Organoruthenaborane Chemistry. Part 6.* The Reaction of $[\{Ru(\eta^6\text{-}C_6Me_6)Cl_2\}_2]$ with the *closo*-$[B_{10}H_{10}]^{2-}$ Anion: Characterisation of Some *closo*-Type Eleven-vertex 1-Ruthenaundecaboranes and the Molecular Structure of $[5\text{-}(\eta^6\text{-}C_6Me_6)\text{-}6\text{-}(OMe)$-*nido*-$5\text{-}RuB_9H_{12}]$†

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The reaction between $[\{Ru(\eta^6\text{-}C_6Me_6)Cl_2\}_2]$ and *closo*-$[B_{10}H_{10}]^{2-}$ in dichloromethane solution gives the eleven-vertex *closo*-type metallaborane $[1\text{-}(\eta^6\text{-}C_6Me_6)\text{-}1\text{-}RuB_{10}H_{10}]$ (**1**; 82% yield) together with trace quantities of its 2-chloro derivative (**2**). When the reaction is carried out in refluxing methanol solution the metallaborane products are the two eleven-vertex species $[1\text{-}(\eta^6\text{-}C_6Me_6)\text{-}2\text{-}(OMe)$-*'isocloso'*-$1\text{-}RuB_{10}H_9]$ (**3**; 52% yield) and its 4-(OMe) isomer (**4**; trace quantities), together with the ten-vertex *nido* compound $[5\text{-}(\eta^6\text{-}C_6Me_6)\text{-}6\text{-}(OMe)\text{-}5\text{-}RuB_9H_{12}]$ (**5**; 32% yield). The new ruthenaboranes (**1**)—(**5**) are all yellow solids, reasonably robust in air, and are characterised by n.m.r. spectroscopy, elemental analysis, and, in the case of (**5**), by single-crystal *X*-ray diffraction analysis. Crystals of (**5**) are monoclinic, space group $P2_1/c$, with a = 1 385.3(2), b = 1 030.7(2), c = 1 419.8(2) pm, β = 103.67(1)°, and Z = 4.

We have found that $[\{Ru(\eta^6\text{-}C_6Me_6)Cl_2\}_2]$ is a versatile metallaborane synthon[1] and in Part 2 of this series[2] we described its reaction with the *arachno* ten-vertex borane anion $[B_{10}H_{14}]^{2-}$ which led to the formation of the interesting triply hydrogen-bridged *nido* eleven-vertex ruthenaborane species $[7\text{-}(\eta^6\text{-}C_6Me_6)$-*nido*-$7\text{-}RuB_{10}H_{13}]^-$ in high yield. We now describe the reactions, in the presence and absence of MeOH, between $[\{Ru(\eta^6\text{-}C_6Me_6)Cl_2\}_2]$ and the *closo* ten-vertex borane anion $[B_{10}H_{10}]^{2-}$ which lead to the formation of some *closo*-type eleven-vertex ruthenaboranes together with the *nido* ten-vertex ruthenaborane $[5\text{-}(\eta^6\text{-}C_6Me_6)\text{-}6\text{-}(OMe)$-*nido*-$5\text{-}RuB_9H_{12}]$ which we have also characterised by *X*-ray diffraction analysis. The numbering systems of the *nido* ten-vertex and *closo*-type eleven-vertex skeletons encountered in this work are given by structures (**I**) and (**II**) respectively. Note that the IUPAC-recommended scheme in (**II**) differs from that previously used by us in earlier papers on this structural type (*e.g.* refs. 3—6).

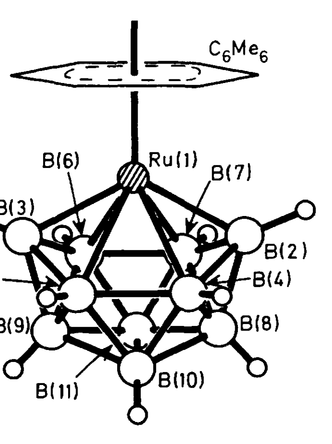
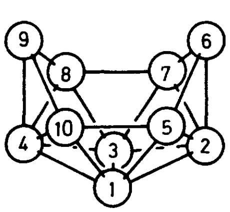


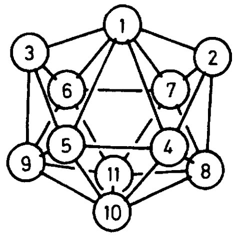
Figure 1. Proposed molecular structure of $[1\text{-}(\eta^6\text{-}C_6Me_6)$-*closo*-$1\text{-}RuB_{10}H_{10}]$ (**1**). Compounds (**2**), (**3**), and (**4**) are, respectively, the 2-Cl, 2-OMe, and 4-OMe substituted derivatives

