Pentamethylcyclopentadienylrhodaborane Chemistry. Part 1. High-yield Planned Synthesis, Molecular Structure, and Nuclear Magnetic Resonance Properties of the Ten-vertex *nido*-6-Rhodadecaborane [(η^5-C_5Me_5)RhB_9H_{13}] *

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The dimeric pentamethylcyclopentadienylrhodium complex [{Rh(η^5-C_5Me_5)Cl_2}$_2$] is potentially a high-yield rhodaborane synthon, and reacts quantitatively with *arachno*-[B_9H_{14}]$^-$ to give [6-(η^5-C_5Me_5)-*nido*-6-RhB_9H_{13}] as an orange-red air-stable solid, which has been examined by *X*-ray crystallography. Crystals are orthorhombic, space group *Pbca*, with a = 1 977.2(3), b = 1 440.1(2), c = 2 450.1(4) pm, and Z = 16; the final R factor is 0.0429 for 3 678 observed reflections. N.m.r. data are also presented and briefly discussed; these together with the molecular structure confirm the complex to be a *nido*-decaborane analogue in which the HB(6) unit is replaced by an isolobal and isoelectronic Rh(η^5-C_5Me_5) centre.

Surveys of polyhedral metallaborane chemistry reveal a large variety of reaction and structural data on cobaltaborane and iridaborane species.[1] In known compounds the cobalt centres used have tended to mimic isoelectronic boron centres to produce structures that are relatively straightforward in terms of the application of the Wade–Williams–Mingos–Rudolph PSEPT rules,[2] but the iridium centres have tended to exhibit a greater variety of behaviour, and produce more exceptions to the PSEPT rules for simple clusters. This is partly a function of the choice of exopolyhedral metal ligands by the various research schools involved, *viz.* cyclopentadienyl for cobalt and non-chelating phosphines and carbonyls for iridium, but is also a function of the greater flexibility of valency state and co-ordination number available to the heavier metal atom.[3] In this context the behaviour of rhodium is of considerable interest, but the amount of reported polyhedral rhodaborane work is surprisingly sparse, known species being limited to *nido*-[$(PPh_3)_2HRhB_4H_8$],[4] *nido*-[(cod)$ClRhB_9H_{13}$] (cod = cyclo-octa-1,5-diene),[5] the *nido*-hexaborane complexes [(acac)Rh(B_6H_{10})$_2$] [acac = acetylacetonate] and [{ClRh(B_6H_{10})$_2$}$_2$],[6] and the very recently reported *closo*-type species [$(PMe_2Ph)_2RhHB_{10}H_8(OMe)_2$] and [$(PMe_2Ph)_2RhHB_{10}H_8Cl(OMe)$];[7] only the last two compounds have been examined crystallographically.

A successful synthetic stratagem for the production of metalloborane compounds in our laboratories has been the reaction of a low-valent transition-metal halide complex with a borane anion.[8,9] This process generally results in halide displacement by the borane anion accompanied by an effective oxidative insertion of the metal into the cluster, the basic reaction type often being accompanied by a variety of other processes such as cluster rearrangement,[10] cluster degradation,[11–20] ligand addition to the cluster,[12,16,20–22] solvent addition to the cluster,[7,12,23,24] cluster closure,[11,24–27] ortho-cycloboronation,[10,12,14,21,26] *etc.*, and this has been applied particularly to iridium(I) substrates such as [$IrCl(PR_3)_3$] and [$Ir(CO)Cl(PR_3)_2$] (*e.g.* R = Me or Ph).[9,21,28,29] In our initial attempts to extend some of these successful reactions to analogous rhodium species, however, we have found that the predominant products are the phosphine–borane adducts such as $BH_3(PR_3)$ and $B_9H_{13}(PR_3)$, and only trace amounts, if any, of isolable metallaboranes are present.[30] The principal exception to this so far is the synthesis of the two *closo*-type eleven-vertex species [$(PMe_2Ph)_2RhHB_{10}H_8(OMe)_2$] and [$(PMe_2Ph)_2RhHB_{10}H_8Cl(OMe)$] [though even these were obtained in the low yields of $\leqslant$ *ca.* 5%, the major products still being $BH_3(PMe_2Ph)$ and $B_9H_{13}(PMe_2Ph)$].[7] In view of this we surmised that the rhodium ligation sphere in the rhodium halide starting complexes such as these was too labile, and that consequently phosphine ligand dissociation followed by phosphine ligand attack on the borane anion often occurred preferentially to metallaborane formation. It seemed reasonable that less competition from such processes might occur with chelating metal ligands such as the polyphosphines or cyclopentadienyls on the starting rhodium halide,[30] and most of our initial siting experiments indicate that this is indeed often the case. In accord with this we have initiated a systematic survey of polyhedral rhodaborane chemistry using the pentamethylcyclopentadienyl moiety as the exopolyhedral rhodium ligand. Here we describe the high-yield preparation of the ten-vertex *nido*-6-metalladecaborane [6-(η^5-C_5Me_5)-*nido*-6-RhB_9H_{13}].

