Pentamethylcyclopentadienylrhodaborane Chemistry. Part 5.[1] Preparation, Molecular Structure, and Nuclear Magnetic Resonance Spectra of the *arachno* Ten-vertex Rhodadecaboranes $[6\text{-}(\eta^5\text{-}C_5Me_5)\text{-}6,9\text{-}(RNC)_2\text{-}arachno\text{-}6\text{-}RhB_9H_{11}]$ (R = Me or $p\text{-}MeC_6H_4$) *

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The reaction of MeNC with $[6\text{-}(\eta^5\text{-}C_5Me_5)\text{-}nido\text{-}6\text{-}RhB_9H_{13}]$ (**1**) results in the formation of yellow air-stable $[6\text{-}(\eta^5\text{-}C_5Me_5)\text{-}6,9\text{-}(MeNC)_2\text{-}arachno\text{-}6\text{-}RhB_9H_{11}]$ (**2**) in 64% yield. The product was characterized by n.m.r. spectroscopy, and the structural type confirmed by a single-crystal *X*-ray diffraction analysis on the $p\text{-}MeC_6H_4NC$ analogue, yellow, air-stable $[6\text{-}(\eta^5\text{-}C_5Me_5)\text{-}6,9\text{-}(p\text{-}MeC_6H_4NC)_2\text{-}arachno\text{-}6\text{-}RhB_9H_{11}]$ (**3**), obtained in the much lower yield of *ca.* 5% from the reaction of the *nido* compound (**1**) with $p\text{-}MeC_6H_4NC$. Crystals of (**3**) were triclinic, space group $P\bar{1}$, with a = 1 307.4(2), b = 1 264.6(2), c = 1 093.1(1) pm, α = 115.23(1), β = 85.05(1), γ = 110.37(1)°, and Z = 2; R factor 0.0312 for 5 138 observed reflections [$I > 2.0\sigma(I)$]. The two $p\text{-}MeC_6H_4NC$ ligands are in the Rh(6)-*endo* and B(9)-*exo* configuration.

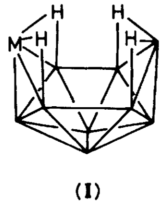
Examination of the reaction chemistry of polyhedral metallaboranes is often inhibited by the low yields in which they are obtained.[2,3] In Part 1 of this series[4] we described the synthesis of the ten-vertex *nido*-6-rhodadecaborane $[6\text{-}(\eta^5\text{-}C_5Me_5)\text{-}nido\text{-}6\text{-}RhB_9H_{13}]$ (**1**) {structure (**I**) [M = $Rh(\eta^5\text{-}C_5Me_5)$ in (**I**) and (**IV**)—(**VII**)]}. In contrast to most known metallaboranes,[3] compound (**1**) is obtainable in high yield from readily available starting materials, which therefore facilitates the examination of its further chemistry.

It is a direct structural analogue of the well examined binary borane *nido*-$B_{10}H_{14}$ (**II**). One of the extensively investigated reactions of *nido*-$B_{10}H_{14}$ is that with Lewis bases L such as PMe_2Ph which results in the elimination of dihydrogen to give bis(ligand) *arachno* species $B_{10}H_{12}L_2$ of schematic configurations (**IIIA**) and (**IIIB**) [equation (1)].[5–7]

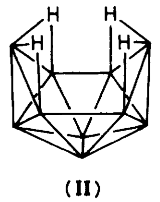
$$B_{10}H_{14} + 2L \longrightarrow B_{10}H_{12}L_2 + H_2 \qquad (1)$$

Analogous behaviour with the many known ten-vertex *nido*-metalladecaboranes however has not previously been reported.[3] For example, reaction of $[6\text{-}(\eta^5\text{-}C_5Me_5)\text{-}nido\text{-}6\text{-}RhB_9H_{13}]$ (**1**) with the tertiary phosphine PMe_2Ph yields the phosphine-substituted and rearranged ten-vertex *nido* cluster compound $[7\text{-}(PMe_2Ph)\text{-}5\text{-}(\eta^5\text{-}C_5Me_5)\text{-}nido\text{-}5\text{-}RhB_9H_{11}]$ (**IV**), together with ten-vertex $[3,10\text{-}(PMe_2Ph)_2\text{-}2\text{-}(\eta^5\text{-}C_5Me_5)\text{-}closo\text{-}2\text{-}RhB_9H_7]$ (**V**) and nine-vertex $[5\text{-}(PMe_2Ph)\text{-}2\text{-}(\eta^5\text{-}C_5Me_5)\text{-}nido\text{-}2\text{-}RhB_8H_{10}]$ (**VI**), as reported in Part 2,[8] whereas reaction with the secondary phosphine $PHPh_2$ results in the PPh_2-bridged *arachno* nine-vertex species $[4,8\text{-}(\mu\text{-}PPh_2)\text{-}4\text{-}(\eta^5\text{-}C_5Me_5)\text{-}9\text{-}(PHPh_2)\text{-}i\text{-}arachno\text{-}4\text{-}RhB_8H_9]$ (**VII**), as reported in Part 4.[1]

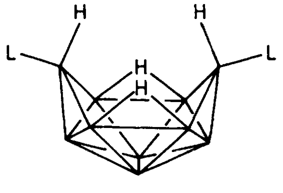
By contrast, we have now found that reactions of compound (**1**) with the ligands MeNC or $p\text{-}MeC_6H_4NC$, which have different Lewis acid–base σ and π characteristics to those of the phosphines, do in fact yield ten-vertex *arachno* metallaborane species (**VIII**) in an analogous manner to that in equation (1). The respective products are $[6\text{-}(\eta^5\text{-}C_5Me_5)\text{-}6,9\text{-}(MeNC)_2\text{-}arachno\text{-}6\text{-}RhB_9H_{11}]$ (**2**) and its corresponding



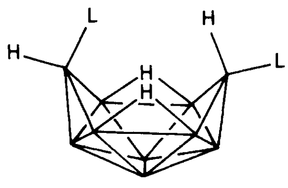
(**I**)



