In memory of T. A. Stephenson

Organoruthenaborane Chemistry. Part 5.* Products of the Reaction between *closo*-$[B_{10}H_{10}]^{2-}$ and $[(\eta^6\text{-}C_6Me_6)ClRuB_3H_8]$. Nuclear Magnetic Resonance Studies and the Crystal and Molecular Structure of $[\{(\eta^6\text{-}C_6Me_6)_2Ru_2H_4\}\text{-}RuB_{10}H_8(OEt)_2]$ †

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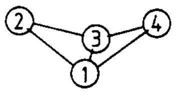
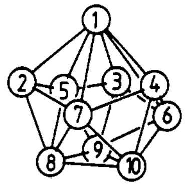
Reaction of $[\{Ru(\eta^6\text{-}C_6Me_6)Cl_2\}_2]$ with $Tl[B_3H_8]$ gives the yellow *arachno* four-vertex species $[2\text{-}(\eta^6\text{-}C_6Me_6)\text{-}2\text{-}Cl\text{-}2\text{-}RuB_3H_8]$ (**1**) in a yield of 66%. Treatment of this with *closo*-$[B_{10}H_{10}]^{2-}$ in refluxing ethanol results in the formation of yellow $[1\text{-}(\eta^6\text{-}C_6Me_6)$-*isocloso*-$1\text{-}RuB_9H_8\text{-}2\text{-}(OEt)]$ (**2**, *ca.* 2% yield), yellow $[1\text{-}(\eta^6\text{-}C_6Me_6)$-*isocloso*-$1\text{-}RuB_{10}H_9\text{-}2\text{-}(OEt)]$ (**3**, *ca.* 5% yield), and the novel dark red triruthenium–decaboron double-cluster compound $[1\text{-}\{(\eta^6\text{-}C_6Me_6)_2Ru_2H_4\}$-*isocloso*-$1\text{-}RuB_{10}H_8\text{-}2,3\text{-}(OEt)_2]$ (**4**, 32% yield). Compounds (**1**)—(**4**) are reasonably air-stable and are characterised by n.m.r. spectroscopy. A single-crystal *X*-ray diffraction analysis of compound (**4**) showed that the crystals were monoclinic, space group $P2_1/c$, with a = 1 081.7(1), b = 1 622.6(3), c = 2 120.4(3) pm, β = 102.07(1)°, and Z = 4. The $(\eta^6\text{-}C_6Me_6)_2Ru_3H_4$ sub-cluster of compound (**4**) exhibits novel features.

In a preliminary communication[2] we have reported the isolation of the interesting double-cluster compound of ruthenium and boron, $[\{(\eta^6\text{-}C_6Me_6)_2Ru_2H_4\}RuB_{10}H_8(OEt)_2]$ which comprises Ru_3 and RuB_{10} units conjoined at a common ruthenium atom. Here we describe the synthetic reaction and its products in more detail. The numbering schemes for the four-, ten-, and eleven-vertex metallaborane clusters described in this work are shown in structures (I)—(III) respectively.‡



(I)



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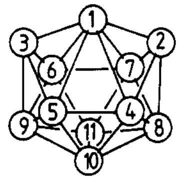

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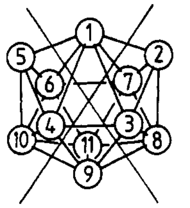

(IV)

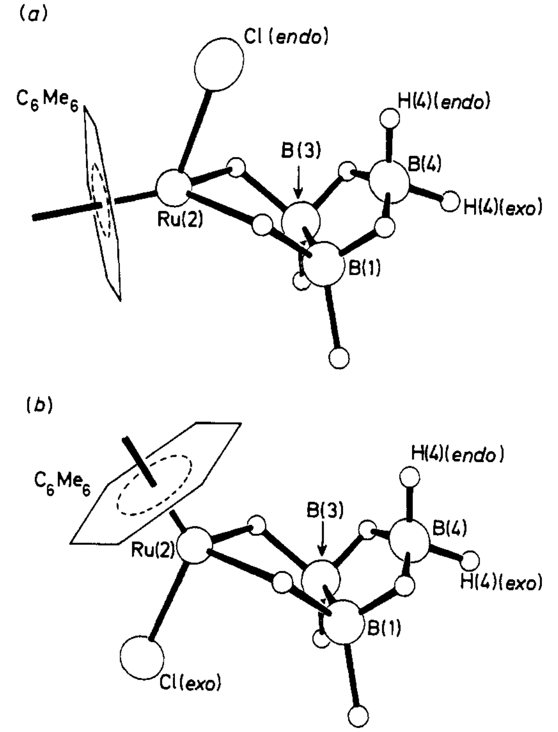

Figure 1. Proposed molecular configuration for $[2\text{-}(\eta^6\text{-}C_6Me_6)\text{-}2\text{-}Cl\text{-}$*arachno*-$2\text{-}RuB_3H_8]$ (**1**). Present evidence cannot distinguish between the *endo* and *exo* chloro forms (*a*) and (*b*) respectively

Results and Discussion

Reaction between the thallium salt of the *arachno*-$[B_3H_8]^-$ anion and $[\{Ru(\eta^6\text{-}C_6Me_6)Cl_2\}_2]$ in dichloromethane solution at room temperature for 1 h, followed by chromatographic separation, resulted in the isolation of an air-stable yellow solid, compound (**1**), in a 66% yield [equation (1)]. This was readily

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* Parts 1—4, previously unnumbered, are refs. 1(*a*)—1(*d*) respectively.