Results and Discussion

The reaction between *arachno*-[B_9H_{14}]$^-$ and [{Rh(η^5-C_5Me_5)Cl_2}$_2$] in dichloromethane solution at room temperature for 50 min results in the quantitative formation of [6-(η^5-C_5Me_5)RhB_9H_{13}] according to the reaction stoicheiometry of equation (1).

$$[\{Rh(\eta^5\text{-}C_5Me_5)Cl_2\}_2] + 2[B_9H_{14}]^- \longrightarrow 2[6\text{-}(\eta^5\text{-}C_5Me_5)RhB_9H_{13}] + 2Cl^- + 2HCl \quad (1)$$

The product is readily isolated as a blood-orange air-stable crystalline solid in essentially quantitative yield (reaction on a scale of *ca.* 1 mmol), and readily yields crystals suitable for single-crystal *X*-ray diffraction analysis. There are two independent molecules, a and b, in the unit cell which differ slightly in the orientation of the C_5Me_5 group. The structure of molecule a is shown in Figure 1, and selected interatomic

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* *nido*-6-(η^5-Pentamethylcyclopentadienyl)-6-rhodadecaborane.

Supplementary data available (No. SUP 56414, 9 pp.): thermal parameters, full list of bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Interatomic distances (pm) for [6-(η^5-C_5Me_5)RhB_9H_{13}] with e.s.d.s in parentheses

Molecule a				Molecule b			
(*i*) To the rhodium atom							
Rh(6)–C(1)	216.1(9)			Rh(6)–C(1)	220.0(8)		
Rh(6)–C(2)	219.3(8)			Rh(6)–C(2)	222.4(8)		
Rh(6)–C(3)	220.2(8)			Rh(6)–C(3)	218.5(8)		
Rh(6)–C(4)	216.9(8)			Rh(6)–C(4)	217.6(8)		
Rh(6)–C(5)	217.3(8)			Rh(6)–C(5)	216.0(8)		
Rh(6)–B(2)	219.2(9)			Rh(6)–B(2)	220.0(10)		
Rh(6)–B(5)	223.9(10)	Rh(6)–B(7)	222.4(10)	Rh(6)–B(5)	223.3(10)	Rh(6)–B(7)	221.8(10)
Rh(6)–H(5,6)	170(4)	Rh(6)–H(6,7)	171(4)	Rh(6)–H(5,6)	170(5)	Rh(6)–H(6,7)	177(4)
(*ii*) Boron–boron							
B(1)–B(2)	178.0(12)	B(2)–B(3)	177.3(12)	B(1)–B(2)	177.7(13)	B(2)–B(3)	177.1(13)
B(1)–B(3)	176.9(12)			B(1)–B(3)	176.2(13)		
B(1)–B(5)	172.2(12)	B(3)–B(7)	173.6(12)	B(1)–B(5)	173.8(13)	B(3)–B(7)	174.1(13)
B(1)–B(4)	176.8(13)	B(3)–B(4)	178.2(13)	B(1)–B(4)	177.0(12)	B(3)–B(4)	179.7(13)
B(1)–B(10)	171.3(13)	B(3)–B(8)	172.5(13)	B(1)–B(10)	172.2(13)	B(3)–B(8)	172.4(15)
B(2)–B(5)	179.9(12)	B(2)–B(7)	181.4(12)	B(2)–B(5)	181.4(13)	B(2)–B(7)	177.9(13)
B(4)–B(9)	169.6(14)			B(4)–B(9)	166.4(14)		
B(4)–B(8)	176.1(14)	B(4)–B(10)	177.2(13)	B(4)–B(8)	174.5(14)	B(4)–B(10)	174.8(13)
B(5)–B(10)	198.8(14)	B(7)–B(8)	202.1(14)	B(5)–B(10)	201.1(14)	B(7)–B(8)	201.6(14)
B(9)–B(10)	178.7(14)	B(8)–B(9)	176.8(15)	B(9)–B(10)	179.0(14)	B(8)–B(9)	175.0(15)
(*iii*) Boron–hydrogen							
B(1)–H(1)	107(5)	B(3)–H(3)	110(5)	B(1)–H(1)	117(5)	B(3)–H(3)	114(6)
B(5)–H(5)	124(5)	B(7)–H(7)	116(4)	B(5)–H(5)	118(4)	B(7)–H(7)	116(5)
B(10)–H(10)	99(5)	B(8)–H(8)	123(4)	B(10)–H(10)	114(5)	B(8)–H(8)	115(5)
B(9)–H(9)	112(6)			B(9)–H(9)	107(6)		
B(4)–H(4)	111(4)			B(4)–H(4)	108(4)		
B(10)–H(9,10)	111(5)	B(8)–H(8,9)	95(5)	B(10)–H(9,10)	120(5)	B(8)–H(8,9)	97(5)
B(9)–H(8,9)	115(5)	B(9)–H(9,10)	115(4)	B(9)–H(8,9)	111(4)	B(9)–H(9,10)	116(4)
(*iv*) Others							
C(ring)—C(ring) range	139.5(9)—144.4(9)			C(ring)—C(ring) range	141.4(9)—143.2(10)		
C(ring)—C(Me) range	148.4(10)—149.8(11)			C(ring)—C(Me) range	148.9(10)—149.9(10)		

