

Polyhedral azaborane chemistry. Nitrogen-vertex incorporation in metallaazaborane formation from 4-(NHEt₂)B₉H₁₃. Two isomers of [(η⁵-C₅Me₅)RhB₉H₁₂(NEt₂)]

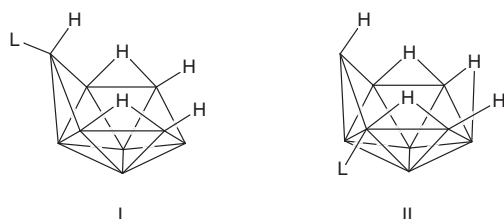
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The reaction of 4-(NHEt₂)-*arachno*-B₉H₁₃ with [{RhCl₂(η⁵-C₅Me₅)}₂] and NaH afforded orange-yellow [6-(η⁵-C₅Me₅)-*nido*-6-RhB₉H₁₂-μ-8,9-(NEt₂)] **1** and yellow [5-(η⁵-C₅Me₅)-*nido*-5-RhB₉H₁₂-μ-9,10-(NEt₂)] **2**. These compounds were characterized by single-crystal X-ray diffraction analysis and NMR spectroscopy and are compared to their non-bridged congeners [6-(η⁵-C₅Me₅)-*nido*-6-RhB₉H₁₃] **3** and [5-(η⁵-C₅Me₅)-*nido*-5-RhB₉H₁₃] **4**. It is concluded that the bridging μ-{NEt₂} groups exhibit bonding to the borane cage that is intermediate between bonding schemes that involve one two-electron three-centre bond and two two-electron two-centre bonds.

It is long established that an extensive ten vertex metallaborane chemistry can derive from the reactions of transition-element centres with the *arachno*-nonaborane anion [B₉H₁₄]⁻.^{1,2} Essentially isostructural in cluster terms with the [B₉H₁₄]⁻ anion are the ligand derivatives 4-L-*arachno*-B₉H₁₃, where L is a two-electron ligand [schematic cluster structure I; in I, II, IV, V and VI unlettered vertices are {BH(*exo*)} units]. These last derivatives have been well established for well over 30 years.^{3,4} Their reaction chemistry with transition-element species has, however, not been well investigated. Reports⁵ are limited to the reactions of [PtCl₂(PMe₂Ph)₂] with the B-substituted species 1-Cl-4-(SMe₂)-*arachno*-B₉H₁₂ and 7-(OMe)-4-(SMe₂)-*arachno*-B₉H₁₂ and the reactions of [Cu(BH₄)(PPh₃)₂] with the anionic species [4-L-*arachno*-B₉H₁₃]⁻, where L⁻ = [NCS]⁻, [NCSe]⁻ or [(NC)BPh₃]⁻.

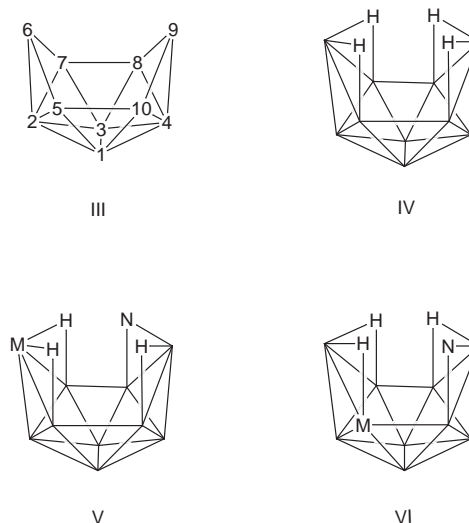


Recently a hitherto unsuspected family of LB₉H₁₃ isomers, the series 5-L-*arachno*-B₉H₁₃ (schematic cluster structure II) has been established.⁶ We are currently investigating some reactions of transition-element centres with 5-(NC₅H₄Ph-4')-*arachno*-B₉H₁₃ as a representative of these new isomers and find that its reactivity is significantly different from its 4 isomer.⁷ As mentioned above, however, the reactivity of the conventionally structured 4 isomers themselves is not well established. It is useful therefore more firmly to establish their reactivity towards metal centres. As part of such a survey we here present some results from the reaction of 4-(NHEt₂)-*arachno*-B₉H₁₃ with [{RhCl₂(η⁵-C₅Me₅)}₂]. The choice of the NHEt₂ species was prompted by the cognate observation that, when L in 4-L-B₉H₁₃ is an *exo*-terminal primary or secondary amine residue, NH₂R or NHR₂, then the nitrogen atom can be incorporated more intimately into the cluster upon treatment with other ligands L' to form the nine-vertex *arachno*-type {NB₉} cluster species L'B₈H₁₁NHR and L'B₈H₁₁NR₂.⁸ On reaction with transition-element complexes, some of these latter can lead in turn to metallaazaboranes that involve complete contiguous cluster incorporation of a nitrogen centre,⁹⁻¹¹ and it is also known that nitrogen-atom incorporation can also be induced to occur in

related systems that do not contain metals.^{3,12} We surmised that the present reaction might also feature partial or complete cluster incorporation of the nitrogen atom, with use of the secondary amine residue perhaps inhibiting a complete cluster incorporation; in view of burgeoning current activity in azaborane¹² and metallaazaborane^{9,10,11,13} chemistry, there is interest in establishing where, along any coordinate for nitrogen-atom cluster assimilation, any products might be.