† 1-[6′,9′-bis(ethoxy)-*nido*-octahydrodecaborato]-2,3-bis(η^6-hexamethylbenzene)-μ_3-hydrido-1,2; 2,3; 1,3-tri-μ-hydrido-*triangulo*-triruthenium.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

‡ We now adopt the IUPAC-recommended numbering rules for the *closo*-type eleven-vertex structure [see (**III**) above]; previous descriptions of clusters of this type from our laboratories (*e.g.* refs. 3—8) have used the alternative numbering scheme depicted in (**IV**) which is related to the non-systematic but universally adopted method of numbering the *nido*-$B_{10}H_{14}$ cluster.

Table 1. Measured n.m.r. parameters for [(η^6-C_6Me_6)ClRuB_3H_8] (**1**), together with those of [(CO)(PPh_3)$_2$HOsB_3H_8]^a for comparison; $CDCl_3$ solution

	Ru compound (1) (302 K)		[(CO)(PPh_3)$_2$HOsB_3H_8] (294 K)^a	
Assignment	$\delta(^{11}B)$/p.p.m.^{b,c}	$\delta(^1H)$/p.p.m.^{c,d,e}	$\delta(^{11}B)$/p.p.m.^{b,c}	$\delta(^1H)$/p.p.m.^{c,d,f}
4	+0.4^g (1 B)	+3.10^h (1 H), +2.60^i (1 H)	+1.0 (1 B)	+4.34^h (1 H), +2.20^i (1 H)
1, 3	−36.5^j (2 B)	+0.59 (2 H)	−40.5 (1 B) −39.5 (1 B)	+0.56 (1 H) −0.83 (1 H)
H(1,2) H(2,3)	—	−9.50 (2 H)	— —	−9.07 (1 H) −10.20 (1 H)
H(1,4) H(3,4)	—	−0.88 (2 H)^k	—	−0.21 (2 H)^{k,l}

[a] Data from ref. 11. [b] ±0.5 p.p.m. to low field (high frequency) of $BF_3(OEt_2)$ in $CDCl_3$. [c] Relative intensities in parentheses. [d] ±0.05 p.p.m. to 'high frequency' of $SiMe_4$; ^1H resonances related to directly bound B atoms by ^1H-{^{11}B(selective)} spectroscopy. [e] $\delta(^1H)(C_6Me_6)$ +2.17 p.p.m. [f] $\delta(^1H)$(OsH)(terminal) −10.10 p.p.m. [g] Approx. 1:2:1 triplet, splitting *ca.* 143 Hz. [h] Probably *exo* (see Figure 1). [i] Probably *endo* (see Figure 1). [j] Doublet; splitting *ca.* 130 Hz. [k] Selectively sharpened by irradiation at $\nu[^{11}B(1,3)]$ but not by irradiation at $\nu[^{11}B(4)]$ in ^1H-{^{11}B(selective)} experiments implying much smaller $^1J[^{11}B-^1H(\text{bridge})]$ for $^{11}B(1,3)$ than for $^{11}B(4)$. [l] Apparently accidentally coincident resonances.

Table 2. Measured n.m.r. parameters for [(η^6-C_6Me_6)RuB_9H_8(OEt)] (**2**), together with those of [(PPh_3)(o-$Ph_2P\overline{C_6H_4)HIrB}_9H_8$]^a for comparison

	Ru compound (2) ($CDCl_3$ solution at 302 K)				Ir compound ($CDCl_3$ solution at 294 K)^a	
Assignment^b	$\delta(^{11}B)$/p.p.m.^{c}	Observed [$^{11}B-^{11}B$]-COSY correlations^d	$\delta(^1H)$/p.p.m.^{e}	$^1J(^{11}B-^1H)$/Hz^f	$\delta(^{11}B)$/p.p.m.^{c}	$\delta(^1H)$/p.p.m.^{e}
1	Ru	—	+2.13^g	—	Ir	−11.79
2	+88.8	(5, 7)s, (8)s	*h*	—	+99.7	*i*
3, 4	+86.4	(5, 7)s, (6)w, (9, 10)s	+8.30	160	+92.5 +86.9	+10.39 +10.04
5, 7	−19.0	(2)s, (3, 4)s, (8)w, (9, 10)w	+0.18	143	−9.6	+1.63
					−13.9	+0.09
6	−18.3	(3, 4)w, (9, 10)w	+0.19	132	−16.0	+1.63
8	+14.8	(2)s, (5, 7)s, (9, 10)s	+3.38	136	+29.8	+5.39
					+25.6	+5.34
9, 10	+22.9	(3, 4)s, (5, 7)w, (6)w, (8)s	+3.64	137	+22.0	+5.15