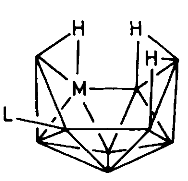
(**II**)



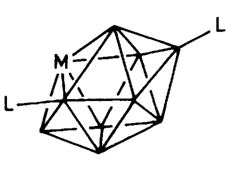
(**III A**)



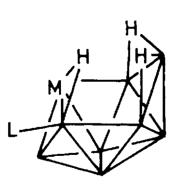
(**IIIB**)



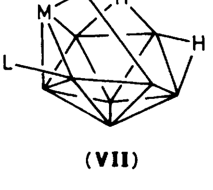
(**IV**)



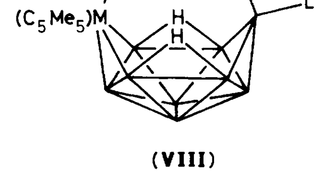
(**V**)



(**VI**)



(**VII**)



(**VIII**)

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* 6-(η^5-Pentamethylcyclopentadienyl)-6,9-bis(p-tolyl isocyanide)-*arachno*-6-rhodadecaborane.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Selected interatomic distances (pm) for $[6\text{-}(\eta^5\text{-}C_5Me_5)\text{-}6,9\text{-}(p\text{-}MeC_6H_4NC)_2\text{-}6\text{-}RhB_9H_{11}]$ (**3**) with e.s.d.s in parentheses

(*i*) To the rhodium atom			
Rh(6)–C(1)	191.0(4)	Rh(6)–B(2)	219.3(5)
Rh(6)–C(17)	222.7(4)	Rh(6)–B(5)	228.3(5)
Rh(6)–C(18)	226.1(4)	Rh(6)–B(7)	226.2(5)
Rh(6)–C(19)	227.4(4)		
Rh(6)–C(20)	224.4(4)		
Rh(6)–C(21)	225.2(4)		
(*ii*) Boron–boron			
B(1)–B(2)	176.1(6)	B(2)–B(3)	174.9(6)
B(1)–B(3)	178.3(6)		
B(1)–B(5)	179.0(6)	B(3)–B(7)	178.3(6)
B(1)–B(4)	175.3(6)	B(3)–B(4)	174.8(6)
B(1)–B(10)	178.7(6)	B(3)–B(8)	177.7(6)
B(2)–B(5)	177.4(6)	B(2)–B(7)	178.8(6)
B(4)–B(9)	173.3(6)		
B(4)–B(8)	177.1(6)	B(4)–B(10)	176.8(6)
B(5)–B(10)	190.3(6)	B(7)–B(8)	186.9(6)
B(9)–B(10)	186.7(6)	B(8)–B(9)	187.6(6)
(*iii*) Boron–hydrogen			
B(1)–H(1)	100(3)	B(3)–H(3)	106(3)
B(2)–H(2)	104(3)	B(4)–H(4)	112(2)
B(5)–H(5)	102(3)	B(7)–H(7)	107(4)
B(8)–H(8)	118(3)	B(10)–H(10)	96(3)
B(9)–H(9)	110(3)		
B(5)–H(5,10)	138(3)	B(7)–H(7,8)	132(3)
B(10)–H(5,10)	127(3)	B(8)–H(7,8)	123(3)
(*iv*) Others			
B(9)–C(9)	154.1(6)		
N(1)–C(1)	116.0(4)	N(2)–C(9)	114.9(4)
N(1)–C(2)	137.3(3)	N(2)–C(10)	137.2(3)
C(8)–C(5)	152.0(5)	C(16)–C(13)	150.3(5)

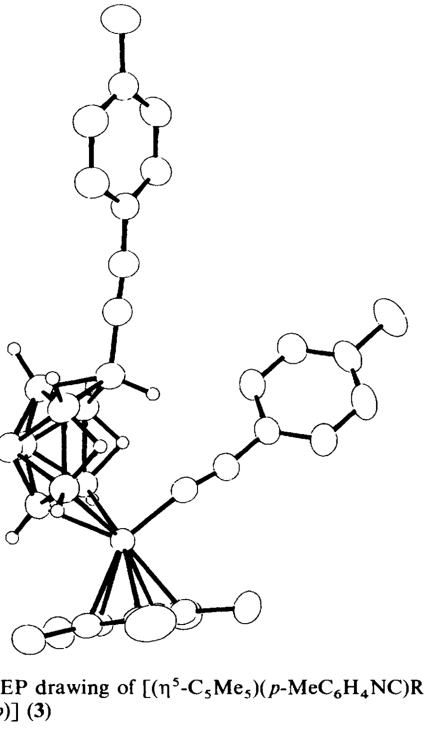


Figure 1. ORTEP drawing of $[(\eta^5\text{-}C_5Me_5)(p\text{-}MeC_6H_4NC)RhB_9H_{11}(CNC_6H_4Me\text{-}p)]$ (**3**)

(p-$MeC_6H_4NC)_2$ analogue (**3**). The work may be viewed in the context of other recent reports on the interaction of isonitriles with ten-vertex boron-containing cluster compounds.[9]

Table 2. Selected angles (°) between interatomic vectors for $[6\text{-}(\eta^5\text{-}C_5Me_5)\text{-}6,9\text{-}(p\text{-}MeC_6H_4NC)_2\text{-}6\text{-}RhB_9H_{11}]$ (**3**) with e.s.d.s in parentheses

(*i*) At the rhodium atom			
B(5)–Rh(6)–B(2)	46.6(1)	B(7)–Rh(6)–B(2)	47.3(1)
B(7)–Rh(6)–B(5)	80.7(2)		
C(1)–Rh(6)–B(5)	84.1(2)	C(1)–Rh(6)–B(7)	97.6(2)
C(1)–Rh(6)–B(2)	117.0(2)		
(*ii*) Rhodium–boron–boron			
Rh(6)–B(5)–B(1)	119.2(3)	Rh(6)–B(7)–B(3)	119.2(3)
Rh(6)–B(5)–B(2)	64.0(2)	Rh(6)–B(7)–B(2)	64.3(2)
Rh(6)–B(5)–B(10)	123.9(3)	Rh(6)–B(7)–B(8)	125.8(3)
Rh(6)–B(2)–B(1)	125.5(3)	Rh(6)–B(2)–B(3)	124.8(3)
Rh(6)–B(2)–B(5)	69.4(2)	Rh(6)–B(2)–B(7)	68.4(2)
(*iii*) Others			
Rh(6)–C(1)–N(1)	168.8(2)	B(9)–C(9)–N(2)	176.8(3)
C(1)–N(1)–C(2)	167.7(2)	C(9)–N(2)–C(10)	169.2(3)
C(9)–B(9)–H(9)	107(2)		
B(5)–H(5,10)–B(10)	92(2)	B(7)–H(7,8)–B(8)	94(2)