Results and Discussion

The reaction between $[NEt_3H]_2[B_{10}H_{10}]$ and $[\{Ru(\eta^6\text{-}C_6Me_6)Cl_2\}_2]$ in dichloromethane solution at ambient temperature for 1 h, followed by chromatographic separation, readily yielded the eleven-vertex *closo*-type species $[1\text{-}(\eta^6\text{-}C_6Me_6)\text{-}1\text{-}RuB_{10}H_{10}]$ (**1**) in high yield (>80%) as a yellow air-stable crystalline compound (Figure 1). This was readily identified as such by elemental analysis, n.m.r. spectroscopy (Table 1), and mass spectrometry. The metallaborane synthesis was quite clean, the only other chromatographically mobile metallaborane product being one present in trace quantities, and tentatively identified by n.m.r. spectroscopy (Table 1) as the 2-chlorinated derivative of (**1**), *viz.* $[2\text{-}Cl\text{-}1\text{-}(\eta^6\text{-}C_6Me_6)\text{-}1\text{-}RuB_{10}H_9]$ (**2**). The high-yield formation of (**1**) is analogous to the previously reported[6] synthesis of its rhodaborane analogue $[1\text{-}(\eta^5\text{-}C_5Me_5)\text{-}1\text{-}RhB_{10}H_{10}]$ from $[\{Rh(\eta^5\text{-}C_5Me_5)Cl_2\}_2]$ and $[B_{10}H_{10}]^{2-}$, this closed eleven-vertex metallaborane structural type being of interest[7–12] because of its contravention[5,12–14] of the simple Williams–Wade[15,16] cluster-geometry and electron-counting rules. The reaction is stoicheiometric, and may well occur *via* the formation of a neutral B–H–Ru bridged intermediate species, equation (1), in which the *closo*-$B_{10}H_{10}$ moiety has remained intact (*cf.* copper and platinum complexes of $[B_{10}H_{10}]^{2-}$ in refs. 17—20, and the ruthenium complex of



(**I**)



(**II**)

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* Part 5 is ref. 4.

† $5\text{-}(\eta^6$-Hexamethylbenzene)-6-methoxy-*nido*-5-ruthenadecaborane.

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

Table 1. Measured n.m.r. parameters for [1-(η^6-C_6Me_6)-*closo*-1-$RuB_{10}H_{10}$] (**1**) and its 2-Cl (**2**),[a] 2-OMe (**3**), and 4-OMe (**4**) substituted derivatives at 294 K in CD_2Cl_2 or $CDCl_3$ solution

	(**1**), CD_2Cl_2 solution		(**2**), $CDCl_3$ solution[a]		(**3**), CD_2Cl_2 solution		(**4**), $CDCl_3$ solution	
Assignment[b]	δ(^{11}B)/p.p.m.[c]	δ(^{1}H)/p.p.m.[d,e]	δ(^{11}B)/p.p.m.[c]	δ(^{1}H)/p.p.m.[d,e]	δ(^{11}B)/p.p.m.[c]	δ(^{1}H)/p.p.m.[d,e]	δ(^{11}B)/p.p.m.[c]	δ(^{1}H)/p.p.m.[d,e]
1	Ru	*ca.* 2.1[f]	Ru	2.12[f]	Ru	2.07[f]	Ru	2.16[f]
2	110.9	10.44	100.3	*a,g*	98.1	4.54[g,h]	112.5	10.80
3	110.9	10.44	104.7	10.01	104.4	9.96	105.4	10.21
4	13.3	0.90	*ca.* 11.2[i]	1.63	9.7	1.54	31.3	3.31[g,h]
5	13.3	0.90	5.3	0.79	4.8	0.69	5.6	1.21
6	13.3	0.90	5.3	0.79	4.8	0.69	*ca.* 14.2[i,j]	1.18[j]
7	13.3	0.90	*ca.* 11.2[i]	1.63	9.7	1.54	*ca.* 11.0[i,j]	1.32[j]
8	11.8	4.14	3.8	3.33	1.0	3.40	*ca.* 14.2[i]	4.28
9	11.8	4.14	*ca.* 11.2[i]	4.06	*ca.* 10.7[i]	3.93	*ca.* 11.0[i]	4.32
10	18.1	2.77	*ca.* 11.2[i]	2.36	*ca.* 10.7[i]	2.18	18.8	3.40
11	18.1	2.77	*ca.* 11.2[i]	2.36	*ca.* 10.7[i]	2.18	18.3	2.73