[a] Data from refs. 17 and 18. [b] By two-dimensional [$^{11}B-^{11}B$]-COSY (column 3) and by analogy with *isocloso* compounds described in references 5, 17, and 18; numbering as in structure (II). [c] ±0.5 p.p.m. to high frequency of $BF_3(OEt_2)$ in $CDCl_3$. [d] s = Stronger and w = weaker. [e] ±0.05 p.p.m. to high frequency of $SiMe_4$; ^1H resonances related to directly bound B atoms by ^1H-{^{11}B(selective)} spectroscopy. [f] ±8 Hz; obtained from ^{11}B spectrum with resolution enhancement to achieve baseline separation of doublet components. [g] C_6Me_6 proton position. [h] Ethoxy-substituted position; $\delta(^1H)$(OEt) +1.48 (triplet) and +4.43 (quartet), $^3J(^1H-^1H)$ *ca.* 7 Hz. [i] P-phenylene C-orthocycloboronated site (effective aromatic substituent site).

$$[\{Ru(\eta^6\text{-}C_6Me_6)Cl_2\}_2] + 2Tl[B_3H_8] \longrightarrow 2[(\eta^6\text{-}C_6Me_6)ClRuB_3H_8] + 2TlCl \quad (1)$$

identified as [2-(η^6-C_6Me_6)-2-Cl-*arachno*-2-RuB_3H_8] [for numbering see structure (I) and Figure 1]. Elemental analytical data were consistent with the formulation, and the n.m.r. properties (Table 1) compared to those of other four-vertex *arachno*-2-metallaboranes of iron,[9] ruthenium,[10] and osmium,[11] clearly show that compound (**1**) is of the same metallaborane structural type, with proton n.m.r. indicating the retention of an unmodified η^6-C_6Me_6 ligand on the metal centre. The proposed structure is therefore as indicated in Figure 1, although present evidence cannot distinguish between the two non-borane stereochemical possibilities of the two isomers shown.

The product (**1**) can be regarded as a straightforward 18-electron octahedral d^6 ruthenium(II) species, with three of the octahedral bonding vectors directed towards the C_6Me_6 moiety, one towards the chlorine atom, and the other two directed one each towards the B–H–Ru bridging bonds. In cluster terms the metallaborane is an *arachno*-B_4H_{10} analogue in which the (η^6-C_6Me_6)ClRu moiety replaces the wingtip BH_2 moiety in the 2 position, these fragments each contributing two orbitals to the cluster bonding proper.

Compound (**1**) is of interest in metallaborane synthesis because it is a metallaborane which still retains halogen bound to the metal and thus in principle permits further reaction with borane anions to build up higher metallaborane species [*e.g.* equation (2)]. With this objective in mind we examined its

$$[(\eta^6\text{-}C_6Me_6)ClRuB_3H_8] + [B_nH_m]^- \xrightarrow{?} Cl^- + \text{'}(\eta^6\text{-}C_6Me_6)RuB_{3+n}H_{8+m}\text{'} \xrightarrow{?} \text{stable metallaboranes} \quad (2)$$

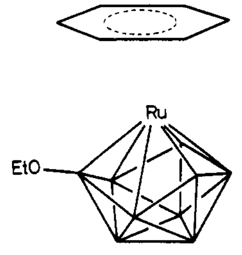
reaction with the *closo*-$[B_{10}H_{10}]^{2-}$ anion in refluxing ethanol, a reaction that works with a variety of metal–halide centres to produce metallaboranes.[1a,3–8,12–14] With compound (**1**) this reaction system resulted in the formation of three predominant metallaborane products, compounds (**2**), (**3**), and (**4**), which were separable by t.l.c. and h.p.l.c.; the only other metallaborane product in a yield viable enough to undergo any characterisation was shown by long-accumulation ^{11}B Fourier-transform n.m.r. spectroscopy to be an eleven-vertex *closo*-type RuB_{10} cluster compound related to compounds (**3**) and (**4**) discussed below.

Compound (**2**), an air-stable yellow solid, obtained in *ca.* 2% yield, was readily identified as the ten-vertex *isocloso*[3,15] metalladecaborane cluster compound [1-(η^6-C_6Me_6)-1-RuB_9H_8-2-(OEt)], structure (V), by n.m.r. spectroscopy (Table 2).