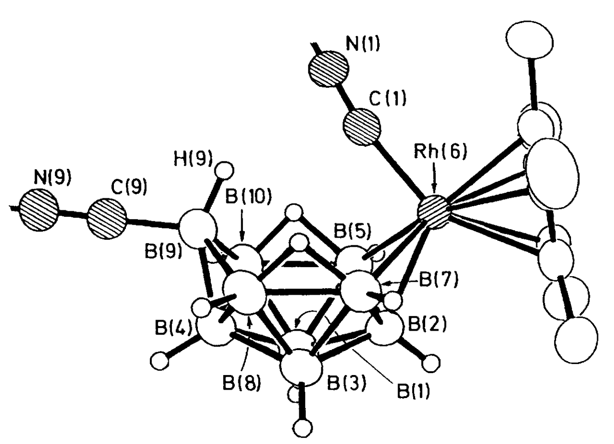


Figure 2. Detailed ORTEP drawing of the metallaborane cluster structure of $[(\eta^5\text{-}C_5Me_5)(p\text{-}MeC_6H_4NC)RhB_9H_{11}(CNC_6H_4Me\text{-}p)]$ (**3**) showing numbering scheme used

Results and Discussion

The reaction between methyl isocyanide and $[6\text{-}(\eta^5\text{-}C_5Me_5)\text{-}$*nido*-$6\text{-}RhB_9H_{13}]$ (**1**) in toluene solution at room temperature readily yielded a yellow air-stable crystalline solid product, tentatively identified by n.m.r. spectroscopy (see Table 3 below) as the 6,9-bis(methyl isocyanide) *arachno* ten-vertex metallaborane species $[6\text{-}(\eta^5\text{-}C_5Me_5)\text{-}6,9\text{-}(MeNC)_2\text{-}$*arachno*-$6\text{-}RhB_9H_{11}]$ (**2**). The isolated yield was 64% (the reaction being conducted on a scale of *ca.* 300 μmol) with an idealised stoicheiometry as in equation (2).

$$[(\eta^5\text{-}C_5Me_5)RhB_9H_{13}]\,(\mathbf{1}) + 2MeNC \longrightarrow [(\eta^5\text{-}C_5Me_5)(MeNC)RhB_9H_{11}(MeNC)]\,(\mathbf{2}) + H_2 \quad (2)$$

The reaction is therefore analogous to the addition of ligands to the binary borane analogue $B_{10}H_{14}$ [equation (1) above],[5–7] but is novel and previously unobserved for a *nido* ten-vertex metallaborane species. Those reactions of two-electron donor ligands with *nido* ten-vertex metallaboranes that have been previously investigated, specifically in some manganese,[10–13] rhenium,[14,15] ruthenium,[16] and (as mentioned above) rhodium[1,8] compounds, generally result in a retention of *nido* ten-vertex character or in a cluster oxidation, either by net electron or vertex loss. The process represented by equation (2), by contrast, is one of effective cluster reduction by net two-electron gain.

Unresolved questions following the n.m.r. identification of compound (**2**), apart from an independent confirmation of the structural type, concerned the dispositions of the two isonitrile ligands: do they occupy *exo,exo* configurations, (**IIIA**), or *endo,exo* ones, (**IIIB**), or are they of some other configuration? Crystals that we have so far obtained of compound (**2**) have not been ideal for single-crystal *X*-ray diffraction analysis, but we obtained suitable crystals of the *p*-tolyl isocyanide analogue $[(\eta^5\text{-}C_5Me_5)(p\text{-}MeC_6H_4NC)RhB_9H_{11}(p\text{-}MeC_6H_4NC)]$ (**3**). This is synthesized in an analogous manner to compound (**2**) [equation (2)], but the isolated yield was much smaller (*ca.* 5%; reaction scale 300 µmol). Compound (**3**) is also an air-stable yellow crystalline solid. The molecular structure is illustrated in Figures 1 and 2, and interatomic distances and angles are in Tables 1 and 2 respectively. All metallaborane cluster hydrogen atoms were readily located and freely refined.

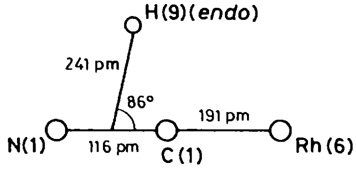
The metallaborane cluster structure is seen to be based on an open ten-vertex cage similar in gross geometric terms to both *nido* and *arachno* cluster geometries. Of these two, the *arachno* nature is indicated by the presence of bridging hydrogen atoms in the B(5)–B(10) and B(7)–B(8) positions, an *endo*-terminal hydrogen atom on B(9), and B(5)–B(10), B(10)–B(9), B(9)–B(8), and B(7)–B(8) interatomic distances mutually similar in magnitude to those observed for *arachno*-$[B_{10}H_{14}]^{2-}$ itself[17] and other *arachno* ten-vertex borane species.[3,18–21] The *arachno* nature is confirmed by the very diagnostic[6,22,23] cluster ^{11}B and ^{1}H n.m.r. shielding patterns (see Table 3 below), and also manifested more subtly in the slightly more open cluster than that of corresponding *nido* analogues such as compound (**1**) [for example B(5)–B(7), B(8)–B(10), and B(9)–Rh(6) are 294, 295, and 404 pm in compound (**3**), compared to 293, 282, and 396 pm respectively in compound (**1**)].

