was carried out using 0.75 mm layers of silica gel G (Merck, GF_{254}) made from water slurries on glass plates of dimensions 20×20 cm^2, followed by drying in air at 100°C. $[B_9H_{13}(SMe_2)]$ [3], $[(EtH_2N)B_8H_{11}NHEt]$ (**1**) [3], $[(^{iso}PrH_2N)B_8H_{11}NH^{iso}Pr]$ (**3**) [5], $[RhCl(PPh_3)_3]$ [21] and $[PtCl_2(PMe_2Ph)_2]$ [22] were prepared by literature methods and all other reagents were obtained commercially. NMR spectroscopy was carried out on Bruker DPX200, AC250 and AM400 instruments operating at ca. 4.7, 5.9 and 9.4 T. Chemical shifts δ are given in ppm relative to $\Xi = 100$ MHz for $\delta(^1H)$ (nominally $SiMe_4$), and $\Xi =$ 32.083 972 MHz for $\delta(^{11}B)$ (nominally $[F_3BOEt_2]$ in $CDCl_3$). Ξ is as defined in Ref. [23]. The mass spectra were recorded on a Finnigan MAT 8200 spectrometer.

3.1. Synthesis of $[(MeH_2N)B_8H_{11}NHMe]$ (2)

A solution of $[B_9H_{13}(SMe_2)]$ (1.20 g; 6.97 mmol) in dry THF (40 ml) was heated to reflux with a fourfold excess of NH_2Me (28 mmol) for 3 h, after which time the reaction mixture was cooled, and the resulting crystalline precipitate filtered off. Recrystallization from ethanol–water (1:1, ca. 10 ml) yielded pure azaborane (**2**) (521 mg, 3.29 mmol, 48%) as white crystalline solid; MS (FAB^+) for compound (**2**): $m/z = 158$ [M^+, 25%].

3.2. Synthesis of $[(Et_2HN)B_8H_{11}NEt_2]$ (4)

$[B_9H_{13}(SMe_2)]$ (100 mg, 0.58 mmol) was dissolved in toluene (10 ml), $NHEt_2$ (0.5 ml, 4.80 mmol) added, and the solution was refluxed for 24 h. The more volatile components were removed in vacuo, the solid residue was redissolved in CH_2Cl_2 and the products were separated and purified by repeated preparative TLC, development with CH_2Cl_2 giving two products. These were $[(Et_2NH)B_8H_{11}NEt_2]$ (**4**) (20 mg, 0.083 mmol, 14%, R_F 0.8) and $[B_9H_{13}(NHEt_2)]$ (88 mg, 0.48 mmol, 82%, R_F 0.9); MS (EI, 70 eV, 200°C) for compound (**4**): $m/z =$ 242 [M^+, 15%], 72 [Et_2N^+, 18%].

3.3. Synthesis of $[(EtMeHN)B_8H_{11}NHEt]$ (5)

A solution of compound (**1**) (60 mg, 0.32 mmol) in THF (5 ml), was cooled to -78°C and then NaH (12

mg, 0.5 mmol) was added. The solution was stirred for 30 min at r.t., cooled to −78°C, and then MeI (72 mg, 0.55 mmol) was added. After stirring a further 1 h the more volatile components were removed in vacuo, the solid residue redissolved in CH_2Cl_2 and the products separated and purified by repeated preparative TLC. Development with hexane–CH_2Cl_2 (3:7) gave [(EtMeHN)B_8H_{11}NHEt] (**5**) (24 mg, 0.12 mmol, 37%, R_F: 0.7) and [(EtH_2N)B_8H_{11}NHEt] (**1**) (25 mg, 0.134 mmol, 42%, R_F 0.4); MS (EI, 70 eV, 200°C) for compound (**5**): $m/z = 200$ [M^+, 12%].

3.4. Synthesis of $(EtMe_2N)B_8H_{11}NHEt]$ (6)

NaH (20 mg, 0.83 mmol) was added to a solution of compound **1** (60 mg, 0.32 mmol) in THF (5 ml) at r.t. The mixture was stirred for 30 min, and then MeI (119 mg, 0.83 mmol) was added. After stirring for 1 h the more volatile components were removed in vacuo, the solid residue redissolved in CH_2Cl_2 and the products separated and purified by repeated preparative TLC. Development in hexane–CH_2Cl_2 (3:7) gave [($EtMe_2N$)B_8H_{11}NHEt] (**6**) (31 mg, 0.144 mmol, 45%, R_F 0.82) and [(EtH_2N)B_8H_{11}NHEt] (**1**) (13 mg, 0.7 mmol, 22%, R_F 0.4); MS (EI, 70 eV, 200°C) for compound (**6**): $m/z = 214$ [M^+, 20%], 73 [$NEtMe_2^+$, 45%].