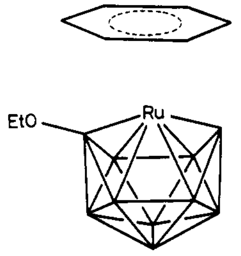
Table 3. Measured n.m.r. parameters for [(η^6-C_6Me_6)$RuB_{10}H_9$(OEt)] (**3**) and [{(η^6-C_6Me_6)$_2Ru_2H_4$}$RuB_{10}H_8(OEt)_2$] (**4**), together with those of [(η^5-C_5Me_5)$RhB_{10}H_9$(OMe)][a] for comparison

	Compound (**3**) ($CDCl_3$ solution at 304 K)			Compound (**4**) (CD_3CN solution at 304 K)			Rh compound ($CDCl_3$ at 297 K)[a]	
Assignment[b]	$\delta(^{11}B)$/ p.p.m.[c]	$^1J(^{11}B$–$^1H)$/ Hz[d]	$\delta(^1H)$/ p.p.m.[e]	$\delta(^{11}B)$/ p.p.m.[c]	$^1J(^{11}B$–$^1H)$/ Hz[d]	$\delta(^1H)$/ p.p.m.[e]	$\delta(^{11}B)$/ p.p.m.[c]	$\delta(^1H)$/ p.p.m.[e]
1	Ru	—	+2.08[f]	Ru	—	+2.14,[f] −13.93[g]	Rh	+1.65[f]
2	+97.0	—	*h,i*	+88.1	—	*h,k*	+96.8	*j*
3	+103.9	167	+9.96				+112.1	+10.10
4, 7	+10.4	131[l]	+1.59	+1.6	135	+2.39	+14.3	+2.08
5, 6	+4.9	144	+0.72				+9.8	+1.39
8	+0.9	140	+3.39	+3.6	134	+3.11	+0.2	+3.49
9	*ca.* +11[m]	134[m]	+4.04				+11.6	+4.08
10, 11	*ca.* +11[m]	134[m]	+2.29	−0.1	134	+1.93	+14.3	+2.54

[a] Data from ref. 8; note that the numbering convention used in reference 8 [structure (**IV**)] differs from that used here [structure (**III**)]. [b] Assignments by two-dimensional [^{11}B–^{11}B]-COSY experiments; correlations very similar to those reported for the related *closo*/*isocloso*-type eleven-vertex rhodium species in ref. 8. [c] ±0.5 p.p.m. to high frequency (low field) of $BF_3(OEt_2)$ in $CDCl_3$. [d] ±8 Hz; obtained from ^{11}B spectrum with resolution enhancement to achieve baseline separation of doublet components. [e] ±0.05 p.p.m. to high frequency of $SiMe_4$; ^1H resonances relative to directly bound B atoms by ^1H-{^{11}B(selective)}spectroscopy. [f] C_nMe_n proton resonance. [g] Relative intensity 4 H; at lower temperatures this separated into two positions, each of relative intensity 2 H, with $\delta(^1H)$ −10.60 and −17.67 p.p.m. at 203 K; coalescence temperature 270 K at 400 MHz (9.4 T). At extreme lower temperatures the higher field resonance (which has 1:2:1 triplet character, splitting *ca.* 3.6 Hz) broadens somewhat and shifts slightly; $\delta(^1H)(CD_2Cl_2)$ −17.67 p.p.m. and $w_{\frac{1}{2}}$ *ca.* 9 Hz at 203 K; $\delta(^1H)(CD_2Cl_2)$ −17.59 p.p.m. and $w_{\frac{1}{2}}$ *ca.* 12.3 Hz at 173 K. [h] Ethoxy-substituted position. [i] $\delta(^1H)$(OEt) +4.86 (q) and +1.67 (t) p.p.m., $^3J(^1H$–$^1H)$ *ca.* 7 Hz. [j] Methoxy-substituted position. [k] $\delta(^1H)$(OEt) +2.97 (q) and +0.90 (t) p.p.m. [l] Accidental overlap with $\delta[^{11}B(9)]$ and $\delta[^{11}B(10, 11)]$ precludes accurate measurement. [m] $\delta[^{11}B(9)]$ and $\delta[^{11}B(10, 11)]$ accidentally near-coincident; precludes accurate estimation of individual $^1J(^{11}B$–$^1H)$ values.



(**V**)



(**VI**)

The overall ^{11}B shielding pattern with 3 B at very low field, 3 B at moderately low field, and 3 B at intermediate to high field is diagnostic of the ten-vertex *isocloso*-1-metalladecaboranes,[5,16–19] and the overall 1:2:2:1:1:2 intensity ratio pattern shows a time-averaged mirror plane rather than three-fold symmetry, the lower symmetry arising from an ethoxy group rather than an *exo* hydrogen on one of the lower-connectivity boron positions on the belt nearest the metal atom [nominally B(2); numbering as in structure (**II**)]. Proton n.m.r. also shows an unmodified η^6-C_6Me_6 grouping, and the resultant [1-(η^6-C_6Me_6)-*isocloso*-1-RuB_9H_8-2-(OEt)] formulation for compound (**2**), as represented in (**V**), is consistent with elemental analysis and mass spectrometry.