The two isonitrile ligands are in the B(9)-*exo*, Rh(6)-*endo* configuration (**VIII**), in contrast to most non-metallaborane $B_{10}H_{12}L_2$ species which are generally held to have the *exo,exo* configuration (**IIIA**).[5,7,18,19,24] However, recent results on the formation of $B_{10}H_{12}(PMe_2Ph)_2$ show that the initial kinetically-favoured product is that of *endo,exo* configuration (**IIIB**),[6] which is also now supported by the observed configurations of compounds (**2**) and (**3**) although in this case the steric bulk of the C_5Me_5 ligand will also affect the sites of ligand attack. Also it may be noted that the reaction of isonitriles with *nido*-6-SB_9H_{11} results in *endo* as well as *exo arachno* ten-vertex products.[25] One consequence of the *endo,exo* configuration for compounds (**2**) and (**3**) is the proximity of the H(9)(*endo*) atom to the Rh(6)-bound C≡N linkage. This results in an anomalously low nuclear shielding for $^{1}H(9)$(*endo*) as discussed below, and also suggests a potentially interesting further reaction chemistry.[25] An additional point of geometrical interest is the B(9)–C(9) internuclear distance to the *exo*-bound isonitrile ligand on C(9), which at 154.1(6) pm is somewhat shorter than those previously found for B–C distances to σ-bound organyl groups in metallaboranes (range 157.8—164.3, average 160.5 pm).[3,26–32] This may indicate contributions from multiple bonding between the borane cluster and the isonitrile ligands. The comparison data are, however, limited.

The $Rh(\eta^5\text{-}C_5Me_5)$ geometry is very similar to those of the other pentamethylcyclopentadienylrhodaboranes discussed in Parts 1—4,[1,4,8,33] and the rhodium–boron distances are similar to those[4] in the *nido* compound (**1**). The (neutral) $Rh(\eta^5\text{-}C_5Me_5)(RNC)$ rhodium centre may be regarded as making a two-orbital two-electron contribution to the cluster bonding proper {like BH_2^- in $[B_{10}H_{14}]^{2-}$ or like neutral BH(RNC) in the 9-position in compound (**2**) itself}, and this may be regarded as a straightforward 'octahedral' d^6 rhodium(III) centre. Compounds (**2**) and (**3**) are entirely in accord with the Williams–Wade cluster-geometry and electron-counting rules,[34,35] the two-electron bond to the *endo* RNC ligand on Rh(6) formally taking the place of an *endo*-terminal B–H bond in the binary borane formalism.

The measured n.m.r. properties for compound (**3**) (Table 3), are consistent with the crystallographically determined structure, confirming that the crystal selected was representative of the bulk sample. It can be seen from Table 3 that the n.m.r. properties for compounds (**2**) and (**3**) are very similar. The more detailed n.m.r. work was done on compound (**2**), for which the ^{11}B spectrum was readily assigned using relative intensities and observed two-dimensional $[^{11}B\text{–}^{11}B]$-COSY correlations (Figure 3). The ^{1}H spectrum was thence assigned by selective $^{1}H\text{-}\{^{11}B\}$ double-resonance experiments, the observed $[^{1}H\text{–}^{1}H]$-COSY correlations then acting as additional confirmation of the $\delta(^{11}B)$ assignments. All nearest-neighbour boron atoms show $[^{11}B\text{–}^{11}B]$-COSY cross-peaks except for the hydrogen-bonded (5)(10) and (7)(8) pairs [and of course the (1)(3) pair because of symmetry]. There is significant variation of intensity among the observed cross-correlation peaks, for example the $^{11}B(4)\text{–}^{11}B(9)$ correlation is weak whereas in *nido* ten-vertex systems it is invariably strong.[4,8,16,36,37] Likewise, there is a marked intensity variation among the $[^{1}H\text{–}^{1}H]$-COSY cross-peaks, the observed intensity patterns again being generally different from those observed[16,38] in *nido* ten-vertex systems.

There is a general parallel between $\delta(^{1}H)$ for the terminal protons and $\delta(^{11}B)$ for the boron atoms to which they were directly bound, the slope of the correlation $\delta(^{11}B):\delta(^{1}H)$ being *ca.* 20:1, the maximum deviation from this being some 0.25 p.p.m. in $\delta(^{1}H)$ (Figure 4). This slope is somewhat larger than that observed for the other pentamethylcyclopentadienylrhodaboranes reported in Parts 1—4 [$\delta(^{11}B):\delta(^{1}H)$ 12:1 to 16:1][1,4,8,33] but very similar to that observed for *arachno* ten-vertex bis(ligand) decaboranes such as $B_{10}H_{12}(PMe_2Ph)_2$-6,9 [$\delta(^{11}B):\delta(^{1}H)$ also *ca.* 20:1].[6] The overall boron nuclear shielding pattern [*e.g.* $\delta(^{11}B)$(1,3) and (6,9) at high field, $\delta(^{11}B)$(2,4) at lower field] is also similar to these and other[22–24,39–41] *arachno*-decaboranyl species, both these factors being confirmatory of the *arachno* ten-vertex character of the rhodaborane reported here. It is of interest that the *endo*-$^{1}H(9)$ resonance adjacent to the B(9)-*exo*-bound isonitrile ligand is also on the $\delta(^{11}B):\delta(^{1}H)$(*exo*-terminal) correlation line. This contrasts to the normal proton shielding behaviour of *arachno* ten-vertex polyhedral borane species, in which the *endo*-terminal proton resonance generally comes some 1—2 p.p.m. above the *exo*-proton plot,[6,22,23] but may be rationalized in this case by the anisotropic deshielding effect of the Rh(6)-bound *endo* *p*-MeC_6H_4NC ligand, the *endo*-H(9) atom being only some 241 pm from the mid-point of the anisotropic N≡C linkage [structure (**IX**)]. This close approach suggests interesting further chemistry.