Results and Discussion

Treatment of 4-(NHEt₂)-*arachno*-B₉H₁₃ with NaH in thf solution (where thf = tetrahydrofuran), followed by reaction with [{RhCl₂(η⁵-C₅Me₅)}₂] for 3 h at room temperature, resulted, after chromatographic separation, in the isolation of two isomeric rhodaboranes. These were orange-yellow [6-(η⁵-C₅Me₅)-*nido*-6-RhB₉H₁₂-μ-8,9-(NEt₂)] **1** and yellow [5-(η⁵-C₅Me₅)-*nido*-5-RhB₉H₁₂-μ-9,10-(NEt₂)] **2**, both air-stable crystalline solids. Yields were low (6 and 2% respectively), but several other coloured products in similarly low yield are isolatable. These latter have so far defied unequivocal characterization. Meanwhile, it is convenient to report on these two compounds **1** and **2**, as they constitute an isomeric pair, and permit useful comparisons. They are characterized by single-crystal X-ray diffraction analysis and by NMR spectroscopy (Tables 1 and 2).



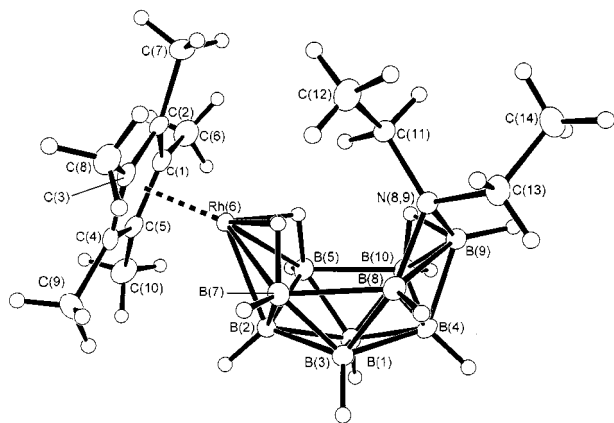


Fig. 1 An ORTEP-type¹⁵ drawing of the crystallographically determined molecular structure of [6-(η^5 -C₅Me₅)-nido-6-RhB₉H₁₂- μ -8,9-(NEt₂)] **1**. Ellipsoids are shown at the 40% probability level

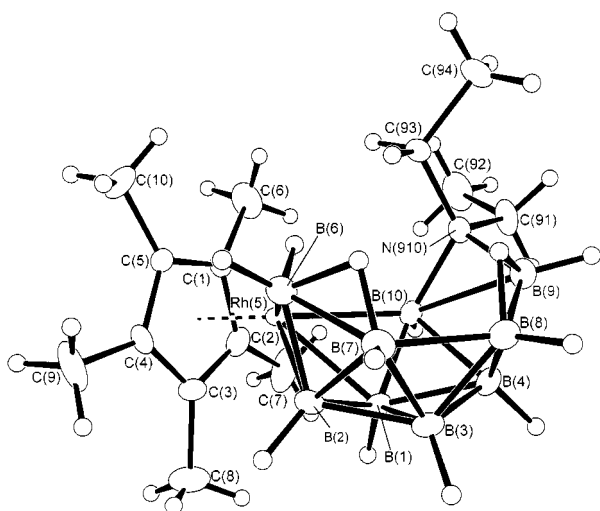


Fig. 2 An ORTEP-type¹⁵ drawing of the crystallographically determined molecular structure of [5-(η^5 -C₅Me₅)-nido-5-RhB₉H₁₂- μ -9,10-(NEt₂)] **2**. Ellipsoids are shown at the 40% probability level

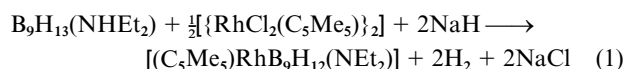
Both compounds are readily seen to be of *nido*-ten vertex {RhB₉} configuration (Figs. 1 and 2, *nido* decaboranyl numbering system as in schematic structure III). Compared to *nido*-B₁₀H₁₄ itself (schematic structure IV), compound **1** has a {Rh(η^5 -C₅Me₅)} centre in the 'prow' 6 position instead of a {BH} unit and a bridging {NEt₂} unit in a distal B–B position [here numbered (8,9)] instead of a hydrogen bridge [schematic V, where M \equiv {Rh(η^5 -C₅Me₅)} and N \equiv {NEt₂}]. Other *exo*-terminal and bridging hydrogen atoms are as in *nido*-B₁₀H₁₄ itself. Compound **1** therefore geometrically resembles [6-(η^5 -C₅Me₅)-nido-6-RhB₉H₁₃] **3**,¹ with a {B–H–B} bridging unit replaced by a [B–(NEt₂)–B] bridging unit. Compound **2** similarly resembles [5-(η^5 -C₅Me₅)-nido-5-RhB₉H₁₃] **4**¹⁴ but now with the {B–H–B} unit in the 9,10 position closest to the metal centre replaced by the {B–{NEt₂}–B} unit [schematic cluster structure VI, where M \equiv {Rh(η^5 -C₅Me₅)} and N \equiv {NEt₂}].