[a] Product found in trace quantities; identification of 2-substituent as Cl not confirmed; a second possibility could be OH (ref. 25). [b] Assignments by [^{11}B–^{11}B]-COSY experiments (correlations observed being similar to those for the same structural type in refs. 4 and 6), and by δ(^{11}B) and δ(^{1}H) chemical shift parallels with other eleven-vertex *closo*-type 1-metallaundecaboranes (refs. 4—6 and 14). [c] δ(^{11}B) ±0.5 p.p.m. to high frequency (low field) of Ξ 32.083 971 MHz [nominally $BF_3(OEt_2)$ in $CDCl_3$ at 294 K]. [d] δ(^{1}H) ±0.05 p.p.m. to high frequency (low field) of Ξ 100 MHz (nominally internal $SiMe_4$). [e] ^{1}J(^{11}B–^{1}H) generally in range 135—175 Hz; ^{1}H resonances assigned to directly bound B atoms in ^{1}H-{^{11}B(selective)} experiments. [f] C_6Me_6 proton resonance. [g] Substituted position. [h] OMe proton resonance; some selective sharpening observed in ^{1}H-{^{11}B} experiments indicating presence of small coupling ^{3}J(^{11}B–O–C–^{1}H). [i] Accidental near-coincidence of different ^{11}B resonances precludes accurate measurement. [j] Assignments between ^{11}B^{1}H(6) and ^{11}B^{1}H(7) uncertain because overlapping ^{11}B resonances obscure individual [^{11}B–^{11}B]-COSY correlations.

$[B_{12}H_{12}]^{2-}$ in ref. 21), followed by ruthenium insertion to form the product (**1**) [equation (2)].

$$\tfrac{1}{2}[\{Ru(\eta^6\text{-}C_6Me_6)Cl_2\}_2] + [B_{10}H_{10}]^{2-} \longrightarrow [(\eta^6\text{-}C_6Me_6)Ru(\mu\text{-}H)_nB_{10}H_{10-n}] + 2Cl^- \quad (1)$$

$$[(\eta^6\text{-}C_6Me_6)Ru(\mu\text{-}H)_nB_{10}H_{10-n}] \longrightarrow \underset{(\mathbf{1})}{[(\eta^6\text{-}C_6Me_6)RuB_{10}H_{10}]} \quad (2)$$

When the reaction is carried out in refluxing methanol solution, by contrast, different products are formed. The principal product, compound (**3**), is an air-stable yellow crystalline compound readily identified by n.m.r. spectroscopy (Table 1), and by comparison with its previously reported[4] ethoxy analogue, as [1-(η^6-C_6Me_6)-2-(OMe)-*closo*-1-$RuB_{10}H_9$]. The isolated yield was 52% (reaction scale 0.3 mmol). A second product, present in trace quantities, was an isomer of this, the presence of 10 separate resonance positions in the ^{11}B n.m.r. spectrum (Table 1) identifying it as the asymmetrically methoxylated species [1-(η^6-C_6Me_6)-4-(OMe)-*closo*-1-$RuB_{10}H_9$] (**4**) [numbering as in structure (**II**) and Figure 1]. This was also an air-stable yellow crystalline solid.

A stoicheiometry for the formation of these methoxy-substituted species is given by equation (3). The reaction

$$\tfrac{1}{2}[\{Ru(\eta^6\text{-}C_6Me_6)Cl_2\}_2] + [B_{10}H_{10}]^{2-} + MeOH \longrightarrow \underset{(\mathbf{3})\text{ and }(\mathbf{4})}{[(\eta^6\text{-}C_6Me_6)RuB_{10}H_9(OMe)]} + 2Cl^- + H_2 \quad (3)$$

presumably occurs *via* attack of methanolic oxygen on the initially formed Ru–H–B bridged intermediate species postulated above, since prolonged heating of the unsubstituted compound (**1**) in refluxing methanol did not form any methoxy-substituted metallaborane.

Consistent with this hypothesis of methanol attack on an initially formed adduct of *closo*-$[B_{10}H_{10}]^{2-}$ is the nature of the third product from the reaction in methanol, *viz.* the methoxy-substituted nine-boron ten-vertex *nido*-5-metalladecaborane [5-(η^6-C_6Me_6)-6-(OMe)-*nido*-5-RuB_9H_{12}] (**5**) [idealised equation (4)]. This is obtained as an air-stable crystalline solid in 32% yield, the combined yield of compounds (**3**), (**4**), and (**5**) from the reaction thus being some 85%.

$$\tfrac{1}{2}[\{Ru(\eta^6\text{-}C_6Me_6)Cl_2\}_2] + [B_{10}H_{10}]^{2-} + 4MeOH \longrightarrow \underset{(\mathbf{5})}{[(\eta^6\text{-}C_6Me_6)RuB_9H_{12}(OMe)]} + 2Cl^- + B(OMe)_3 + H_2 \quad (4)$$

The results of multi-element, multiple resonance, and multi-dimensional n.m.r. spectroscopy (Table 2) indicated a 6-methoxy substituted *nido*-5-ruthenadecaborane configuration, this being substantiated by the results of a single-crystal *X*-ray diffraction analysis. A drawing of the molecular structure of compound (**5**) is in Figure 2, and salient interatomic distances and angles are listed in Tables 3 and 4 respectively.