Table 2. Selected angles (°) between interatomic vectors for [6-(η^5-C_5Me_5)RhB_9H_{13}] with e.s.d.s in parentheses

Molecule a				Molecule b			
(*i*) At the rhodium atom							
B(5)–Rh(6)–B(2)	47.9(3)	B(7)–Rh(6)–B(2)	48.5(3)	B(5)–Rh(6)–B(2)	48.3(3)	B(7)–Rh(6)–B(2)	47.5(3)
B(7)–Rh(6)–B(5)	82.8(4)			B(7)–Rh(6)–B(5)	82.1(4)		
H(5,6)–Rh(6)–H(6,7)	88(2)			H(5,6)–Rh(6)–H(6,7)	88(2)		
(*ii*) Rhodium–boron–boron							
Rh(6)–B(5)–B(1)	118.3(6)	Rh(6)–B(7)–B(3)	118.0(6)	Rh(6)–B(5)–B(1)	118.1(6)	Rh(6)–B(7)–B(3)	119.6(6)
Rh(6)–B(5)–B(2)	64.7(4)	Rh(6)–B(7)–B(2)	64.8(4)	Rh(6)–B(5)–B(2)	64.9(4)	Rh(6)–B(7)–B(2)	65.7(5)
Rh(6)–B(5)–B(10)	120.6(5)	Rh(6)–B(7)–B(8)	121.3(6)	Rh(6)–B(5)–B(10)	121.6(5)	Rh(6)–B(7)–B(8)	112.3(6)
Rh(6)–B(2)–B(1)	117.9(5)	Rh(6)–B(2)–B(3)	117.8(6)	Rh(6)–B(2)–B(1)	118.0(6)	Rh(6)–B(2)–B(3)	119.1(6)
Rh(6)–B(2)–B(5)	67.4(4)	Rh(6)–B(2)–B(7)	66.7(4)	Rh(6)–B(2)–B(5)	66.8(4)	Rh(6)–B(2)–B(7)	66.8(5)
(*iii*) Others							
Rh(6)–H(5,6)–B(5)	99(3)	Rh(6)–H(6,7)–B(7)	94(3)	Rh(6)–H(5,6)–B(5)	96(3)	Rh(6)–H(6,7)–B(7)	96(3)
B(9)–H(9,10)–B(10)	104(4)	B(9)–H(8,9)–B(8)	114(5)	B(9)–H(9,10)–B(10)	99(4)	B(9)–H(8,9)–B(8)	115(4)

distances and angles are given in Tables 1 and 2 respectively. The compound is readily seen to be *nido*-6-metalladecaborane, *i.e.* it has a *nido*-$B_{10}H_{14}$ configuration in which the HB(6) vertex has been replaced by an isoelectronic and isolobal Rh(η^5-C_5Me_5) entity.[31,32] An overall description of the molecular structure in cluster terms is that it consists of a *nido* six-vertex RhC_5 cluster and a *nido* ten-vertex RhB_9 cluster conjoined at the common metal atom. There is sandwich character to the compound in that the Rh-bound C_5 and B_3 planes are nearly parallel (dihedral angle 3.95° for molecule a, and 5.5° for molecule b), and the five methyl groups on the cyclopentadienyl ring are bent away somewhat from the metal atom (mean angular deviation from the C_5 plane 3.3° for molecule a, and 5° for molecule b).[33,34] There is variation among the Rh–C distances, which may arise from differential *trans* or steric effects of the nearest-neighbour components of the B_9H_{13} clusters, although this variation is not too significant statistically [range 216.0(8)—222.4(8) pm]. There is also a variation among the angles between the C-methyl vectors and the central C_5 mean plane (deviations from 180° in the range 1.6—6.0°), but this does

Table 3. Proton and boron-11 n.m.r. data for $[6\text{-}(\eta^5\text{-}C_5Me_5)RhB_9H_{13}]$ (CD_2Cl_2 solution at +21 °C, this work) and for $[6\text{-}(\eta^5\text{-}C_5Me_5)CoB_9H_{13}]$ ($CDCl_3$ solution at ambient temperature, data from ref. 33)