(**IX**)

Experimental

General.—[6-$(\eta^5\text{-}C_5Me_5)$-*nido*-6-RhB_9H_{13}] (**1**),[1] MeNC,[42] and *p*-MeC_6H_4NC[42] were prepared according to the literature

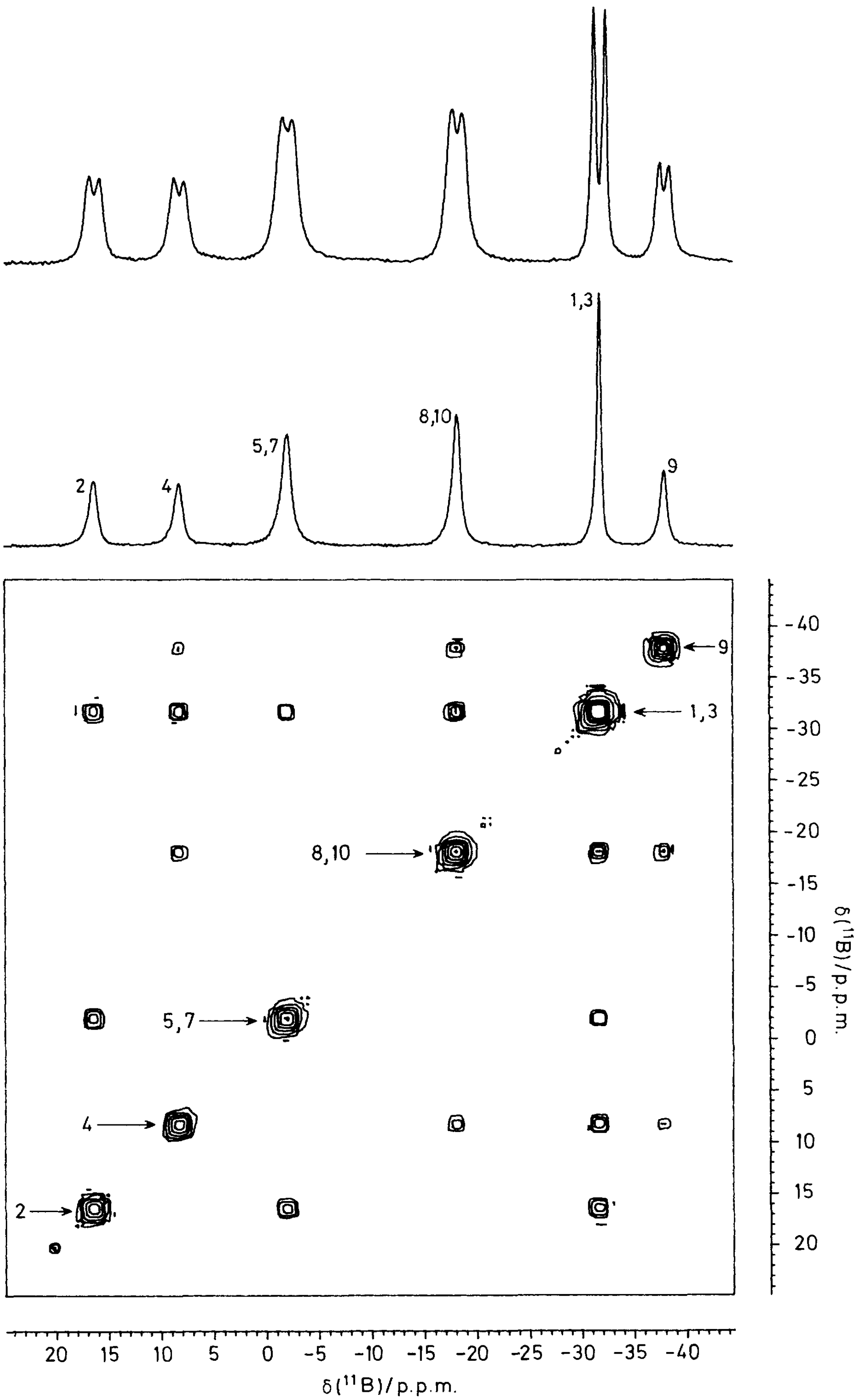


Figure 3. 128-MHz ^{11}B n.m.r. spectra for [(η^5-C_5Me_5)(MeNC)RhB_9H_{11}(CNMe)] (**2**). The top trace is the straightforward ^{11}B spectrum, and the second trace is the same spectrum recorded with {^{1}H(broad-band noise)} decoupling. The lowest diagram is an equiscalar two-dimensional [^{11}B–^{11}B]-COSY90 plot, presented with the same scale as the 'one-dimensional' plots, and also recorded with {^{1}H(broad-band noise)} decoupling

procedures. Reactions were carried out under an atmosphere of dry nitrogen, although subsequent manipulations and separations were carried out in air. Preparative t.l.c. was carried out on silica gel G (Fluka, type GF 254) as a stationary phase on plates of dimensions 200 × 200 × 1 mm, made in these laboratories as required from distilled water slurries followed by drying in air at 373 K for $\geqslant$48 h. Infrared spectra were obtained using commercially available instrumentation on samples prepared as Nujol or hexachlorobutadiene mulls. Mass spectrometry was performed using an AEI (now Kratos) MS30 instrument using the solid-sample introduction probe and 70 eV electron-impact ionization.

Table 3. Measured n.m.r. parameters for $[6\text{-}(\eta^5\text{-}C_5Me_5)\text{-}6,9\text{-}(MeNC)_2\text{-}arachno\text{-}6\text{-}RhB_9H_{11}]$ (**2**) and $[6\text{-}(\eta^5\text{-}C_5Me_5)\text{-}6,9\text{-}(p\text{-}MeC_6H_4NC)_2\text{-}arachno\text{-}6\text{-}RhB_9H_{11}]$ (**3**) in CD_2Cl_2 solution at 194 K