In each case, therefore, a conversion of the *exo*-terminal {B(NHEt₂)} unit of the starting substrate to give a {B–(NEt₂)–B} bridging unit has occurred. This demonstrates an initial step towards a more complete cluster assimilation of a nitrogen vertex as is observed, for example, in the reaction of [RhCl₂(η^5 -C₅Me₅)] with (NHEt₂)₂B₉H₁₁NHEt.^{9,10} In terms of nitrogen-vertex cluster assimilation, it may be noted that the compounds can also be regarded as *arachno* eleven-vertex {RhNB₉} cluster compounds^{16,17} as well as {B–B}-bridged *nido* ten-vertex {RhB₉} compounds. However, in view of the geometric and NMR similarities to the classical *nido* ten-vertex structural type, it is more convenient to discuss them in terms of

Table 1 Selected interatomic distances (in Å) for [6-(η^5 -C₅Me₅)-nido-6-RhB₉H₁₂- μ -8,9-(NEt₂)] **1**, [5-(η^5 -C₅Me₅)-nido-5-RhB₉H₁₂- μ -9,10-(NEt₂)] **2** and [6-(η^5 -C₅Me₅)-nido-6-RhB₉H₁₃] **3**, data from ref. 1, with estimated standard deviations (e.s.d.s) in parentheses

	1 6-Rh (μ -NEt ₂)	2 5-Rh (μ -NEt ₂)	3 6-Rh (parent)
B(1)–B(2)	1.775(3)	1.808(5)	1.780(12)
B(1)–B(3)	1.781(3)	1.781(5)	1.781(12)
B(1)–B(4)	1.782(3)	1.783(5)	1.768(13)
B(1)–B(5)	1.734(3)	—	1.722(12)
B(1)–B(10)	1.749(3)	1.808(5)	1.713(13)
B(2)–B(3)	1.789(3)	1.773(5)	1.773(12)
B(2)–B(5)	1.829(3)	—	1.799(12)
B(2)–B(6)	—	1.754(5)	—
B(2)–B(7)	1.815(3)	1.792(5)	1.814(12)
B(3)–B(4)	1.766(3)	1.760(5)	1.782(13)
B(3)–B(7)	1.722(3)	1.766(5)	1.736(12)
B(3)–B(8)	1.769(3)	1.734(5)	1.725(13)
B(4)–B(8)	1.883(3)	1.781(5)	1.761(14)
B(4)–B(9)	1.767(3)	1.785(5)	1.696(14)
B(4)–B(10)	1.790(3)	1.968(5)	1.772(13)
B(5)–B(10)	1.986(3)	—	1.988(14)
B(6)–B(7)	—	1.778(5)	—
B(7)–B(8)	2.022(3)	1.983(5)	2.021(14)
B(8)–B(9)	2.096(3)	1.809(5)	1.768(15)
B(9)–B(10)	1.820(3)	2.211(5)	1.787(14)
B(1)–Rh(5)	—	2.162(3)	—
B(2)–Rh(6)	2.175(2)	—	2.192(9)
B(2)–Rh(5)	—	2.207(3)	—
B(5)–Rh(6)	2.256(2)	—	2.239(10)
B(6)–Rh(5)	—	2.159(4)	—
B(7)–Rh(6)	2.245(2)	—	2.224(10)
B(10)–Rh(5)	—	2.284(3)	—
B(9)–N(8,9)	1.552(3)	—	—
B(8)–N(8,9)	1.625(2)	—	—
B(9)–N(9,10)	—	1.553(4)	—
B(10)–N(9,10)	—	1.606(4)	—
N(8,9)–C(11)	1.491(2)	—	—
N(8,9)–C(13)	1.515(2)	—	—
N(9,10)–C(93)	—	1.493(4)	—
N(9,10)–C(91)	—	1.518(4)	—

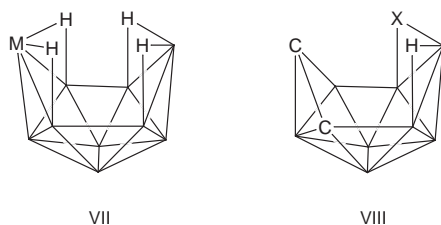
the *nido* ten-vertex approach. Mechanistically and stoichiometrically each can be visualized as arising by simple addition of the metal vertex to the *arachno* nine-vertex {B₉} cluster, followed by 'vertex-swing' processes and conversion of {BH-*exo*-NHEt₂} into {B,B- μ -(NEt₂)} by dihydrogen elimination [equation (1)]. Vertex-swing processes are well documented in



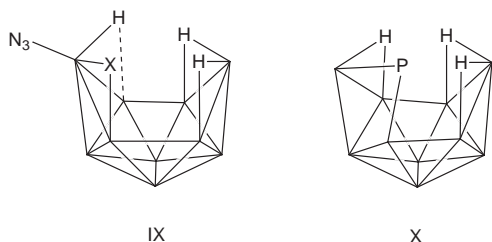
nido and *arachno* ten-vertex systems.¹⁸ The reaction may be initiated by the formation of a discrete or incipient [B₉H₁₂-(NHEt₂)][−] anion, which then displaces halide ion from the rhodium centre.