	$[6\text{-}(\eta^5\text{-}C_5Me_5)RhB_9H_{13}]$			$[6\text{-}(\eta^5\text{-}C_5Me_5)CoB_9H_{13}]$		
Assignment	$\delta(^{11}B)$/p.p.m.[a,b]	$^1J(^{11}B-^1H)$/Hz[c]	$\delta(^1H)$[d,e]	$\delta(^{11}B)$/p.p.m.[b]	$^1J(^{11}B-^1H)$/Hz	$\delta(^1H)$[d,f]
5,7	+19.4 (2 B)	149, 54	+4.07 (2 H); −8.15 (2 H)[g]	+20.5 (2 B)	107 [f]	+4.3
1,3	+12.7 (2 B)	138	+3.59 (2 H)	+15.4 (2 B)	136	+3.7
9	+4.7 (1 B)	158	+3.39 (1 H) } −2.76 (2 H)[h]	+5.2 (1 B)	143	+2.7
8,10	−0.9 (2 B)	152	+2.78 (2 H)	−1.2 (2 B)	143	+0.8
2	−10.8 (1 B)	141	+0.69 (1 H)	−12.4 (1 B)	139	−3.3 [h]
4	−30.6 (1 B)	150	+1.01 (1 H)	−29.8 (1 B)	148	−11.8[i]
C_5Me_5	—	—	+2.02 (15 H)	—	—	+1.89

[a] ±0.5 p.p.m. [b] To high frequency of $BF_3(OEt_2)$. [c] ±5 Hz; measured from ^{11}B spectrum with resolution enhancement to achieve baseline separation of doublet components. [d] ±0.05 p.p.m. to high frequency of $SiMe_4$. [e] ^1H resonances related to directly bound ^{11}B resonances by selective $^1H\text{-}\{^{11}B\}$ experiments. [f] Relative intensities and $^{11}B-^1H$ correlations not specified in ref. 33. [g] H(5,6;6,7) (bridge); doublet, splitting 28 Hz, ascribed to $^1J(^{103}Rh-^1H)$. [h] H(8,9;9,10) (bridge). [i] H(5,6;6,7) (bridge); doublet, splitting 35 Hz, ascribed to $J(^1H-^1H)$ (bridge–terminal) (ref. 33).

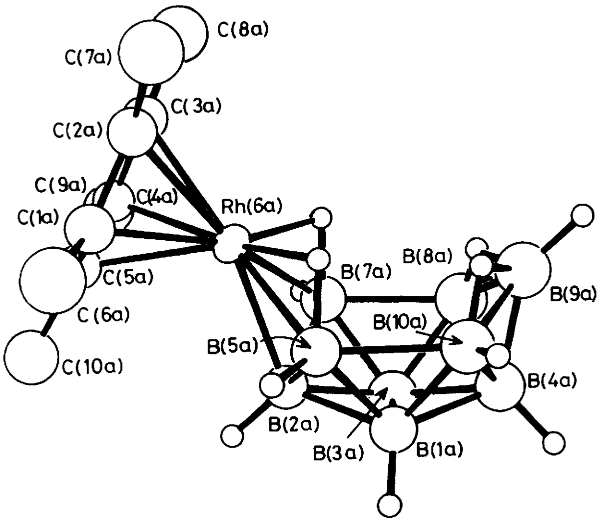

Figure 1. Crystallographically determined molecular structure of $[6\text{-}(\eta^5\text{-}C_5Me_5)RhB_9H_{13}]$ (molecule a). There is a second crystallographically distinct molecule which differs in the angle of twist about the pseudo-C_5 axis of the C_5Me_5 group relative to the rest of the molecule

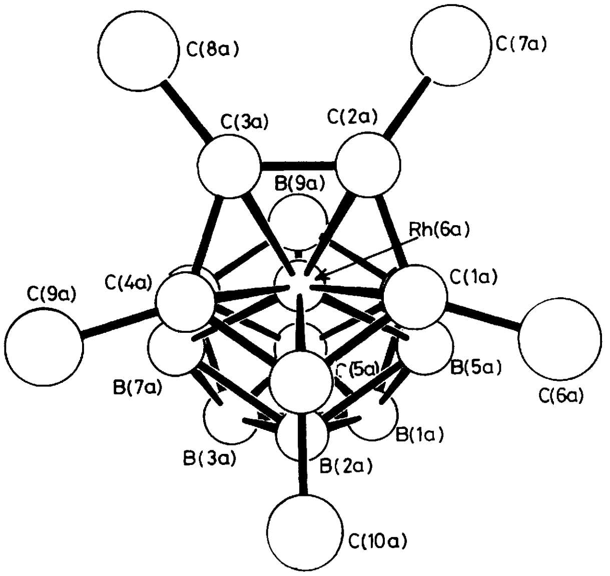

Figure 2. View of molecule a perpendicular to the C_5Me_5 ring showing the approximate C_s symmetry of the non-H-atom framework (H atoms omitted for clarity). In molecule b there is a rotational twist (*ca.* 12°) of the C_5Me_5 moiety relative to the ideal RhB_9 mirror plane

not seem to correlate with any intramolecular features, and therefore presumably arises from crystal-packing forces, *etc.*