All hydrogen atoms on the ruthenaborane cluster were located and freely refined, and the compound can be seen to be of the *nido*-decaborane $B_{10}H_{14}$-type configuration, but with a σ-bound methoxy substituent on B(6) instead of an *exo*-terminal hydrogen atom, and with the BH(5) position subrogated by an isoelectronic and isolobal Ru(η^6-C_6Me_6) moiety entirely in accordance with the Williams–Wade[15,16] cluster rules. The metal centre is formally octahedral 18-electron d^6 ruthenium(II), and the compound has some sandwich character in that the aromatic C_6 and the B(1)B(2)B(6)B(10) planes are near-parallel, the angle between them being 2.5°. As with the previously reported[2] ruthenaborane anion [7-(η^6-C_6Me_6)-*nido*-7-$RuB_{10}H_{13}$]$^-$ the six methyl carbon atoms in the hexamethylbenzene ligand are essentially coplanar with the aromatic ring carbon atoms (range of deviation 0.1—4.0° away from the metal). This contrasts to the known η^5-C_5Me_5 rhodaboranes in which they bend away more definitively from the metal atom,[6,22,23] and to known methylarene cobalta- and ferra-boranes in which the deviation is definitely towards the metal atom.[13] In this context it would be of interest to have comparable structural data on Os(η^6-C_6Me_6) and Ir(η^5-C_5Me_5) analogues that have recently been synthesised.[1,24,25] Within the metallaborane cluster the interatomic distances are generally within expected ranges[26,27] for polyhedral boron-

Table 2. Measured n.m.r. parameters for [5-(η^6-C_6Me_6)-*nido*-6-(OMe)-5-RuB_9H_{12}] (**5**) in CD_2Cl_2 solution at 294 K

				Observed two-dimensional COSY correlations^{f}	
Assignment^{a}	$\delta(^{11}B)$/p.p.m.^{b}	$^{1}J(^{11}B-^{1}H)$/Hz^{c,d}	$\delta(^{1}H)$/p.p.m.^{e}	$[^{11}B-^{11}B]^{g,h}$	$[^{1}H-^{1}H]^{i,j,k}$
1	+17.4	134	+3.26	2s 3m 4m 10s	{[2,10]w^{k} 3w 7w$_4$ 9w$_4$ (9,10)w}^{i}
2	−18.0	134	+2.31	(1s 3s 6s)^{h}	[1w 7w (5,6)w (6,7)s (8,9)w (9,10)m]^{k}
3	−1.1	*d*	+2.16	1s 4s 8w	1w 7m 8w (6,7)vw?
4	−43.6	145	−0.19	1m 3s 8w 9s 10w	(3w 8w 9w)^{i}
5	Ru	—	+2.16^{l}	—	—
6	+45.3	—	+3.80^{m}	2s	—
7	−17.3^{n}	141	+1.08	(3m 8w)^{h}	1w [2,10]w^{k} 3w (6,7)w
8	+8.4	154	+3.13	3m 4m 7w 9vw?	[2,10]w$_4$^{k} 3w 8w 9w (8,9)m (9,10)w
9	−6.0	153	+2.98	4s 8vw? 10vw?	1w$_4$ 4w (8,9)s$_2$ (9,10)s$_2$
10	−1.9	*d*	+2.31	1s 4w 9vw?	[1w 7w (5,6)w (6,7)w (8,9)w (9,10)m]^{k}
(5,6)(bridge)	—		−16.45	—	[2,10]w^{k} (6,7)w$_2$
(6,7)(bridge)	—		−1.05^{n}	—	[2,10]s^{k} 3vw? (8,9)w
(8,9)(bridge)	—		−2.41^{o}	—	[2,10]w^{k} 3vw? 8s 9s$_2$ (6,7)w (9, 10)s$_2$
(9,10)(bridge)	—		−1.59^{o}	—	3w 9s$_2$ (8,9)w$_2$

[a] Assignments by $^{1}H-\{^{11}B\}$ and two-dimensional $[^{1}H-^{1}H]$- and $[^{11}B-^{11}B]$-COSY experiments. Numbering as in structure (**1**) and Figure 2. [b] ±0.5 p.p.m. to high field (low frequency) of $BF_3(OEt_2)$ in $CDCl_3$. [c] ±8 Hz; measured from ^{11}B spectra with resolution enhancement to achieve baseline separation of doublet components. [d] Accurate estimation of 3 and 10 positions precluded by overlap of these two ^{11}B resonances. [e] ±0.05 p.p.m. to high frequency (low field) of $SiMe_4$; ^{1}H resonances assigned to directly bound B positions by $^{1}H-\{^{11}B\}$ selective spectroscopy. [f] s = Stronger, w = weaker, m = intermediate, v = very, ? = uncertain. [g] Measured with $\{^{1}H$(broad-band noise)$\}$ decoupling. Note that observed intensities depend on *both* $^{1}J(^{11}B-^{11}B)$ *and* $T_2{}^{*}(^{11}B)$ and therefore upon solution conditions. [h] Some uncertainty in correlations with and between $^{11}B(2)$ and $^{11}B(7)$ because of peak overlap of these two resonances. [i] Measured with $\{^{11}B$(broad-band noise)$\}$ decoupling; due to the difficulty of decoupling over entire ^{11}B spectrum range, correlations involving $^{1}H(1)$ and $^{1}H(4)$ appear weaker than with complete decoupling. [j] Subscripts refer to *n* in $^{n}J(^{1}H-^{1}H)$; $n = 3$ if not specified. [k] $^{1}H(2)$ and $^{1}H(10)$ resonances accidentally coincident under these conditions and so their individual correlations are not distinguishable. [l] Refers to $\delta(^{1}H)(C_6Me_6)$. [m] Refers to $\delta(^{1}H)$(OMe); O-methyl ^{1}H resonance sharpened by $\nu[^{11}B(6)]$ in $^{1}H-\{^{11}B\}$ experiments, implying small but finite $^{3}J(^{11}B-O-C-^{1}H)$. [n] $\delta(^{1}H)(6,7)$ related to $\delta(^{11}B)$ at −17.3 rather than −18.0 by two-dimensional $[^{1}H-^{11}B]$-COSY heteronuclear experiments (with simultaneous heteronuclear decoupling in both dimensions; ref. 39). Note no correlation observed in these experiments or in $^{1}H-\{^{11}B$(selective)$\}$ work between $\delta(^{1}H)(6,7)$ and $^{11}B(6)$ implying very small coupling if any for $^{1}J[^{11}B(6)-^{1}H(6,7)]$ in (**5**) (*cf.* footnote *o*). [o] Selectively sharpened by resonance frequencies of *both* bridged ^{11}B atoms in $^{1}H-\{^{11}B$(selective)$\}$ experiments (*cf.* footnote *n*).