Table 1 lists selected crystallographically determined interatomic dimensions. Except for the nitrogen-bridged interboron distances, the molecular dimensions of both compounds **1** and **2** are within those of normal¹⁹ *nido*-decaboranyl ranges. The nitrogen-bridged distances of 2.096(3) and 2.211(5) Å respectively are however substantially longer than conventional hydrogen-bridged interboron distances. For example the equivalent hydrogen-bridged distance in *nido*-B₁₀H₁₄ itself (schematic IV) is 1.776(5) Å.²⁰ For conventionally hydrogen-bridged [6-(η^5 -C₅Me₅)-nido-6-RhB₉H₁₃] **3** (schematic cluster structure VII) single-crystal X-ray diffraction data are available.¹ These data permit a direct geometrical comparison of compound **3** with its {NEt₂}-bridged analogue **1** of schematic structure V (Table 1). Here it can be seen that, in addition to the *ca.* 0.3 Å increase in the bridged interboron distance, there is also a general increase in distances involving the other atoms in the bridged link. These increases vary from a marginal +0.01 Å

for B(7)–B(8) to nearly +0.12 Å for B(4)–B(8). There is also a general flexing in the rest of the cluster, with differences ranging from *ca.* –0.02 through zero to *ca.* +0.07 Å. It is interesting that these geometrical differences upon replacement of the {BHB} by a {B–(NEt₂)–B} unit are much less marked than those for the only other similarly related *nido* ten-vertex pair for which structural comparisons have been made, namely *nido*-5,6-C₂B₈H₁₂ **5** (schematic VIII, where X = H) and *nido*-5,6-C₂B₈H₁₁-μ-(8,9)-(NH₂) **6** (schematic VIII, where X = {NH₂}).¹⁶ The geometry of compound **5** is not available, but the {*nido*-5,6-C₂B₈H₁₁} subcluster of structurally characterized²¹ 8-(3'-*closo*-1,2-C₂B₁₀H₁₁)-*nido*-5,6-C₂B₈H₁₁ **7** may be used for comparison. The available geometry of compound **6** is computed by *ab initio* methods rather than being experimentally determined by diffraction work, but the MP2(fc)/6-31G* computational level used is currently regarded as giving reasonable molecular dimensions. For this dicarbaborane pair the increase from **7** to **6** is +0.191 Å for the (8,9)-bridged interboron linkage and distances to the bridged boron atoms B(8) and B(9) from the adjacent boron atoms are increased, the largest increase being in B(7)–B(8) at +0.059 Å; the general interboron and boron-carbon cluster flexing distant from the bridged site for compound **7** versus **6** is also now much bigger than for **1** versus **3**, ranging from –0.041 to +0.035 Å. Of these, the C(5)–C(6) intercarbon linkage changes by +0.027 Å. The relatively smaller geometric perturbations of the rhodaborane **1** upon replacement of the {BHB} bridge by a {B–(NEt₂)–B} bridge to give compound **3** seems also to be reflected in smaller differences in NMR properties (see below, Table 2 and Fig. 3).



An additional type of cluster flexing worth mentioning concerns the nature of the B(6)–B(7) bridging hydrogen character in the position adjacent to the B(5)–B(6) μ-{B–(NH₂)–B} link in 6-(N₃)-*nido*-B₁₀H₁₂-μ-(5,6)-NH₂ **8** (schematic IX, where X = {NH₂}).²² Here the nitrogen-bridged linkage is also long, at 2.077(2) Å, though not quite as long as in compounds **1** and **2**. However, in compound **8** there is now a tendency for the adjacent μ-(6,7) bridging hydrogen atom to exhibit BH(6)*endo* character. Thus the B(6)–H(6,7) and B(7)–H(6,7) distances are considerably differentiated, at 1.429(16) and 1.193(17) Å respectively. This effect appears not to be significant in compounds **1** [1.33(2) and 1.23(2) Å] and **2** [1.32(2) and 1.26(3) Å], however. The differentiation may be influenced by the electronegative {N₃} grouping that is bound *exo* to B(6) in compound **8**. A possibly related diversion towards *endo* character upon electronegative substitution has, for example, also been noted for the equivalent bridging hydrogen atom in conventionally *exo*-substituted [5-(η⁵-C₅Me₅)-*nido*-5-RhB₉H₁₂-6-(OMe)].²³