3.5. Synthesis of $(EtMe_2N)B_8H_{11}NMeEt]$ (7)

A sample of compound (**1**) (40 mg, 0.22 mmol) was dissolved in THF (5 ml), and NaH (18 mg, 0.75 mmol) was added. The solution was stirred for 30 min at r.t., and MeI (107 mg, 0.75 mmol) was added. After stirrings for a further 2 h, the more volatile components were removed in vacuo, the solid residue redissolved in CH_2Cl_2, and the products separated and purified by repeated preparative TLC. Development in hexane–CH_2Cl_2 (3:7) gave [($EtMe_2N$)B_8H_{11}NMeEt] (**7**) (28 mg, 0.12 mmol, 57%, R_F 0.9) and [(EtH_2N)B_8H_{11}NHEt] (**1**) (4 mg, 0.18 mmol, 9%, R_F 0.4); MS (EI, 70 eV, 200°C) for compound (**7**): $m/z = 228$ [M^+, 11%].

3.6. Synthesis of $(Et_2HN)B_8H_{11}NHEt]$ (8)

$NHEt_2$ (56 μl, 0.54 mmol) was added to a solution of compound (**1**) (50 mg, 0.27 mmol) in benzene (10 ml). After heating at reflux for 8 h, the more volatile components were removed in vacuo, the solid residue redissolved in CH_2Cl_2 and the products separated and purified by repeated preparative TLC. Development with CH_2Cl_2 gave [(Et_2HN)B_8H_{11}NHEt] (**8**) (18 mg, 0.084 mmol, 31%, R_F 0.50) and [(EtH_2N)B_8H_{11}NHEt] (**1**) (26 mg, 0.14 mmol, 52%, R_F 0.3); MS (EI, 70 eV, 200°C) for compound (**8**): $m/z = 214$ [M^+, 28%], 199 [$M^+ - Me$, 5%].

3.7. Synthesis of $[(Et_2HN)B_8H_{11}NHMe]$ (9)

A sample of compound (**1**) (50 mg, 0.31 mmol) was dissolved in benzene (10 ml), and $NHEt_2$ (65 μl, 0.62 mmol) was added. After 3 h at reflux temperature the more volatile components were removed in vacuo, the solid residue redissolved in CH_2Cl_2 and the products separated and purified by repeated preparative TLC. Development in CH_2Cl_2 gave [(Et_2HN)B_8H_{11}NHMe] (**9**) (38 mg, 0.19 mmol, 61%, R_F 0.53) and [$BH_3(NHEt_2)$] (5 mg, 0.006 mmol, 19%, R_F 0.49); MS (EI, 70 eV, 200°C) for compound (**9**): $m/z = 200$ [M^+, 34%].

3.8. Synthesis of $[(C_5H_5N)B_8H_{11}NHEt]$ (10)

Pyridine (22 μl, 0.268 mmol) was added to a solution of compound (**1**) (25 mg, 0.134 mmol) in benzene (10 ml), and the solution was then heated at reflux for 3 h. The more volatile components were removed in vacuo, the solid residue redissolved in CH_2Cl_2 and the products separated and purified by repeated preparative TLC. Development in CH_2Cl_2 gave [(C_5H_5N)B_8H_{11}-NHMe] (**10**) (38 mg, 0.08 mmol, 61%, R_F 0.74) and [$BH_3(NC_5H_5)$] (2 mg, 0.02 mmol, 16%, R_F 0.57); MS (EI, 70 eV, 200°C) for compound (**10**): $m/z = 221$ [M^+, 22%], 217 [$M^+ - 3H$, 30%].

3.9. Synthesis of $[(Ph_3P)B_8H_{11}NHEt]$ (11)

Route (a): PPh_3 (140 mg, 0.53 mmol) was added to a solution of [(EtH_2N)B_8H_{11}NHEt] (**1**) (100 mg, 0.53 mmol) in toluene (10 ml). The solution was then heated at reflux for 14 h. Examination of the product mixture by integrated NMR spectroscopy revealed a ca. 40:60 mol% mixture of [(Ph_3P)B_8H_{11}NHEt] (**11**) and [(EtH_2N)B_8H_{11}NHEt] (**1**). Route (b): [$RhCl(PPh_3)_3$] (100 mg, 0.25 mmol) was added to a solution of compound (**1**) (20 mg, 0.108 mmol) in toluene (10 ml), and the mixture then was heated at reflux for 2 h. The more volatile components were removed in vacuo, the solid residue redissolved in CH_2Cl_2 and the products separated and purified by repeated preparative TLC. Development with hexane–CH_2Cl_2 (3:7) gave [(Ph_3P)B_8H_{11}NHEt] (**11**) (26 mg, 0.064 mmol, 60%, R_F 0.55); MS (EI, 70 eV, 200°C) for compound (**11**): $m/z = 392$ [M^+, 11%], 262 [PPh_3^+, 22%].