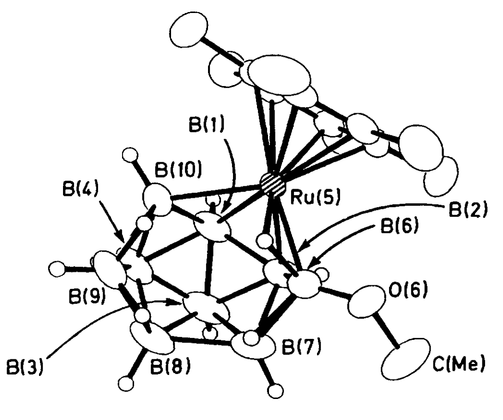

Figure 2. Crystallographically determined molecular structure of [5-(η^6-C_6Me_6)-6-(OMe)-*nido*-5-RuB_9H_{12}] (**5**)

containing species, although the observation that the Ru–H–B bridged distance Ru(5)–B(6) is *shorter* than the unbridged distances Ru(5)–B(1) and Ru(5)–B(2) is noteworthy, as is the fact that the '*nido*-decaboranyl' interboron distance B(7)–B(8) of 196.2(9) pm [*cf.* $B_{10}H_{14}$ 197.3(4) pm[28]] is not paralleled by a similarly longer Ru(5)–B(10) interatomic distance on the other side of the molecule.

The measured n.m.r. properties of compound (**5**) were in accord with the crystallographic structure, confirming that the crystal selected for *X*-ray analysis was representative of the bulk sample. As for compounds (**1**)—(**4**) above (Table 1) the assignments for compound (**5**) were made by the use of $[^{11}B-^{11}B]$-COSY[29] and $[^{1}H-^{1}H]$-COSY[30] n.m.r. spectroscopy, the observed COSY correlations under the experimental conditions used being summarised in Table 2. The compound exhibits a typical *nido*-5-metalladecaborane cluster shielding pattern,[13,25,29–33] with the methoxy-substituted $^{11}B(6)$ resonance being some 12 p.p.m. less shielded (*i.e.* $\Delta\sigma = -12$ p.p.m.) than that[25] of the parent unsubstituted [5-(η^6-C_6Me_6)-*nido*-5-RuB_9H_{13}]. This is in accord with the α-deshielding effect by electronegative substituents generally observed for ^{11}B resonances in polyhedral boron-containing species,[34] but in this context the positive methoxy α-shielding effect at B(2) observed for compound (**3**) (Table 1) is thereby of interest. Comparison with the results for compound (**1**) shows this shielding change to be of the order of +12 p.p.m. This positive change is, however, associated with a boron resonance which has a very low shielding $\{\delta[^{11}B(2)] = +98.1$ p.p.m.$\}$ which suggests an empirical dependence of the α-shielding effect upon the chemical shift of the boron atom at the substituent site. The results for the 4-methoxy *closo*-type compound (**4**) $\{\delta[^{11}B(4)] = +31.3$ p.p.m., $\Delta\sigma = -18$ p.p.m.$\}$ are in accord with this and furthermore suggest an approximately linear relationship of the form of equation (5).

$$\Delta\sigma(^{11}B)_{OMe} = +0.3\delta(^{11}B) - 22 \text{ p.p.m.} \qquad (5)$$

It will be instructive to have more data to investigate the generality of this type of behaviour.