Compound (**3**), also an air-stable yellow solid, was obtained in the somewhat higher yield of *ca.* 5%, and was similarly identified, now as the eleven-vertex *closo*-type metallaundecaborane cluster compound [1-(η^6-C_6Me_6)-1-$RuB_{10}H_9$-2-(OEt)] of configuration as represented in (**VI**) [numbering as in (**III**) above]. The results of n.m.r. spectroscopy (Table 3), with two ^{11}B resonances at very low field and the others closely grouped around $\delta(^{11}B)$ = zero, readily identify the eleven-vertex *closo*-type 1-metallaundecaborane cluster character,[4,8,19] and the 1:1:1:2:2:2:1 relative intensity pattern indicates a time-averaged mirror plane rather than C_{2v} symmetry. The ethoxy group and the η^6-C_6Me_6 ligand follow from the proton spectra, and again the overall formulation is supported by elemental analysis and mass spectrometry. Compounds (**2**) and (**3**) belong to the interesting class of '*isocloso*' metallaborane compounds,[3] first discovered by Bould,[15,17,18,20] that do not conform to the simple Williams–Wade[21,22] cluster-geometry and electron-counting rules, and there is consequently some discussion in the literature as to the nature of the cluster bonding in these species.[23–27] One view is that the metal centre contributes principally three orbitals to the cluster-bonding scheme so that these metallaborane clusters are therefore two electrons short of the formal Wadian *closo* electron counts,[16,24,25,27] whereas another view is that the metallaborane clusters can be regarded as having full *closo* electron counts so that the metal centre therefore contributes principally four orbitals to the cluster-bonding scheme.[17,18,23,28]

The third metallaborane product, compound (**4**), a dark claret-red crystalline compound, was obtained in much larger yield (32% based on Ru content) than compounds (**2**) and (**3**). N.m.r. spectroscopy (Table 3) showed that this also has an eleven-vertex *closo*-type 1-metallaundecaborane cluster, like compound (**3**), but now with an ethoxy substituent on each of the B(2) and B(3) positions [numbering as in (**III**) above], giving a time-averaged C_{2v} symmetry. The room-temperature proton n.m.r. spectrum, however, also revealed a proton resonance of relative intensity 4 H at −13.93 p.p.m., *i.e.* in the metal–hydride region, and this together with the high molecular weight (by osmometry) and low boron content (by elemental analysis) suggested other than a straightforward (η^6-C_6Me_6)Ru moiety at the cluster 1-position.

Single-crystal *X*-ray diffraction analysis revealed the molecular structure drawn in Figure 2, interatomic distances and angles being summarized in Tables 4 and 5 respectively. The collected data set was of sufficient quality for both the metal–hydride and borane hydrogen atoms to be readily located and freely refined. It can be seen that the *closo*-type 2,3-ethoxy-1-metallaundecaboranyl nature of the compound deduced from n.m.r. spectroscopy is confirmed, and the dimensions within this metallaborane cluster are similar to those reported previously for related compounds of ruthenium,[3–5] osmium,[7] and rhodium.[8] These geometrical similarities, together with the n.m.r. similarities,[3–8] suggest that the bonding within this metallaborane cluster unit is unexceptional for this eleven-vertex *closo*-type of compound.

Table 4. Selected interatomic distances (pm) for compound (**4**) with estimated standard deviations (e.s.d.s) in parentheses

(*i*) Ruthenium–ruthenium

Ru(1)–Ru(2)	282.7(4)	Ru(1)–Ru(3)	279.2(4)
Ru(2)–Ru(3)	268.4(4)		

(*ii*) Ruthenium–carbon

Ru(2)–C(1)	218.5(5)	Ru(2)–C(2)	217.7(6)
Ru(2)–C(3)	219.3(6)	Ru(2)–C(4)	221.7(5)
Ru(2)–C(5)	222.5(6)	Ru(2)–C(6)	220.9(5)
Ru(3)–C(13)	217.8(5)	Ru(3)–C(14)	220.5(5)
Ru(3)–C(15)	224.2(5)	Ru(3)–C(16)	225.1(5)
Ru(3)–C(17)	222.4(5)	Ru(3)–C(18)	218.7(5)

(*iii*) Ruthenium–boron

Ru(1)–B(2)	206.5(8)	Ru(1)–B(3)	205.4(8)
Ru(1)–B(4)	236.9(8)	Ru(1)–B(5)	233.3(8)
Ru(1)–B(6)	228.9(8)	Ru(1)–B(7)	236.5(8)