3.10. Synthesis of $[(PhMe_2P)B_8H_{11}NHEt]$ (12)

[$PtCl_2(PMe_2Ph)_2$] (30 mg, 0.05 mmol) was added to a solution of compound **1** (10 mg, 0.053 mmol) in toluene (10 ml) and the solution then was heated at reflux for 2

Table 3
Crystal data and details of refinement of $[(Et_2HN)B_8H_{11}NEt_2]$ (**4**)

Empirical formula	$C_8H_{32}B_8N_2$
Formula weight	242.84
Colour	Colourless
Temperature (K)	223(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	9.26470(10)
b (Å)	9.89090(10)
c (Å)	10.76610(10)
α (°)	111.1930(10)
β (°)	93.3870(10)
γ (°)	126.7710(10)
V (Å^3)	805.73(27)
Z	2
D_{calc}(M gm^{-3})	1.001
μ (mm^{-1})	0.051
Crystal size (mm)	$0.20 \times 0.20 \times 0.40$
θ_{min}, θ_{max} (°)	2.09, 27.00
Index ranges	$-12 \le h \le 12$, $-26 \le k \le 12$, $0 \le l \le 27$
Reflections collected	17 127
Independent reflections	3518 [$R_{int} = 0.05$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3497/0/211
Goodness-of-fit on F^2	1.055
Final R indices (observed data)	$R_1 = 0.055$, $wR_2 = 0.2628$
R indices (all data)	$R_1 = 0.0828$, $wR_2 = 0.1529$
Largest difference map peak and hole (e Å^{-3})	+0.217, −0.246

h. The more volatile components were removed in vacuo, the solid residue redissolved in CH_2Cl_2, and the products separated and purified by repeated preparative TLC. Development in hexane–CH_2Cl_2 (3:7) gave $[(PhMe_2P)B_8H_{11}NHEt]$ (**12**) (10 mg, 0.035 mmol, 68%, R_F 0.6); MS (EI, 70 eV, 200°C) for compound (**12**): $m/z = 279$ [M$^+$, 17%], 138 [$PhPMe_2^+$, 26%].

3.11. Crystal structure determination of $[(Et_2HN)B_8H_{11}NEt_2]$ (4)

A crystal of appropriate dimension was mounted on a glass fibre in a random orientation. Preliminary examination and data collection were performed using a Siemens SMART CCD-Detector X-Ray diffractometer and graphite-monochromated Mo–K_α radiation ($\bar{\lambda} =$ 0.71073 Å). Preliminary unit-cell constants were determined with a set of 45 narrow-frame scans (0.3° in ϖ). A typical data set collected consisted of 4028 frames of intensity data, collected with a frame width of 0.3° in ϖ and a counting time of 15 s per frame, at a crystal-to-detector distance of 4.930 cm. The double-pass method of scanning was used to exclude any noise. The collected frames were integrated using an orientation matrix determined from the narrow-frame scans. SMART and SAINT software packages [24] were used for data collection and data integration. Analysis of the integrated data did not show any decay. Final cell constants were determined by a global refinement of xyz centroids of 8192 reflections ($\theta < 27.5°$). Collected data were corrected for systematic errors using SADABS [25] based upon the Laue symmetry using equivalent reflections. Crystal data, and data-collection and refinement parameters, are listed in Table 3. Structure solution and refinement were carried out using the SHELXTL-PLUS software package [26]. The structure was solved by direct methodsand refined successfully in the space group $P\bar{1}$. Full-matrix least-squares refinement was carried out by minimising $\Sigma\, w(F_o^2 - F_c^2)^2$. The non-hydrogen atoms were refined anisotropically to convergence. All cage and N-bound hydrogen atoms were located from the difference Fourier synthesis and were refined freely. The remaining hydrogen atoms were treated using the appropriate riding model (AFIX m3).

4. Supplementary material

Complete listings of the atomic coordinates, geometrical parameters and anisotropic displacement coefficients for non-hydrogen atoms, together with positional and isotropic displacement coefficients for hydrogen atoms, are deposited with the Cambridge Crystallographic Data Centre, CCDC no. 146817. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Tables of observed and calculated structure factors are available in electronic format.

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