The dimensions of those parts of the borane cluster that are not contiguous to the metal atom are very similar to those in $B_{10}H_{14}$ itself,[32,35] and the overall structure is very similar to that of the cobalt analogue $[6\text{-}(\eta^5\text{-}C_5Me_5)CoB_9H_{13}]$.[33] The Rh–B distances are each some 10—11 pm longer than their Co–B counterparts, however, and the two crystalline forms are not isomorphous. The cobalt species crystallizes in the orthorhombic space group $P2_12_12_1$ with cell dimensions a = 1 053.5(3), b = 1 283.0(3), c = 1 303.7(3) pm, and Z = 4,[33] whereas the rhodaborane is *Pbca*, with a = 1 977.2(3), b = 1 440.1(2), c = 2 450.1(4) pm, and Z = 16, and there are two crystallographically distinct molecules in the unit cell, which differ from each other in the angle of twist of the C_5Me_5 moiety relative to the B_9H_{13} moiety. It is of interest that in the solid state the configuration of molecule a approximates to mirror-plane symmetry, with one of the C(aryl)–C(methyl) bonds eclipsing Rh(6)–B(2) (see Figure 2), but presumably in the solution state there will be relatively free mutual contrarotational fluxional behaviour about the effective five-fold axis of the pentamethylcyclopentadienyl group.

The boron and proton n.m.r. chemical shifts and coupling constants are also consistent with the structure and are similar to those of the cobalt species.[33] The data are summarized in Table 3, which also includes data for $[6\text{-}(\eta^5\text{-}C_5Me_5)CoB_9H_{13}]$[33] for comparison, and a ^{11}B two-dimensional COSY-90 spectrum is given in Figure 3. The assignments for the ^{11}B chemical shifts readily follow from their relative intensities, comparison with known species,[5,10,21,31–33] *etc.*, and the assignments are in addition confirmed by the interboron correlations in the two-dimensional COSY spectrum. In the two-dimensional plot reasonably strong correlations are seen between all adjacent and chemically distinct sites, except for those between B(5,7) and B(8,10), and between B(9) and B(8,10), which are not observed, implying coupling constants $J(^{11}B-^{11}B)$ significantly smaller than the others. This is expected for the *nido*-decaboranyl electronic structure,[36–39] but it should be noted that the apparent absence of a correlation between positions such as B(9) and B(8,10) is by no means

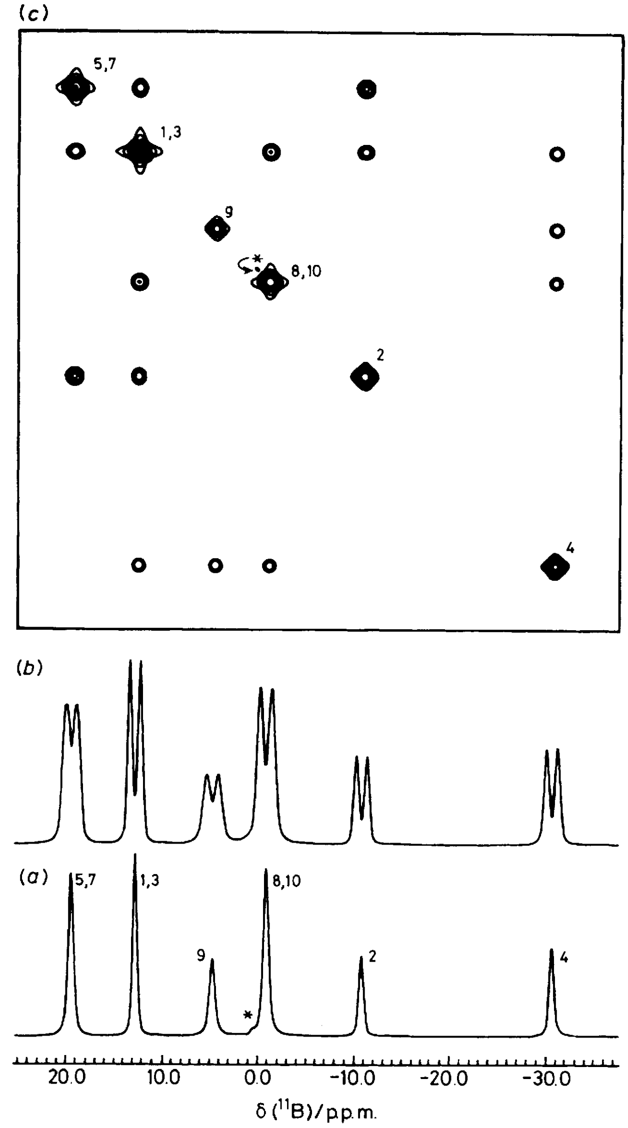

Figure 3. 128-MHz boron-11 n.m.r. spectra for $[6\text{-}(\eta^5\text{-}C_5Me_5)RhB_9H_{13}]$: (*a*) ^{11}B-{^{1}H(broad band noise)} spectrum, (*b*) normal ^{11}B spectrum, and (*c*) a (symmetrised) homonuclear two-dimensional COSY-90 plot using data acquired under conditions of {^{1}H(broad band noise)} decoupling. * Signifies impurity