(*iv*) Ruthenium–hydrogen

Ru(1)–H(1,2)	171.6(65)	Ru(1)–H(1,3)	190.1(51)
Ru(1)–H(2,3)	230.0(50)		
Ru(2)–H(1,2)	170.3(64)	Ru(3)–H(1,3)	169.3(50)
Ru(2)–H(2,3A)	173.7(50)	Ru(3)–H(2,3A)	188.2(50)
Ru(2)–H(2,3B)	175.1(60)	Ru(3)–H(2,3B)	156.2(61)

(*v*) Boron-boron

B(2)–B(4)	178.2(10)	B(2)–B(7)	177.3(10)
B(2)–B(8)	174.0(11)	B(3)–B(5)	181.2(10)
B(3)–B(6)	181.3(11)	B(3)–B(9)	177.1(11)
B(4)–B(5)	172.6(11)	B(4)–B(8)	183.2(11)
B(4)–B(10)	178.4(11)	B(5)–B(9)	183.3(10)
B(5)–B(10)	178.0(11)	B(6)–B(7)	171.2(11)
B(6)–B(9)	184.9(10)	B(6)–B(11)	177.3(11)
B(7)–B(8)	182.6(10)	B(7)–B(11)	177.4(11)
B(8)–B(10)	177.6(12)	B(8)–B(11)	177.8(12)
B(9)–B(10)	177.0(11)	B(9)–B(11)	175.3(12)
B(10)–B(11)	178.2(11)		

(*vi*) Others

B(2)–O(2)	137.8(8)	B(3)–O(3)	136.2(8)
O(2)–C(2A)	136.2(9)	O(3)–C(34)	142.4(8)
C(2A)–C(2B)	137.5(12)	C(3A)–C(3B)	149.8(10)

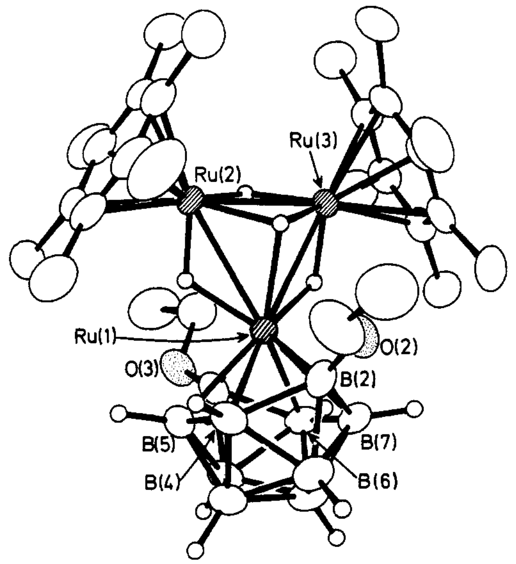


Figure 2. ORTEP drawing of the crystallographically determined molecular structure of $[\{(\eta^6\text{-}C_6Me_6)_2Ru_2H_4\}RuB_{10}H_8(OEt)_2]$ (**4**)

Table 5. Selected interatomic angles (°) for compound (**4**) with e.s.d.s in parentheses

(*i*) About the ruthenium atom

Ru(1)–Ru(2)–Ru(3)	60.8	Ru(2)–Ru(3)–Ru(1)	62.1
Ru(3)–Ru(1)–Ru(2)	57.1	Ru(3)–Ru(1)–H(1,2)	88.1(22)
Ru(2)–Ru(1)–H(1,3)	85.3(16)	Ru(3)–Ru(1)–H(1,3)	36.4(14)
Ru(1)–Ru(2)–H(1,2)	34.4(22)	Ru(3)–Ru(2)–H(1,2)	92.0(22)
Ru(1)–Ru(3)–H(1,3)	41.8(17)	Ru(2)–Ru(3)–H(1,3)	94.1(18)
Ru(2)–Ru(1)–H(2,3A)	37.9(12)	Ru(3)–Ru(1)–H(2,3A)	42.2(12)
Ru(3)–Ru(2)–H(2,3A)	44.3(16)	Ru(1)–Ru(2)–H(2,3A)	52.1(22)
Ru(1)–Ru(2)–H(2,3B)	78.2(19)	Ru(3)–Ru(2)–H(2,3B)	33.6(19)
Ru(1)–Ru(3)–H(2,3A)	52.7(16)	Ru(2)–Ru(3)–H(2,3A)	40.1(15)
Ru(1)–Ru(3)–H(2,3B)	82.1(21)	Ru(2)–Ru(3)–H(2,3B)	38.3(21)
B(2)–Ru(1)–B(4)	46.8(2)	B(4)–Ru(1)–B(5)	43.1(2)
B(3)–Ru(1)–B(5)	48.3(2)	B(3)–Ru(1)–B(6)	49.0(2)
B(6)–Ru(1)–B(7)	43.1(2)	B(2)–Ru(1)–B(7)	46.6(2)