The bonding behaviour within the nitrogen bridges in compounds **1** and **2** is of interest. A non-hydrogen main-group atom bridging this type of *nido*-decaboranyl position is well

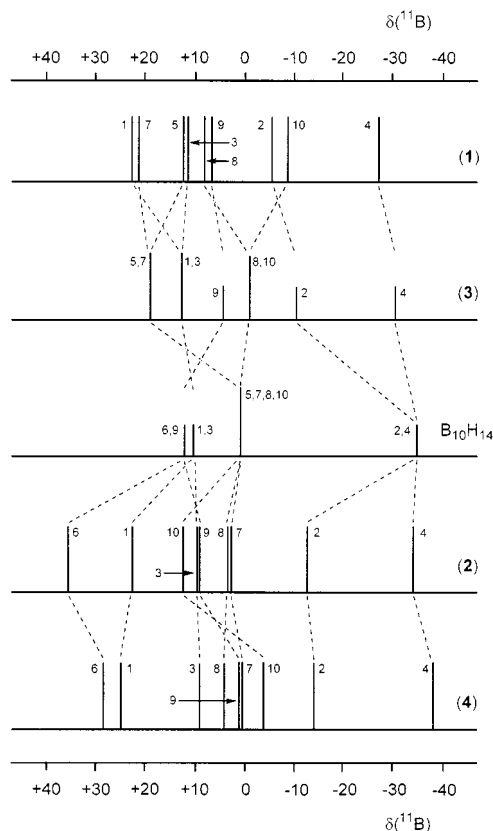


Fig. 3 Stick diagrams of the chemical shifts and relative intensities in the ¹¹B NMR spectra of (top to bottom) [6-(η⁵-C₅Me₅)-*nido*-6-RhB₉H₁₂-μ-8,9-(NEt₂)] **1**, [6-(η⁵-C₅Me₅)-*nido*-6-RhB₉H₁₃] **3**,¹ B₁₀H₁₄, [5-(η⁵-C₅Me₅)-*nido*-5-RhB₉H₁₂-μ-9,10-(NEt₂)] **2** and [5-(η⁵-C₅Me₅)-*nido*-5-RhB₉H₁₃] **4**.¹⁴ Hatched lines join resonance lines for equivalent positions in the five species

recognized, and in known compounds a bridge involving an element to the right of boron in the Periodic Table generally induces a lengthening of the interboron separation above the 1.776(5) Å observed²⁰ in the model *nido*-B₁₀H₁₄ parent. There is, however, considerable variation among observed bridged distances. Thus it is 2.69(2) Å in B₁₀H₁₃-μ-(5,6)-(PPh₂) (schematic X, where P ≡ {PPh₂}),²⁴ 2.096(3) in **1** and 2.211(5) Å in **2**, 2.077(2) Å in 6-(N₃)-*nido*-B₁₀H₁₂-μ-(5,6)-NH₂ **8** (as mentioned above),²² 1.973 Å in 5,6-C₂B₈H₁₁-μ-(NH₂) **6**,¹⁶ 1.872 Å in B₁₀H₁₂-μ-{PHC(Bu^t)B₁₀H₁₂(SMe₂)},²⁵ and 1.864(4) Å in the oxygen-bridged [OB₁₈H₂₁][–] anion (although this had some crystallographic disorder);¹⁷ in the nine-vertex *arachno*-type {NB₈} species (EtNH₂)B₈H₁₁-μ-(NH₂), (PrⁿNH₂)B₈H₁₁-μ-(NHP^r), (PrⁿNH₂)B₈H₁₁-μ-(NH₂^t) and (Et₂NH)B₈H₁₁-μ-(NEt₂) the nitrogen-bridged interboron distances are 1.989(9), 1.963(2), 1.964(4) and 1.987(3) Å respectively,⁸ and in the related platinumborane [(PMe₂Ph)₂PtB₇H₁₁-μ-(NH₂)] 1.92(2) Å.¹¹ In the phosphorus-bridged eleven-vertex monocarbaborane (Me₃N)CB₁₀H₁₀-μ-(PPh) the bridged interboron distance is 1.839(7) Å,²⁶ and in the carbon-bridged eleven-vertex monocarbaborane anions [PhCB₁₀H₁₀-μ-(CHPh)][–] and [MeCB₁₀-H₁₀-μ-(CHMe)][–] 1.86(2) and 1.847(2) Å respectively.²⁷ In the smaller clusters B₅H₁₀-μ-(NH₂^t)²⁸ and [(η⁵-C₅H₅)(OC)₂-FeB₅H₇-μ-(PPh₂)]²⁹ the bridged interboron distances are 2.080(4) and 2.683(5) Å respectively. Of all these, the two {PPh₂}-bridged interboron distances of 2.683(5) and 2.69(2) Å are clearly non-bonding, suggesting two two-electron two-centre phosphorus–boron bonds in the bridge,³⁰ whereas the other phosphorus-, oxygen- and carbon-bridged interboron distances of 1.839(7)–1.872(2) Å are within normal deltahedral borane ranges that perhaps suggest essentially three-centre two-electron involvement of the two bridged boron atoms with the bridging heteroatom. The nitrogen-bridged distances of