Experimental

General.—The starting materials [{Ru(η^6-C_6Me_6)Cl_2}$_2$][35] and $[NEt_3H]_2[B_{10}H_{10}]$[36] were prepared according to literature methods. Reactions were carried out under an atmosphere of dry nitrogen, although manipulatory and separatory procedures were generally carried out in air. Preparative t.l.c. was carried out using silica gel G (Fluka, type GF254) on plates of dimensions 200 × 200 × 1 mm, made in

Table 3. Selected interatomic distances (pm) for [5-(η^6-C_6Me_6)-6-(OMe)-*nido*-5-RuB_9H_{12}] (**5**) with estimated standard deviations (e.s.d.s) in parentheses

(*i*) From the ruthenium atom			
Ru(5)–C(1)	230.1(5)	Ru(5)–B(1)	221.1(5)
Ru(5)–C(2)	226.1(5)	Ru(5)–B(2)	223.0(5)
Ru(5)–C(3)	226.5(5)	Ru(5)–B(6)	215.2(5)
Ru(5)–C(4)	225.9(5)	Ru(5)–B(10)	227.3(6)
Ru(5)–C(5)	224.4(5)	Ru(5)–H(5,6)	165(3)
Ru(5)–C(6)	226.8(5)		
(*ii*) Interboron			
B(1)–B(2)	177.7(8)	B(2)–B(3)	177.9(8)
B(1)–B(3)	176.5(7)	—	
B(1)–B(4)	179.7(7)	B(3)–B(4)	174.2(9)
B(1)–B(10)	180.0(8)	B(3)–B(8)	172.8(8)
B(2)–B(6)	177.3(7)	B(4)–B(9)	170.4(8)
B(3)–B(7)	174.8(8)	—	
B(4)–B(8)	177.4(8)	B(4)–B(10)	180.6(7)
B(7)–B(8)	196.2(9)	—	
B(9)–B(10)	179.7(7)	B(8)–B(9)	178.9(9)
(*iii*) Boron–hydrogen			
B(1)–H(1)	102(3)	B(3)–H(3)	120(4)
B(2)–H(2)	112(4)	B(4)–H(4)	109(4)
B(7)–H(7)	108(4)	—	
B(10)–H(10)	108(3)	B(8)–H(8)	113(3)
—		B(9)–H(9)	105(4)
B(6)–H(5,6)	144(3)	B(6)–H(6,7)	153(3)
—		B(7)–H(6,7)	113(3)
B(8)–H(8,9)	132(4)	B(10)–H(9,10)	124(3)
B(9)–H(8,9)	113(4)	B(9)–H(9,10)	123(3)
(*iv*) Others			
B(6)–O(6)	137.2(5)	O(6)–C(Me)	143.4(5)
C–C(cyclic)	140.7(5)— 142.7(5)	C–C(terminal)	151.8(6)— 153.6(6)

Table 4. Selected angles between interatomic vectors (°) for [5-(η^6-C_6Me_6)-6-(OMe)-*nido*-5-RuB_9H_{12}] (**5**), with e.s.d.s in parentheses

(*i*) Boron–ruthenium–boron			
B(1)–Ru(5)–B(2)	47.2(2)	B(2)–Ru(5)–B(6)	47.7(1)
B(1)–Ru(5)–B(6)	87.5(2)	B(2)–Ru(5)–B(10)	85.3(2)
B(1)–Ru(5)–B(10)	47.3(1)	B(6)–Ru(5)–B(10)	100.2(1)
(*ii*) Ruthenium–boron–boron			
Ru(5)–B(1)–B(2)	67.0(3)	Ru(5)–B(2)–B(1)	65.9(3)
Ru(5)–B(1)–B(4)	115.7(3)	Ru(5)–B(2)–B(3)	114.2(4)
Ru(5)–B(1)–B(4)	120.6(3)	Ru(5)–B(2)–B(6)	63.8(2)
Ru(5)–B(1)–B(10)	68.2(3)	Ru(5)–B(2)–B(7)	111.5(3)
Ru(5)–B(6)–B(2)	68.5(3)	Ru(5)–B(10)–B(4)	117.1(3)
Ru(5)–B(6)–B(7)	113.9(3)	Ru(5)–B(10)–B(9)	123.3(3)
Ru(5)–B(10)–B(1)	64.5(3)		
(*iii*) Others			
B(6)–B(7)–B(8)	119.1(4)	B(7)–B(8)–B(9)	119.4(4)
B(8)–B(9)–B(10)	105.6(4)	—	
Ru(5)–H(5,6)–B(6)	88(2)	B(6)–H(6,7)–B(7)	86(2)
B(8)–H(8,9)–B(9)	93(3)	B(9)–H(9,10)–B(10)	93(2)
O(6)–B(6)–B(2)	133.7(3)	—	
O(6)–B(6)–Ru(5)	123.8(3)	O(6)–B(6)–B(7)	121.4(4)
O(6)–B(6)–H(5,6)	111(1)	O(6)–B(6)–H(6,7)	109(1)
B(6)–O(6)–C(Me)	120.7(4)		

these laboratories from acetone slurries followed by drying in air at 80 °C. Column chromatography was carried out using silica gel 60 (Fluka, 0.063—0.200 mm mesh) as the stationary phase.