(*ii*) Ruthenium–hydrogen–ruthenium

Ru(1)–H(1,2)–Ru(2)	111.5(36)	Ru(1)–H(1,3)–Ru(3)	101.8(26)
Ru(1)–H(2,3A)–Ru(2)	90.0(22)	Ru(1)–H(2,3A)–Ru(8)	85.1(20)
Ru(2)–H(2,3A)–Ru(3)	95.6(23)	Ru(2)–H(2,3B)–Ru(3)	108.1(33)

(*iii*) Boron–boron–boron

B(2)–B(4)–B(5)	119.8(5)	B(3)–B(5)–B(4)	122.6(5)
B(5)–B(3)–B(6)	98.2(5)	B(3)–B(6)–B(7)	124.1(5)
B(2)–B(7)–B(6)	119.0(6)	B(7)–B(2)–B(4)	102.0(5)

(*iv*) Others

B(2)–O(2)–C(2A)	122.9(6)	O(2)–C(2A)–C(2B)	120.7(9)
B(3)–O(3)–C(3A)	122.7(5)	O(3)–C(3A)–C(3B)	109.8(6)

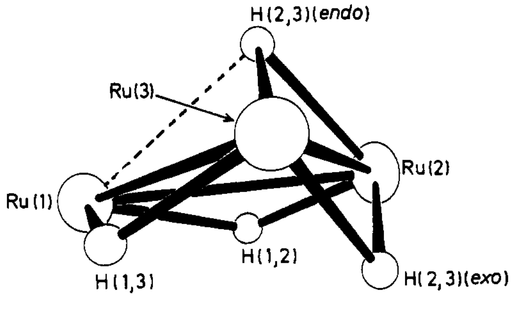
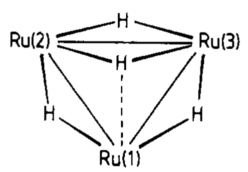
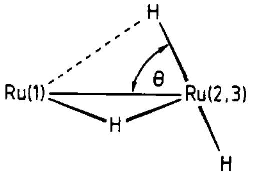


Figure 3. ORTEP drawing of the triangular $H_2Ru_3H_2$ sub-cluster of compound (**4**) (A = *endo* and B = *exo* in Tables 4, 5, and 8)

In contrast, the *exo*-polyhedral ligation sphere of the Ru(1) metal atom (see Figure 3 for detail) is quite unprecedented, because it is based on a Ru_3 triangular cluster that does not have carbonyl groups associated with it, as well as having other unusual features. The disposition of the Ru(1) atom, together with the two other mutually similar ruthenium atoms Ru(2) and Ru(3), approximates very closely to an idealized isosceles triangular arrangement [structure (**VII**)]. The Ru(2) and Ru(3) atoms are linked by two mutually *trans* Ru–H–Ru bridging atoms (dihedral angle between the two RuHRu planes *ca.* 179°), with one of these bridges, designated H(2,3) (*endo*), bent somewhat over the plane {angle of tilt [θ in (**VIII**)] *ca.* 64°}, and the other *exo* to it [structures (**VII**) and (**VIII**)]. Each of these ruthenium atoms is bound to Ru(1) by a Ru–H–Ru bridge, these bridges being out of the Ru_3 plane by *ca.* 65 pm and on the opposite side to H(2,3) (*endo*). The Ru(2) and Ru(3) atoms are each additionally bound to a separate η^6-C_6Me_6 group, the only other ligand on the Ru_3 triangle being the boat η^6-$B_{10}H_8(OEt)_2$ moiety as described in the previous paragraph. The Ru_3 triangle is approximately on what would be one of the



(VII)

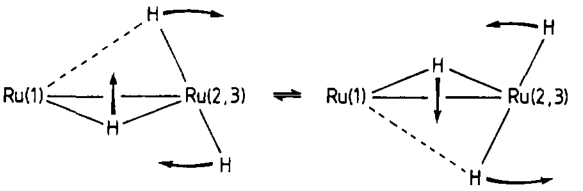


(VIII)

mirror planes of the $RuB_{10}H_8$ unit if the latter conformed to the C_{2v} symmetry to which it approximates, the dihedral angle between Ru(1)Ru(2)Ru(3) and Ru(1)B(10)B(11) being 15°. The twist component of this angle is probably due to crystal-packing forces, whereas any bending component will result also from the asymmetric bonding manifested in the positioning of the bridging H atoms about the Ru_3 plane.