Table 2 Selected ^{11}B , ^1H and ^{13}C NMR parameters for [6-($\eta^5\text{-C}_5\text{Me}_5$)-*nido*-6-RhB $_9$ H $_{12}$ - μ -8,9-(NEt $_2$)] **1** and [5-($\eta^5\text{-C}_5\text{Me}_5$)-*nido*-5-RhB $_9$ H $_{12}$ - μ -9,10-(NEt $_2$)] **2**, together with those for [6-($\eta^5\text{-C}_5\text{Me}_5$)-*nido*-6-RhB $_9$ H $_{13}$] **3**¹ and [5-($\eta^5\text{-C}_5\text{Me}_5$)-*nido*-5-RhB $_9$ H $_{13}$] **4**¹⁴ for comparison

Position	1 6-Rh (μ -NEt $_2$) ^a		2 5-Rh (μ -NEt $_2$) ^b		3 6-Rh (non-aza) ^c		4 5-Rh (non-aza) ^c	
	$\delta(^{11}\text{B})$	$\delta(^1\text{H})$	$\delta(^{11}\text{B})$	$\delta(^1\text{H})$	$\delta(^{11}\text{B})$	$\delta(^1\text{H})$	$\delta(^{11}\text{B})$	$\delta(^1\text{H})$
(1)	+21.7	+4.51	+22.9	+3.61	+12.7	+3.59	+25.3	+3.87
(2)	-6.4	+0.89	-13.1	+0.61	-10.8	+0.69	-13.5	+0.70
(3)	+11.7	+3.47	+9.5	+3.08	+12.7	+3.59	+9.5	+2.77
(4)	-27.4	+1.87	-34.3	+1.18	-30.6	+1.01	-38.3	+0.27
(5)	+11.9	+3.29	—	—	+19.4	+4.07	—	—
(6)	—	—	+36.4	+5.07	—	—	+28.7	+4.55
(7)	+20.6	+4.07	+3.6	+3.46	+19.4	+4.07	+1.6	+3.63
(8)	+8.8	+3.47	+3.2	+2.89	-0.9	+2.78	+4.5	+3.02
(9)	+6.2	+2.97	+9.5	+3.45	+4.7	+3.39	+0.6	+3.15
(10)	-8.7	+2.23	+12.3	+3.32	-0.9	+2.78	-4.0	+2.33
(5,6)		-7.60 ^d		-13.52 ^e		-8.15 ^f		-12.50 ^g
(6,7)		-8.90 ^h		-2.14		-8.15 ^f		-2.42
(8,9)		—		-1.65		-2.76		-2.75
(9,10)		-2.55		—		-2.76		-1.85
C $_5$ Me $_5$		+2.01 ⁱ		+1.88		+2.02		+1.94

^a In CDCl $_3$ at 294–297 K, NHEt $_2$ group: $\delta(^{13}\text{C})$ [$\delta(^1\text{H})$] +57.7 [+2.82] (CH $_2$), +9.8 [+1.14] (CH $_3$), +42.4 [+2.47, +2.11] (CH $_2$) and +8.4 [+0.94] (CH $_3$). ^b In CDCl $_3$ at 294–297 K, NHEt $_2$ group: $\delta(^1\text{H})$ +2.93 (CH $_2$), +1.18 (CH $_3$), +1.90, 1.53 (CH $_2$) and +1.01 (CH $_3$). ^c In CD $_2$ Cl $_2$ at room temperature. ^d $^1J(^{103}\text{Rh}-^1\text{H}) = 29.6$ Hz. ^e $^1J(^{103}\text{Rh}-^1\text{H}) = 35.0$ Hz. ^f $^1J(^{103}\text{Rh}-^1\text{H}) = 28.0$ Hz. ^g $^1J(^{103}\text{Rh}-^1\text{H}) = 33.0$ Hz. ^h $^1J(^{103}\text{Rh}-^1\text{H}) = 30.2$ Hz. ⁱ $\delta(^{13}\text{C})$ at +100.9 [$^1J(^{103}\text{Rh}-^{13}\text{C}) = 6.5$ Hz] (quaternary C) and +10.0 (CH $_3$).

1.963(4)–2.211(5) Å are intermediate between these extremes and may effectively constitute a central part of a spectrum of bonding behaviour that progresses from two-electron three-centre {BBN} bonding, thence with an increasing involvement of the nitrogen-based lone pair, ultimately to give a {B–N–B} bridge involving two two-electron two-centre bonds.