		(**2**)					(**3**)		
Assignment[a]	Relative intensity	$\delta(^{11}B)$/ p.p.m.[b]	Observed $[^{11}B-^{11}B]$-COSY correlations[c,d]	$^1J(^{11}B-^1H)$/ Hz[e]	$\delta(^1H)$/ p.p.m.[f,g]	Observed $[^1H-^1H]$-COSY correlations[d,h]	$\delta(^{11}B)$/ p.p.m.[b]	$\delta(^1H)$/ p.p.m.[f,i]	$^1J(^{11}B-^1H)$/ Hz[e]
(2)	1 BH	+16.3	(5,7)s, (1,3)s	134	+3.36	(1,3)s	+17.1	+3.51	135
(4)	1 BH	+8.2	(8,10)m, (1,3)s, (9)w	130	+3.12	(9)s	+8.5	+3.29	133
(5,7)	2 BH	−2.1	(2)s, (1,3)m	139	+2.14	(1,3)w, (5,10;8,7)s[j]	−1.7	+2.26	*ca.* 140
(8,10)	2 BH	−18.2	(4)m, (1,3)s, 9(m)	151	+1.86	(1,3)w, (5,10;8,7)s[j]	−17.0	+2.06	148
(1,3)	2 BH	−31.7	(2)s, (4)s, (5,7)m, (8,10)s	138	+0.66	(2)s, (5,7)w, (8,10)w (5,10;8,7)w	−31.2	+0.78	140
(9)	1 BH	−37.9	(4)w, (8,10)m	119	+0.47[k]	(4)s	−37.1	+0.90	120
(5,10;8,7) (bridge)	2 H	–		*l*	−3.17	(5,7)s,[j] (8,10)s,[j] (1,3)w	–	−2.82	—

[a] By relative intensities, $^1H\text{-}\{^{11}B(\text{selective})\}$ experiments, and two-dimensional COSY cross-peaks. [b] ±0.5 p.p.m. to high frequency (low field) of $BF_3(OEt_2)$ in $CDCl_3$. [c] Measured with $\{^1H(\text{broad-band noise})\}$ decoupling; other experimental details are in Table 4. [d] s = Stronger, w = weaker, m = intermediate intensity. [e] ±8 Hz, measured from resolution-enhanced ^{11}B spectrum. [f] ±0.05 p.p.m. to high frequency of $SiMe_4$; ^1H resonances assigned to directly-bound B positions by $^1H\text{-}\{^{11}B(\text{selective})\}$ experiments. [g] Additional ^1H data: MeNC at δ +3.34 and +3.46; C_5Me_5 at +1.77 p.p.m. [h] Measured with $\{^{11}B(\text{broad-band noise})\}$ decoupling; other experimental details are in Table 4. [i] Additional ^1H data; *p*-Me at δ +2.37 and +2.39; C_5Me_5 at +2.13; C_6H_4 at +7.12—+7.33 p.p.m. [j] Correlation arises from $^2J(^1H-^{11}B-^1H)$; all others from $^3J(^1H-B-B-^1H)$ pathways. [k] Doublet structure, splitting 8 Hz, presumably arising from $^3J[^1H(4)-^1H(9)]$. [l] Not resolved.

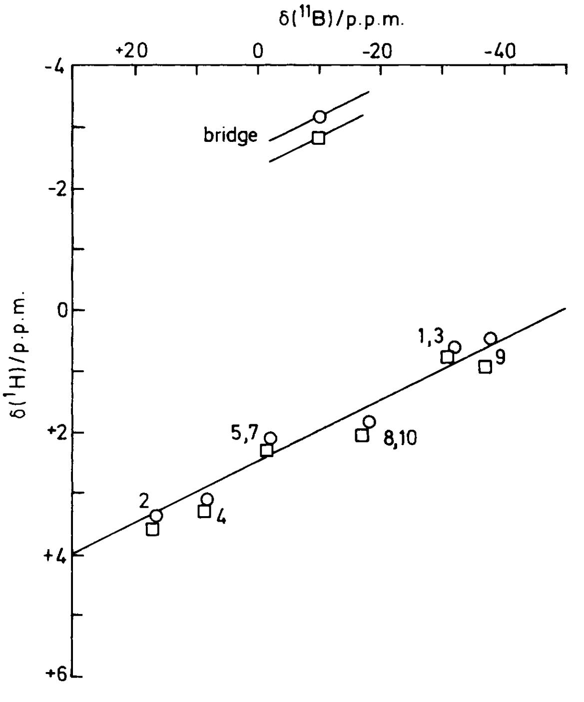


Figure 4. Plot of $\delta(^{11}B)$ *versus* $\delta(^1H)$ for directly bound boron and hydrogen atoms in $[(\eta^5\text{-}C_5Me_5)(RNC)RhB_9H_{11}(CNR)]$ [○, R = Me (**2**); and □, R = *p*-MeC_6H_4 (**3**)]. The line drawn has slope $\delta(^{11}B):\delta(^1H)$ 20:1 and intercept $\delta(^1H)$ +2.50 p.p.m.

Nuclear Magnetic Resonance Spectroscopy.—N.m.r. work was carried out at 2.35 and 9.40 Tesla using JEOL FX-100 and Bruker AM400 instrumentation respectively. The techniques of $^1H\text{-}\{^{11}B\}$,[6,8,43,44] $[^{11}B-^{11}B]$-COSY,[4,16,33,36,37] and $[^1H-^1H]$-COSY[1,16,33,38,45] n.m.r. spectroscopy as used in this work were essentially as described elsewhere, the specific experimental parameters used in the COSY work being summarized in Table 4. In the $^1H\text{-}\{^{11}B\}$ experiments use was made of the technique in which a $^1H\text{-}\{^{11}B(\text{off resonance})\}$ spectrum is subtracted from a $^1H\text{-}\{^{11}B(\text{on resonance})\}$ spectrum in order to remove resonance lines from protons not coupled to the ^{11}B nuclei of interest.[46,47]

Table 4. Experimental details for two-dimensional n.m.r. experiments on compound (**2**)

	$[^{11}B-^{11}B]$-COSY	$[^1H-^1H]$-COSY
Data size (t_2,t_1/words)	512, 64	1 024, 128
Transform size (F_2,F_1/words)	512, 256	1 024, 512
t_2 sweep width (= 2 × t_1 sweep width/Hz)	8 928.6	4 237.3
Digital resolution (F_2/Hz per point)	34.9	8.28
No. of transients per t_1 increment	4 800	128
Recycling time/s	0.05	0.62
Mixing pulse/°	90	45
Window* (t_2 and t_1)	sine-bell squared	sine-bell squared
Other details	$\{^1H$(broad-band-noise decoupling)$\}$	$\{^{11}B$(broad-band-noise decoupling)$\}$

* Centred on centre of free induction decay prior to zero-filling to transform size (*cf.* D. F. Gaines, G. M. Edvenson, T. G. Hill, and B. R. Adams, *Inorg. Chem.*, 1987, **26**, 1813).