Table 4. Non-hydrogen atomic co-ordinates (× 10^4) for $[6\text{-}(\eta^5\text{-}C_5Me_5)\text{-}RhB_9H_{13}]$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Rh(6a)	3 190	−1 535	5 024
Rh(6b)	4 294	5 790	2 427
C(1a)	2 964(3)	−68(5)	4 988(2)
C(2a)	2 681(3)	−494(4)	4 517(2)
C(3a)	2 199(3)	−1 141(4)	4 685(2)
C(4a)	2 179(3)	−1 135(4)	5 274(2)
C(5a)	2 638(3)	−458(4)	5 457(2)
C(6a)	3 467(4)	709(6)	4 990(3)
C(7a)	2 832(4)	−239(5)	3 942(3)
C(8a)	1 752(4)	−1 721(5)	4 331(3)
C(9a)	1 699(3)	−1 668(5)	5 619(3)
C(10a)	2 732(3)	−150(5)	6 032(3)
C(1b)	5 334(3)	5 451(4)	2 181(2)
C(2b)	4 891(3)	4 921(4)	1 852(2)
C(3b)	4 496(3)	4 348(4)	2 202(3)
C(4b)	4 711(3)	4 504(4)	2 750(3)
C(5b)	5 223(3)	5 207(4)	2 738(3)
C(6b)	5 858(4)	6 125(5)	1 986(3)
C(7b)	4 873(3)	4 891(5)	1 245(3)
C(8b)	3 994(4)	3 636(5)	2 025(3)
C(9b)	4 459(4)	3 995(5)	3 243(3)
C(10b)	5 636(4)	5 539(5)	3 209(3)
B(1a)	4 706(4)	−2 376(5)	5 466(3)
B(2a)	3 883(4)	−2 006(5)	5 665(3)
B(3a)	4 099(4)	−3 201(5)	5 682(3)
B(4a)	4 757(4)	−3 531(5)	5 224(3)
B(5a)	4 320(4)	−1 520(5)	5 087(3)
B(7a)	3 305(4)	−2 902(5)	5 436(3)
B(8a)	3 916(5)	−3 898(6)	5 128(4)
B(9a)	4 454(5)	−3 607(6)	4 578(4)
B(10a)	4 866(4)	−2 561(6)	4 787(3)
B(1b)	2 809(4)	6 645(5)	2 933(3)
B(2b)	3 620(4)	6 194(5)	3 101(3)
B(3b)	3 435(4)	7 385(6)	3 203(4)
B(4b)	2 792(4)	7 836(5)	2 757(3)
B(5b)	3 167(4)	5 838(5)	2 492(3)
B(7b)	4 212(4)	7 073(6)	2 924(4)
B(8b)	3 639(5)	8 162(7)	2 693(4)
B(9b)	3 099(5)	8 017(6)	2 134(4)
B(10b)	2 640(4)	6 972(6)	2 271(3)

universally diagnostic of a B–H–B bridge.[37,40,41] Indeed, with an appropriate choice of conditions the B(6)–B(5,7)/B(9)–B(8,10) correlation in *nido*-$B_{10}H_{14}$ itself can be observed.[42] Other noteworthy points include a similarity of the δ(^{11}B) behaviour with that[43] of $B_{10}H_{14}$, except for the B(2) and B(5,7) positions adjacent to the metal atom, which are deshielded relative to the $B_{10}H_{14}$ values by some 25 and 20 p.p.m. respectively. This contrasts with the behaviour of the series of compounds $[(PMe_2Ph)_3H_2WB_9H_{13}]$, $[(PMe_2Ph)_3HReB_9H_{13}]$, $[(PMe_2Ph)_3OsB_9H_{13}]$, and $[(PMe_3)_2HIrB_9H_{13}]$, in which these shieldings are much less shifted from their *nido*-$B_{10}H_{14}$ values.[32] The observation of a splitting of *ca.* 28 Hz of the Rh–H–B bridging proton resonance is also of interest: we would tentatively ascribe this to $^1J(^{103}\text{Rh}\text{-}^1\text{H})$. A splitting of some 35 Hz is also apparently observed in the cobalt species $[6\text{-}(\eta^5\text{-}C_5Me_5)CoB_9H_{13}]$, and ascribed in this case to $J(\text{H}_{\text{bridge}}\text{-}\text{H}_{\text{terminal}})$.[33] This latter does not appear to be the source of splitting in the rhodium analogue, however, because none of the other resonances exhibits such a large coupling structure in the ^{1}H-{^{11}B} spectra.