In view of these geometric considerations it was of interest to compare NMR shielding differences, which are intimately dependent upon changes in electronic structure associated with geometric differences. The NMR data for compounds **1** and **2** are gathered in Table 2, which also contains equivalent data^{1,14} for the parent compounds that do not have the {NEt $_2$ } bridge, *i.e.* the 6 and 5 isomers of [($\eta^5\text{-C}_5\text{Me}_5$)RhB $_9$ H $_{13}$] (compounds **3** and **4** respectively). Spectra for compounds **1** and **2** were readily assigned by one- and two-dimensional homo- and heteronuclear correlation techniques and were consistent with the molecular structures determined in the X-ray work. Fig. 3 shows stick representations of the ^{11}B spectra of compounds **1**, **2**, **3** and **4**. Data for the parent *nido*-B $_{10}$ H $_{14}$ are also included, which enables the basic ten-vertex *nido* cluster shielding characteristics to be traced through. Compared to B $_{10}$ H $_{14}$, the most predominant effects are the α -deshielding effects of the {Rh-($\eta^5\text{-C}_5\text{Me}_5$)} cluster constituents. These have been discussed elsewhere for compounds **3** and **4**^{1,14} and carry through to the {NEt $_2$ }-bridged species **1** and **2**. By contrast, the influence of the {NEt $_2$ } bridge on the basic shielding patterns of compounds **3** and **4** is relatively minor, and appears to be relatively localized. In the 6-{Rh(C $_5$ Me $_5$)} isomer **1** the bridged ^{11}B (8) resonance is shifted to low field by *ca.* 9 ppm compared to that of compound **3**, but the other bridged resonance, that of ^{11}B (9), is barely affected. Adjacent chemical shift effects are perhaps a little bigger: the apical ^{11}B (1) resonance is shifted downfield by *ca.* 9 ppm and the open-face ^{11}B (10) resonance upfield by the same amount. The only other significant change is for the ^{11}B (5) position next to the rhodium atom, which is shielded by *ca.* 8 ppm. For the 5-{Rh(C $_5$ Me $_5$)} species **2** the differences, now compared to compound **4**, are even less marked. The bridged ^{11}B (9) and ^{11}B (10) resonances are shifted downfield by *ca.* 9 and *ca.* 16 ppm respectively, all others being very similar except for ^{11}B (6) next to the rhodium atom that is deshielded by 8 ppm. Overall the similarities between bridged and non-bridged shielding patterns are quite striking for these rhodaboranes. By contrast, for example, analogous comparison between 5,6-

C $_2$ B $_8$ H $_{11}$ - μ -(NH $_2$) **6** and unbridged 5,6-C $_2$ B $_8$ H $_{12}$ (**5/7**)³¹ shows much more marked differences.¹⁶ These dicarbaboranes also exhibit bigger relative geometric differences distant from the bridged site, as discussed above, even though the nitrogen-bridged interboron distance in 5,6-C $_2$ B $_8$ H $_{11}$ - μ -(NH $_2$) **6** at 1.973 Å is less than those in compounds **1** and **2** and much more similar to that in its direct hydrogen-bridged analogue in the {5,6-C $_2$ B $_8$ H $_{11}}$ fragment of compound **7** mentioned above. This may mean that the more flexible rhodium centres are acting as better sinks for cluster changes induced by bridging {NR $_2$ } groups.

Experimental

General

The reaction was carried out in dry solvents under dry nitrogen but the subsequent manipulatory and separatory procedures were carried out in air. The compounds [(RhCl $_2$ ($\eta^5\text{-C}_5\text{Me}_5$)) $_2$]³² and 4-(NHEt $_2$)-*arachno*-B $_9$ H $_{13}$ ³ were prepared according to literature methods; NaH was obtained commercially. Preparative thin-layer chromatography (TLC) was carried out using 1 mm layers of silica gel G (Fluka, type GF254), made from water slurries on glass plates of dimensions 20 × 20 cm followed by drying in air at 80 °C.

Preparation of [6-($\eta^5\text{-C}_5\text{Me}_5$)-*nido*-6-RhB $_9$ H $_{12}$ - μ -8,9-(NEt $_2$)] **1** and [5-($\eta^5\text{-C}_5\text{Me}_5$)-*nido*-5-RhB $_9$ H $_{12}$ - μ -9,10-(NEt $_2$)] **2**

A sample of 4-(NHEt $_2$)-*arachno*-B $_9$ H $_{13}$ (100 mg, 546 μmol) was dissolved in thf (20 cm 3), and then NaH (26.2 mg, 1.092 mmol) was added. The solution was stirred for 15 min at room temperature, then [(RhCl $_2$ ($\eta^5\text{-C}_5\text{Me}_5$)) $_2$] (165 mg, 546 μmol) was added and stirring continued for 3 h. The more volatile components were removed, the solid residue dissolved in CH $_2$ Cl $_2$ (*ca.* 5 cm 3) and the products separated and purified by repeated preparative TLC, development with hexane–CH $_2$ Cl $_2$ (3 : 7) giving [5-($\eta^5\text{-C}_5\text{Me}_5$)-*nido*-5-RhB $_9$ H $_{12}$ - μ -9,10-(NEt $_2$)] **2** as a yellow solid (R_F 0.84, 5 mg, 2%) and [6-($\eta^5\text{-C}_5\text{Me}_5$)-*nido*-6-RhB $_9$ H $_{12}$ - μ -8,9-(NEt $_2$)] **1** as an orange-yellow solid (R_F 0.75, 14 mg, 6%). Several other coloured products (total weight *ca.* 50 mg) were apparent, but at present these have so far proved impossible to purify and thence unequivocally to characterise.