Nuclear Magnetic Resonance Spectroscopy.—This was performed at 2.35 and/or 9.40 T on JEOL FX-100 and Bruker AM 400 instrumentation respectively. The techniques of ^1H-{^{11}B},[33,37,38] [^{11}B–^{11}B]-COSY,[6,22,24,29] and [^1H–^1H]-COSY[6,24,30] spectroscopy were used essentially as described elsewhere and the [^1H–^{11}B]-COSY experiment (footnote *n* in Table 2) was performed with simultaneous heteronuclear decoupling in both dimensions essentially as described in ref. 39. Other spectroscopy was straightforward. Chemical shifts $\delta(^1H)$ and $\delta(^{11}B)$ are given in p.p.m. to high frequency (low field) of Ξ 100 ($SiMe_4$) and 32.083 971 MHz [nominally $BF_3(OEt)_2$ in $CDCl_3$] respectively.

Mass Spectrometry.—This was performed on an AEI (now KRATOS) MS30 instrument using the solid-sample introduction probe and 70 eV electron-impact ionisation.

Reaction of [{Ru(η^6-C_6Me_6)Cl_2}$_2$] *with* [$NEt_3H]_2[B_{10}H_{10}$] *in* CH_2Cl_2.—[{Ru(η^6-C_6Me_6)Cl_2}$_2$] (200 mg, 0.3 mmol) and [$NEt_3H]_2[B_{10}H_{10}$] (482 mg, 1.5 mmol) were stirred in dry degassed dichloromethane (80 cm^3) under an atmosphere of dry nitrogen. After 2.5 h the dichloromethane was reduced in volume (rotary evaporator, 40 °C, water pump), and the reaction mixture separated by column chromatography. Elution with CH_2Cl_2 gave yellow (**1**) (186 mg, 0.49 mmol, 82%). Elution in MeCN gave yellow (**2**) (trace) [Found for (**1**): C, 36.7; H, 7.3; B, 26.6. $C_{12}H_{28}B_{10}Ru$ requires C, 37.7; H, 7.3; B, 28.2%; *m*/*e* (max.) 384 (385, 386 present but weak); $^{12}C_{12}{}^1H_{28}{}^{11}B_{10}{}^{104}Ru$ requires 386; principal other fragmentations $C_6Me_6{}^+$ at 162 and doubly charged ions around M^{2+} at 180—190].

Reaction of [{Ru(η^6-C_6Me_6)Cl_2}$_2$] *with* [$NEt_3H]_2[B_{10}H_{10}$] *in Methanol.*—[{Ru(η^6-C_6Me_6)Cl_2}$_2$] (200 mg, 0.3 mmol) and [$NEt_3H]_2[B_{10}H_{10}$] (482 mg, 1.5 mmol) were brought to reflux in dry degassed methanol (60 cm^3) under an atmosphere of dry nitrogen. After 16 h the methanol was removed under reduced pressure (rotary evaporator, 40 °C, water pump). The resulting solid was dissolved in CH_2Cl_2 and applied to preparative t.l.c. plates. Development with CH_2Cl_2–n-hexane (7:3) gave three bands: yellow (**5**) (76 mg, 0.19 mmol, 32%) (R_f = 0.81), yellow (**3**) (129 mg, 0.31 mmol, 52%) (R_f = 0.65), and yellow (**4**) (trace) (R_f = 0.14) [Found for (**5**): C, 37.55; H, 7.85. $C_{13}H_{33}B_9ORu$ requires C, 38.5; H, 8.25%; *m*/*e* (max.) 408; $^{12}C_{13}{}^1H_{33}{}^{11}B_9{}^{16}O^{104}Ru$ requires 408. Found for (**3**): C, 40.3; H, 7.65. $C_{13}H_{30}B_{10}ORu$ requires C, 37.9; H, 7.35%. *m*/*e* (max.) 416; $^{12}C_{13}{}^1H_{30}{}^{11}B_{10}{}^{16}O^{104}Ru$ requires 416].

X-*Ray Crystallography.*—A sample of compound (**5**) suitable for single-crystal diffraction analysis was obtained by slow diffusion of n-pentane into a solution of (**5**) in dichloromethane.