Other spectroscopy was straightforward, chemical shifts $\delta(^1H)$ and $\delta(^{11}B)$ being given in p.p.m., positive to high freqency (low field) of Ξ100 ($SiMe_4$) and Ξ32.083 971 MHz [nominally $BF_3(OEt_2)$ in $CDCl_3$ at 294 K][23] respectively (Ξ being defined as in ref. 48).

Preparation of $[6\text{-}(\eta^5\text{-}C_5Me_5)\text{-}6,9\text{-}(MeNC)_2\text{-}arachno\text{-}6\text{-}RhB_9H_{11}]$ (**2**).—$[6\text{-}(\eta^5\text{-}C_5Me_5)\text{-}nido\text{-}6\text{-}RhB_9H_{13}]$ (**1**) (102 mg, 293 μmol) was dissolved in toluene (20 cm³) with gentle warming. A solution of MeNC in toluene (0.49 mol dm⁻³, 1.5 cm³, corresponding to *ca.* 740 μmol of MeNC) was added. The solution darkened rapidly, and over 24 h deposited a precipitate. This was collected, dissolved in CH_2Cl_2, and the resulting solution filtered. The filtrate was concentrated (rotary evaporator, 323 K, water-pump pressure) and applied to a series of preparative t.l.c. plates. Elution with CH_2Cl_2–MeCN (95:5) gave a broad yellow band (R_f = 0.7), which was removed, extracted with CH_2Cl_2, and the extract evaporated to dryness. Recrystallisation of this residue from CH_2Cl_2–hexane gave pure $[(\eta^5\text{-}C_5Me_5)(MeNC)RhB_9H_{11}(MeNC)]$ (**2**) as a yellow crystalline solid (80 mg, 187 μmol, 64%) (Found: C, 39.0; H, 7.55; B, 22.3; N, 6.3. $C_{14}H_{32}B_9N_2Rh$ requires C, 39.2; H, 7.55; B, 22.7;

N, 6.5%). Infrared: 2 895w, 2 510s, 2 490s(sh), 2 450m, 2 296s, 2 168s, 1 422m, 1 362m, 1 330m, 1 082m, 1 030w, 1 002m, 975w, 945w(br), 880w, 852m, 810w, 728w, and 510w cm^{-1}. Mass spectrum: *m/e* (max.) 430 (very weak); $^{12}C_{14}{}^{1}H_{32}{}^{11}B_{9}{}^{14}N_{2}$-$^{103}Rh$ requires *m/e* 430; the highest mass feature in the base envelope was at *m/e* 390; [M^+ − MeNC] requires 389 for $^{12}C_{12}{}^{1}H_{29}{}^{11}B_{9}{}^{14}N^{103}Rh$. Small single crystals were obtained by slow evaporation of a solution in CH_2Cl_2, but these were not as satisfactory for a single-crystal *X*-ray diffraction analysis as those from compound (**3**) (see below).

Preparation of [6-(η^5-C_5Me_5)-6,9-(*p*-MeC_6H_4NC)$_2$-*arachno*-6-RhB_9H_{11}] (**3**).—[6-(η^5-C_5Me_5)-*nido*-6-RhB_9H_{13}] (**1**) (100 mg, 287 µmol) was dissolved in toluene (20 cm^3) with gentle warming. A solution of *p*-MeC_6H_4NC in toluene (0.63 mol dm^{-3}, 0.9 cm^3, corresponding to 570 µmol of *p*-MeC_6H_4NC) was added by syringe. The solution immediately darkened and was left to stir for 3.5 h. The solvent was removed under reduced pressure (rotary evaporator, 353 K, water-pump pressure), the residue dissolved in CH_2Cl_2 (*ca.* 3 cm^3), and applied to a series of preparative t.l.c. plates. These were developed using CH_2Cl_2 as the liquid phase, and the yellow band at R_f 0.7 was removed, extracted with CH_2Cl_2, and purified by repeated t.l.c. using CH_2Cl_2–hexane (80:20) as the liquid phase. This yielded pure [(η^5-C_5Me_5)(*p*-MeC_6H_4NC)RhB_9H_{11}(CNC_6H_4Me-*p*)] (**3**) as a yellow crystalline solid (8 mg, 15 µmol, *ca.* 5%). Single crystals suitable for *X*-ray diffraction analysis were grown by the slow diffusion of hexane into a solution of compound (**3**) in CH_2Cl_2.

X-Ray Crystallography.—All crystallographic measurements were made on a Nicolet *P*3/F diffractometer operating in the ω scan mode using graphite-monochromatised Mo-K_α radiation (λ = 71.069 pm) following a standard procedure described in detail elsewhere.[49] The data set was corrected for absorption empirically once the structure had been determined.[50] The structure was solved *via* standard heavy-atom methods and refined by full-matrix least squares using the SHELX program system.[51] All non-hydrogen atoms were refined with anisotropic thermal parameters with the phenyl groups treated as rigid bodies with idealised hexagonal symmetry (C–C = 139.5 pm). The phenyl and methyl hydrogen atoms were included in calculated positions (C–H = 108 pm) and were assigned to an overall isotropic thermal parameter. The borane hydrogen atoms were located in a Fourier difference map and were freely refined with individual isotropic thermal parameters. The weighting scheme $w = [\sigma^2(F_o) + g(F_o)^2]^{-1}$ was used at the end of the refinement in which the parameter *g* was included in the refinement in order to obtain satisfactory agreement analyses.