Table 3 Crystal data and details of refinement for [6-(η^5 -C₅Me₅)-*nido*-6-RhB₉H₁₂- μ -8,9-(NEt₂)] **1** and [5-(η^5 -C₅Me₅)-*nido*-5-RhB₉H₁₂- μ -9,10-(NEt₂)] **2**

	1	2
Empirical formula	C ₁₄ H ₃₇ B ₉ NRh	C ₁₄ H ₃₇ B ₉ NRh
Formula weight	419.65	419.65
Crystal system	Orthorhombic	Monoclinic
Space group	<i>P</i> 2 ₁ 2 ₁	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	10.3219(6)	8.1876(5)
<i>b</i> /Å	12.9165(7)	14.3398(9)
<i>c</i> /Å	15.9291(8)	17.9158(11)
β /°	—	93.248(2)
<i>U</i> /Å ³	2123.7(2)	2100.1(2)
<i>Z</i>	4	4
<i>D</i> _c /Mg m ⁻³	1.312	1.327
μ /mm ⁻¹	0.801	0.810
<i>F</i> (000)	872	872
Crystal size/mm	0.40 × 0.15 × 0.14	0.65 × 0.06 × 0.03
θ_{\min} , θ_{\max} /°	2.03, 28.31	1.82, 28.44
<i>hkl</i> Ranges	−13, 13; −16, 16; −19, 20	−10, 10; −18, 18; −23, 20
Reflections collected	15 201	16 927
Independent reflections, <i>n</i>	4845	4904
<i>R</i> _{int} ^a	0.0222	0.0514
Reflections with <i>F</i> _o ² > 2σ <i>F</i> _o ²	4747	3706
Weighting scheme ^b parameters <i>a</i> , <i>b</i>	0.0227, 0.207	0.0305, 0.5523
Extinction coefficient, <i>x</i> ^c	0.0010(2)	0.0008(2)
No. parameters, <i>p</i>	282	282
Goodness of fit ^d on <i>F</i> ² , <i>S</i>	1.062	1.059
<i>R</i> 1 ^e	0.0171	0.0377
<i>wR</i> 2 ^f	0.0415	0.0741
Largest difference map peak and hole/e Å ⁻³	0.379, −0.313	0.441, −0.768
Enantiopole parameter ^g	−0.02(2)	—

^a $\sum|F_o^2 - F_c^2(\text{mean})|/\sum F_o^2$. ^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 $k[1 + 0.001x F_c^2 \lambda^3/\sin(2\theta)]^4$ where *k* is the overall scale factor. ^d $[\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$. ^e $\sum|F_o| - |F_c|/\sum|F_o|$ for reflections with *F*_o² > 2σ(*F*_o²). ^f $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ for all data.

^g See ref. 37.

Nuclear magnetic resonance spectroscopy

The NMR spectroscopy was performed at *ca.* 5.9 and 9.4 T (corresponding to 250 and 400 MHz ¹H frequencies respectively) using commercially available instrumentation and techniques and procedures described and enunciated elsewhere.^{32–35}

Chemical shifts δ are given in ppm relative to $\Xi = 100$ MHz for $\delta(^1\text{H})$ (± 0.05 ppm) (nominally SiMe₄), $\Xi = 32.083\,972$ MHz for $\delta(^{11}\text{B})$ (± 0.5 ppm) (nominally F₃B·OEt₂ in CDCl₃)³⁵ and $\Xi = 25.145\,004$ MHz for $\delta(^{13}\text{C})$ (± 0.5 ppm) (nominally SiMe₄); Ξ is as defined in ref. 36.

Crystallography

Crystals of [6-(η^5 -C₅Me₅)-*nido*-6-RhB₉H₁₂- μ -8,9-(NEt₂)] **1** and [5-(η^5 -C₅Me₅)-*nido*-5-RhB₉H₁₂- μ -9,10-(NEt₂)] **2** suitable for the single-crystal X-ray work were obtained by diffusion of CH₂Cl₂ into a hexane solution at room temperature. Crystallographic data for both complexes were collected at 160 K on a Siemens SMART CCD area-detector diffractometer with 0.3° ω -rotation frames using Mo-K α radiation ($\lambda = 0.710\,73$ Å). Crystal data and refinement parameters for both structures are listed in Table 3. Data were corrected for absorption empirically using repeated and symmetry-equivalent reflections.

Both structures were solved by direct methods using SHELXS 86³⁸ and were refined by full-matrix least squares (against all the unique *F*² data) using SHELXL 93.³⁹ Refinement procedures were 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 freely refined isotropically.

CCDC reference number 186/1006.

See <http://www.rsc.org/suppdata/dt/1998/2353/> for crystallographic files in .cif format.

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