All crystallographic measurements were made on a Nicolet *P*3/*F* diffractometer operating in the $\omega/2\theta$ scan mode using graphite-monochromated Mo-K_α radiation (λ = 71.069 pm) following a procedure described elsewhere in detail.[40] The data set was corrected for absorption once the structure had been solved.[41] The structure was solved *via* standard heavy-atom procedures and refined by full-matrix least squares using SHELX 76.[42] All non-hydrogen atoms were assigned anisotropic thermal parameters. 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 readily located in Fourier difference maps and these were freely refined with individual isotropic thermal parameters. The weighting scheme $w = [\sigma^2(F_o) + g(F_o)^2]^{-1}$ was used in which the parameter *g* was included in refinement in order to obtain satisfactory agreement analyses. Non-hydrogen and hydrogen atom fractional co-ordinates are listed in Tables 5 and 6 respectively. Additional material available from the

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

Atom	*x*	*y*	*z*
Ru(5)	562.2(1)	1 136.8(2)	2 885.3(1)
C(1)	417(2)	3 213(3)	2 273(2)
C(2)	766(2)	3 258(3)	3 287(2)
C(3)	1 646(2)	2 590(3)	3 749(2)
C(4)	2 156(2)	1 820(3)	3 198(2)
C(5)	1 781(2)	1 720(3)	2 174(2)
C(6)	917(2)	2 427(3)	1 717(2)
C(7)	−468(3)	4 028(3)	1 770(3)
C(8)	206(4)	4 081(3)	3 887(3)
C(9)	2 063(3)	2 733(4)	4 834(2)
C(10)	3 102(3)	1 107(4)	3 680(3)
C(11)	2 327(3)	884(3)	1 585(3)
C(12)	532(3)	2 391(4)	620(2)
O(6)	1 393(2)	−272(2)	4 864(2)
C(61)	1 921(3)	−1 399(4)	5 303(3)
B(1)	−52(3)	−375(4)	1 804(3)
B(2)	806(3)	−999(3)	2 839(3)
B(3)	−273(4)	−1 898(4)	2 281(3)
B(4)	−1 291(3)	−978(4)	1 690(3)
B(6)	735(3)	−350(3)	3 977(3)
B(7)	90(3)	−1 870(4)	3 547(3)
B(8)	−1 290(3)	−1 801(4)	2 787(3)
B(9)	−1 874(3)	−259(4)	2 484(3)
B(10)	−1 004(3)	694(4)	2 019(3)

Table 6. Hydrogen atomic co-ordinates (× 10^4) for compound (**5**)

Atom	*x*	*y*	*z*
H(7A)	−454(3)	3 971(3)	1 014(3)
H(7B)	−334(3)	5 017(3)	2 018(3)
H(7C)	−1 185(3)	3 718(3)	1 860(3)
H(8A)	268(4)	3 746(3)	4 619(3)
H(8B)	−564(4)	4 061(3)	3 495(3)
H(8C)	485(4)	5 061(3)	3 902(3)
H(9A)	1 628(3)	3 455(4)	5 101(2)
H(9B)	2 805(3)	3 099(4)	4 890(2)
H(9C)	2 098(3)	1 859(4)	5 261(2)
H(10A)	3 076(3)	875(4)	4 415(3)
H(10B)	3 741(3)	1 709(4)	3 686(3)
H(10C)	3 156(3)	222(4)	3 288(3)
H(11A)	1 922(3)	910(3)	835(3)
H(11B)	2 370(3)	−104(3)	1 844(3)
H(11C)	3 068(3)	1 257(3)	1 647(3)
H(12A)	893(3)	1 623(4)	315(2)
H(12B)	682(3)	3 310(4)	319(2)
H(12C)	−260(3)	2 221(4)	449(2)
H(61A)	2 507(3)	−1 081(4)	5 903(3)
H(61B)	2 238(3)	−1 942(4)	4 798(3)
H(61C)	1 409(3)	−2 007(4)	5 568(3)
H(1)	166(19)	−328(26)	1 169(20)
H(2)	1 565(27)	−1 313(28)	2 793(25)
H(3)	−62(26)	−2 932(33)	2 004(24)
H(4)	−1 728(26)	−1 347(29)	1 002(26)
H(7)	334(25)	−2 774(34)	3 903(24)
H(8)	−1 736(24)	−2 674(33)	2 917(23)
H(9)	−2 646(27)	−99(33)	2 333(24)
H(10)	−1 384(21)	1 424(25)	1 520(21)
H(5,6)	84(23)	754(29)	3 804(22)
H(6,7)	−155(25)	−1 176(28)	4 064(25)
H(8,9)	−1 610(29)	−786(38)	3 198(31)
H(9,10)	−1 368(22)	720(30)	2 737(22)

Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond parameters.

Crystal data. $C_{13}H_{33}B_9ORu$, $M = 403.78$, $a = 1\,385.3(2)$, $b = 1\,030.7(2)$, $c = 1\,419.8(2)$ pm, $\beta = 103.67(1)°$, $U = 1.970$ nm^3, $Z = 4$, space group $P2_1/c$, $D_c = 1.36$ g cm^{-3}, $\mu = 7.06$ cm^{-1}, $F(000) = 824$.

Data collection. Scans running from 1° below $K_{\alpha 1}$ to 1° above $K_{\alpha 2}$, scan speeds 2.0—29.3° min^{-1}, $4.0 < 2\theta < 45.0°$. 2 937 Data collected, 2 367 observed $[I > 2.0\sigma(I)]$, $T = 290$ K.

Structure refinement. Number of parameters 288, weighting factor $g = 0.000\,14$, $R = 0.0215$, $R' = 0.0237$.

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