The quantitative nature of the synthesis augurs well for the high-yield generation of other new rhodaboranes by the use of other suitable anionic boranes as starting materials, and also permits the ready use of the metallaboranes themselves as starting materials to develop further the chemistry of the system. We hope to report further on some of these implications shortly.† The high-yield specific synthesis from the defined starting metal halide complex $[\{Rh(\eta^5\text{-}C_5Me_5)Cl_2\}_2]$ at room temperature is of additional significance because it is in sharp contrast to the ostensibly similar cobalt systems which use a (retrospectively) more arbitrary mixture of $CoCl_2$ and *arachno*-$[C_5H_5]^-$ with the borane anion, often at low temperatures, and which typically yield a complex (though often fascinating) mixture of metallaboranes and related species, though sometimes in excruciatingly small yields.[33,34,44,45]

Experimental

General.—Reactions were carried out under dry nitrogen,

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† *Note added in proof.* See now, for example, *J. Chem. Soc., Chem. Commun.*, 1985, 1165, 1722.

Table 5. Hydrogen atom co-ordinates (× 10^4) for $[6\text{-}(\eta^5\text{-}C_5Me_5)RhB_9H_{13}]$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
H(61a)	3 591(4)	890(6)	5 406(3)	H(102b)	5 613(4)	6 287(5)	3 230(3)
H(62a)	3 253(4)	1 305(6)	4 786(3)	H(103b)	6 155(4)	5 323(5)	3 156(3)
H(63a)	3 920(4)	493(6)	4 779(3)	H(1a)	5 096(22)	−2 120(27)	5 729(20)
H(71a)	3 228(4)	277(5)	3 933(3)	H(2a)	3 842(22)	−1 619(26)	6 028(20)
H(72a)	2 382(4)	39(5)	3 753(3)	H(3a)	4 109(23)	−3 492(27)	6 095(20)
H(73a)	2 996(4)	−349(5)	3 722(3)	H(4a)	5 195(22)	−3 913(26)	5 397(18)
H(81a)	1 434(4)	−2 155(5)	4 583(3)	H(5a)	4 580(25)	−742(30)	5 085(22)
H(82a)	2 060(4)	−2 153(5)	4 071(3)	H(7a)	2 850(22)	−3 227(27)	5 668(19)
H(83a)	1 439(4)	−1 274(5)	4 083(3)	H(8a)	3 681(25)	−4 689(29)	5 140(21)
H(91a)	1 412(3)	−2 138(5)	5 365(3)	H(9a)	4 532(28)	−3 937(32)	4 168(28)
H(92a)	1 359(3)	−1 194(5)	5 822(3)	H(10a)	5 249(24)	−2 293(29)	4 583(21)
H(93a)	1 977(3)	−2 060(5)	5 920(3)	H(5,6a)	3 945(21)	−1 628(25)	4 697(19)
H(101a)	3 120(3)	377(5)	6 048(3)	H(6,7a)	3 094(23)	−2 710(29)	4 945(19)
H(102a)	2 882(3)	−736(5)	6 279(3)	H(8,9a)	3 924(23)	−3 758(27)	4 747(20)
H(103a)	2 263(3)	132(5)	6 185(3)	H(9,10a)	4 529(23)	−2 836(28)	4 463(20)
H(61b)	5 832(4)	6 181(5)	1 547(3)	H(1b)	2 366(22)	6 375(27)	3 203(19)
H(62b)	6 353(4)	5 884(5)	2 104(3)	H(2b)	3 668(21)	5 679(26)	3 448(19)
H(63b)	5 765(4)	6 798(5)	2 166(3)	H(3b)	3 399(24)	7 497(31)	3 664(23)
H(71b)	5 221(3)	5 397(5)	1 082(3)	H(4b)	2 408(22)	8 278(27)	2 931(18)
H(72b)	4 367(3)	5 047(5)	1 105(3)	H(5b)	2 987(24)	5 062(29)	2 445(21)
H(73b)	5 016(3)	4 207(5)	1 107(3)	H(7b)	4 680(24)	7 275(29)	3 184(21)
H(81b)	3 928(4)	3 676(5)	1 589(3)	H(8b)	3 812(27)	8 913(31)	2 759(25)
H(82b)	3 515(4)	3 765(5)	2 224(3)	H(9b)	2 889(27)	8 344(31)	1 782(25)
H(83b)	4 174(4)	2 953(5)	2 135(3)	H(10b)	2 173(26)	6 792(30)	2 020(22)
H(91b)	4 709(4)	4 259(5)	3 603(3)	H(5,6b)	3 554(26)	5 935(30)	2 080(23)
H(92b)	4 566(4)	3 264(5)	3 200(3)	H(6,7b)	4 349(22)	7 013(27)	2 463(18)
H(93b)	3 919(4)	4 095(5)	3 282(3)	H(8,9b)	3 613(22)	8 144(26)	2 300(19)
H(101b)	5 438(4)	5 246(5)	3 582(3)	H(9,10b)	3 005(22)	7 304(28)	1 933(19)