Crystal data for (**3**). $C_{26}H_{40}B_9N_2Rh$, *M* = 580.82, triclinic, space group $P\bar{1}$, *a* = 1 307.4(2), *b* = 1 264.6(2), *c* = 1 093.1(1)

Table 5. Fractional atomic co-ordinates (× 10^4) for compound (**3**)

Atom	*x*	*y*	*z*
Rh(6)	2 814.8(1)	1 940.9(1)	204.4(2)
C(1)	1 594(2)	2 380(2)	1 063(2)
N(1)	953(2)	2 713(3)	1 779(2)
C(2)	178(1)	3 216(2)	2 441(2)
C(3)	−65(1)	4 039(2)	2 079(2)
C(4)	−868(1)	4 537(2)	2 719(2)
C(5)	−1 429(1)	4 210(2)	3 722(2)
C(6)	−1 186(1)	3 386(2)	4 084(2)
C(7)	−383(1)	2 889(2)	3 444(2)
C(8)	−2 296(3)	4 763(4)	4 428(5)
C(9)	−421(2)	2 595(3)	−1 976(3)
N(2)	−1 205(2)	2 636(2)	−2 324(2)
C(10)	−2 151(1)	2 478(2)	−2 941(2)
C(11)	−2 552(1)	1 449(2)	−4 180(2)
C(12)	−3 497(1)	1 276(2)	−4 853(2)
C(13)	−4 041(1)	2 130(2)	−4 287(2)
C(14)	−3 640(1)	3 159(2)	−3 048(2)
C(15)	−2 695(1)	3 332(2)	−2 375(2)
C(16)	−5 033(3)	1 976(4)	−5 035(4)
C(17)	3 096(2)	1 488(3)	1 876(3)
C(18)	3 993(2)	2 574(3)	1 980(3)
C(19)	4 555(2)	2 241(2)	788(3)
C(20)	3 995(2)	942(2)	−57(3)
C(21)	3 107(2)	473(2)	630(3)
C(22)	2 337(2)	1 398(4)	2 979(4)
C(23)	4 332(3)	3 840(3)	3 166(3)
C(24)	5 584(2)	3 077(3)	507(3)
C(25)	4 380(3)	180(3)	−1 355(3)
C(26)	2 370(3)	−862(3)	160(5)
B(1)	2 914(3)	3 169(3)	−2 169(3)
B(2)	3 221(2)	2 141(3)	−1 692(3)
B(3)	2 289(3)	1 525(3)	−3 085(3)
B(4)	1 524(2)	2 500(3)	−2 731(3)
B(5)	3 080(2)	3 524(3)	−412(3)
B(7)	2 026(2)	813(3)	−1 936(3)
B(8)	915(3)	1 044(3)	−2 652(3)
B(9)	594(2)	2 472(3)	−1 506(3)
B(10)	1 939(3)	3 766(3)	−1 115(3)
H(3A)	369(1)	4 292(2)	1 302(2)
H(4A)	−1 056(1)	5 174(2)	2 438(2)
H(6A)	−1 620(1)	3 133(2)	4 861(2)
H(7A)	−195(1)	2 251(2)	3 724(2)
H(8A)	−2 747(3)	4 421(4)	5 138(5)
H(8B)	−2 843(3)	4 489(4)	3 575(5)
H(8C)	−1 942(3)	5 766(4)	4 921(5)
H(11)	−2 131(1)	788(2)	−4 618(2)
H(12)	−3 808(1)	480(2)	−5 812(2)
H(14)	−4 062(1)	3 820(2)	−2 610(2)
H(15)	−2 385(1)	4 128(2)	−1 416(2)
H(16A)	−5 184(3)	1 171(4)	−5 998(4)
H(16B)	−4 923(3)	2 789(4)	−5 203(4)
H(16C)	−5 721(3)	1 833(4)	−4 429(4)
H(22A)	2 286(3)	2 304(4)	3 615(4)
H(22B)	2 801(3)	1 159(4)	3 529(4)
H(22C)	1 524(3)	712(4)	2 693(4)
H(23A)	3 581(3)	3 816(3)	3 670(3)
H(23B)	4 528(3)	4 516(3)	2 748(3)
H(23C)	4 987(3)	4 096(3)	3 888(3)
H(24A)	5 786(2)	2 663(3)	−530(3)
H(24B)	6 225(2)	3 225(3)	1 184(3)
H(24C)	5 503(2)	3 958(3)	717(3)
H(25A)	4 928(3)	785(3)	−1 772(3)
H(25B)	3 687(3)	−468(3)	−2 074(3)
H(25C)	4 805(3)	−328(3)	−1 149(3)
H(26A)	1 604(3)	−923(3)	631(5)
H(26B)	2 780(3)	−1 342(3)	442(5)
H(26C)	2 215(3)	−1 287(3)	−928(5)
H(1)	3 457(27)	3 598(30)	−2 664(33)
H(2)	4 017(26)	2 146(29)	−1 839(31)
H(3)	2 498(22)	1 044(26)	−4 081(28)
H(4)	1 211(18)	2 637(21)	−3 554(22)
H(5)	3 638(25)	4 319(29)	279(31)
H(7)	1 950(29)	−138(34)	−2 263(36)
H(8)	213(22)	233(26)	−3 463(28)
H(9)	410(22)	2 365(25)	−556(27)
H(10)	1 877(22)	4 559(27)	−886(27)
H(5,10)	2 120(25)	3 756(29)	0(30)
H(7,8)	1 011(23)	779(27)	−1 714(29)

pm, $\alpha = 115.23(1)$, $\beta = 85.05(1)$, $\gamma = 110.37(1)°$, $U = 1.5285(4)$ nm^3, $Z = 2$, $\mu = 5.09$ cm^{-1}, and $F(000) = 600$.

Data collection. Scan widths 1.0° + α-doublet splitting, scan speeds 2.0—29.3° min^{-1} and $4.0 < 2\theta < 50.0°$. Total data collected = 5 499, number observed = 5 138 [$I > 2.0\sigma(I)$].

Structure refinement. Number of parameters = 387, weighting factor $g = 0.0002$, $R = 0.0312$, $R' = 0.0346$.

Atomic co-ordinates are given in Table 5. Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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