using dried and degassed solvents, but subsequent manipulations and separations were carried out in air. $[\{Rh(\eta^5\text{-}C_5Me_5)Cl_2\}_2]$ was made from $[RhCl_3(H_2O)_n]$ and hexamethylbicyclo[2.2.0]hexa-2,5-diene in refluxing methanol according to a literature method,[46] and $[NBu^n_4][B_9H_{14}]$ was made from $B_{10}H_{14}$ and $[NBu^n_4]OH$ in methanol at room temperature, essentially according to a procedure described previously for $[NEt_4][B_9H_{14}]$.[11] Preparative t.l.c. used 1-mm layers of silica (Kieselgel GF54; Fluka) on plates of dimensions 20 × 20 cm; these were made in the laboratory as required from an acetone slurry, followed by drying in air at *ca.* 100 °C.

Preparation of $[6\text{-}(\eta^5\text{-}C_5Me_5)RhB_9H_{13}]$.—$[\{Rh(\eta^5\text{-}C_5Me_5)Cl_2\}_2]$ (1.0 g; 0.16 mmol) was added to a solution of $[NBu^n_4][B_9H_{14}]$ (1.12 g, 0.32 mmol) in CH_2Cl_2 (20 cm^3), and the resulting mixture stirred under N_2 at room temperature for 50 min, during which time its colour changed from red to orange. The solvent and other volatile components were then removed under reduced pressure, the solid residue was redissolved in CH_2Cl_2 (5 cm^3), and purified by t.l.c. using 80:20 CH_2Cl_2–light petroleum (b.p. 60–80 °C) as the liquid phase. The product was eluted as a dark orange band, R_f *ca.* 0.86, and was identified as described in the text (yield 1.0 g, 93%). A crystal suitable for single-crystal *X*-ray diffraction analysis was obtained from CH_2Cl_2 *via* slow liquid–liquid diffusion of light petroleum.

Crystallographic Studies.—Unit-cell and intesity data were recorded on a Syntex $P2_1$ diffractometer operating in the ω—2θ scan mode using graphite-monochromated Mo-K_α radiation (λ = 71.069 pm) following a procedure described elsewhere in detail.[47] The resultant data set was corrected for absorption empirically after the structure had been solved.[48]

The structure was determined by routine heavy-atom methods and refined by full-matrix least squares using the SHELX program system.[49] The two rhodium atoms were assigned anisotropic thermal parameters while all other non-hydrogen atoms were refined isotropically. All methyl hydrogen atoms were included in calculated positions using AFIX routines in SHELX and these were refined with an overall isotropic thermal parameter for each pentamethylcyclopentadienyl group. The weighting scheme $w = 1/[\sigma^2(F_o) + g(F_o)^2]$ was used at the end of refinement to give acceptable agreement analyses.

Crystal data for $[6\text{-}(\eta^5\text{-}C_5Me_5)RhB_9H_{13}]$. $C_{10}H_{28}B_9Rh$, M = 348.62, orthorhombic, a = 1 977.2(3), b = 1 440.1(2), c = 2 450.1(4) pm, U = 6.977 nm^3, space group *Pbca*, Z = 16, D_c = 1.327 g cm^{-3}, μ(Mo-K_α) = 8.64 cm^{-1}, $F(000)$ = 2 776, T = 290 K.

Data collection. Scans from 1° below $K_{\alpha 1}$ to 1° above $K_{\alpha 2}$, scan speeds 2.0—29.3° min^{-1}, $4.0 > 2\theta > 45.0°$, 5 111 unique data, 3 678 observed [$I > 2.0\sigma(I)$].

Structure refinement. Number of parameters = 307, weighting factor g = 0.0003, R = 0.0429, R' = 0.0472.

Non-hydrogen and hydrogen atomic positions are in Tables 4 and 5 respectively.

Nuclear Magnetic Resonance Spectroscopy.—100-MHz ^1H and 32-MHz ^{11}B single and multiple resonance work was carried out on a JEOL FX-100 spectrometer, using general techniques adequately described elsewhere;[5,11,43,50,51] spectroscopy was straightforward. 128-MHz ^{11}B, $^{11}B\text{-}\{^1H$(broad band noise)$\}$, and ^{11}B homonuclear COSY spectroscopy (Figure 3) were carried out on a Bruker AM-400 instrument.

The COSY experiment was acquired with a 90° mixing pulse using 256 and 128 words of data in the t_2 and t_1 dimensions respectively (32 transients were collected for each of the 128 t_1 values, giving a total acquisition time of less than 15 min); uninterrupted broad band noise proton decoupling was applied throughout. The time-domain matrix was multiplied by a sine-bell function and zero-filled four times prior to Fourier transformation in both dimensions. The frequency domain matrix was symmetrised along its (F1 = F2) diagonal. In the probe configuration used the ^{11}B 90° pulse duration was 8.5 μs.

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