The disposition of the ruthenium–hydrogen moieties Ru(2)-H(1,2) and Ru(3)H(1,3) with respect to Ru(1) is analogous to the disposition of the two phosphine ligands in the previously reported [3,5] monometallic analogue $[(PPh_3)_2RuB_{10}H_8(OEt)_2]$. This, together with the other metallaborane cluster similarities discussed above, suggests that the *exo*-polyhedral ligation to the metallaborane cluster ruthenium atom Ru(1) in compound (**4**) is similar to that in the bis(phosphine) species, *i.e.* Ru(2)H(1,2) and Ru(3)H(1,3) each form a two-electron bond with Ru(1) so that the (neutral) $(\eta^6\text{-}C_6Me_6)_2Ru_2H_4$ moiety can be regarded as a bidentate ligand to the Ru(1) centre. This metal centre can be regarded as being formally ruthenium(II) if the '*hypercloso*' view [24,25,27] of the cluster electronics is adopted, or ruthenium(IV) in the '*isocloso*' system.[3,5–7,26]

The compound exhibits time-averaged C_{2v} symmetry in solution, as judged by n.m.r. spectroscopy (Table 3). In particular, the Ru–H–Ru bridging hydrogen atoms exhibit two proton resonance positions, of relative intensity 2 H:2 H, at lower temperatures, whereas a retention of the solid-state configuration (Figure 3) would require a 2:1:1 intensity pattern; this we attribute to a process as depicted in equation (3), in which the two H(2,3) bridging atoms do not mutually exchange, but oscillate between *endo* and *exo* positions, this being accompanied by a flipping of H(1,2) and H(2,3) through the Ru_3 plane [equation (3)]. This motion could not be stopped by cooling to 170 K, implying an activation energy $\Delta G^‡$ of < *ca.* 31 kJ mol^{-1} for this process, although at lower temperatures there was some broadening of the highest field resonance, perhaps suggesting an incipient separation of this into two components, and therefore assigning it to the H(2,3) bridge position. At higher temperatures there is a mutual exchange of all four bridging hydrogen atoms, with $\Delta G^‡$ 46.0 kJ mol^{-1} as judged by peak coalescence in the ^1H n.m.r. spectrum. A number of mechanisms could be written down for this process, the recently reported cluster structure of $[(\eta^5\text{-}C_5Me_5)H_3\text{-}Ir_2BH_4]$ [29] (Figure 4) suggesting models for transition states involving Ru–H terminal hydride character.



(3)

(IX) (X)

The ruthenium triangular sub-cluster is of high interest because, first, it does not have carbonyl ligands associated with it. The very extensively investigated sub-discipline of ruthenium triangle chemistry has so far been dominated by carbonyl derivatives; all the structural work reported to date (at least 150 single-crystal *X*-ray diffraction analyses!) containing either bridging or terminal carbonyl groups. The stability of the *triangulo*-triruthenium compound (**4**) reported here therefore is an augury for an extensive arene–ruthenium cluster chemistry that will complement and extend the large amount of carbonyl cluster work, and probably generate much novel and fascinating chemistry. This supposition is enhanced by the second point about the triangular sub-cluster of compound (**4**), which is that it is electronically unsaturated and should therefore exhibit unusual reactivities. The two C_6Me_6 ligands each contribute six electrons, the formal borane ligand four, the hydrogen atoms one each, and the ruthenium atoms eight each, to the transition metal 'triangular cluster count.' This total 44, four less than the 48 usually associated [30] with triangular clusters implying at least two 16-electron ruthenium centres. This deficiency can be regarded as being mitigated by the bridging nature of the two hydrogen atoms between Ru(2) and Ru(3) [H(2,3) (*exo*) and H(2,3) (*endo*)] which renders each of these two ruthenium atoms as formally an 18-electron transition-metal centre, and by the looser agostic interaction of H(2,3) (*endo*) with the borane-bound Ru(1) atom, which thereby gives this hydrogen atom some capping character and Ru(1) also some 18-electron character. These considerations suggest that nucleophilic addition to the cluster supported by bridge ⟶ terminal hydride conversion could readily occur, which has many important implications for the development of the further chemistry of this type of system.

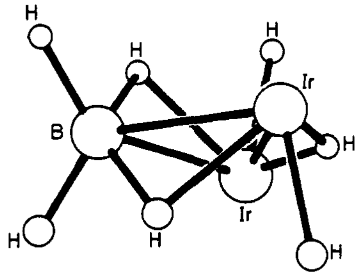


Figure 4. Drawing of the structure of the $H_3Ir_2H_2BH_2$ cluster unit of $[(\eta^5\text{-}C_5Me_5)_2H_3Ir_2H_2BH_2]$.[29] Cluster hydride configurations such as this provide a model for transition states in the high-temperature total hydride fluxionality of the $H_2Ru_3H_2$ sub-cluster of compound (**4**)

The yield of compound (**4**) was surprisingly high (*ca.* 32% based on ruthenium content), and the precedent of the straightforward reaction of $[\{Ru(\eta^6\text{-}C_6Me_6)Cl_2\}_2]$ with *closo*-$[B_{10}H_{10}]^{2-}$ in methanol to form methoxy-substituted *closo*-type $[(\eta^6\text{-}C_6Me_6)RuB_{10}H_{10}]$ species in good yield [1a,31] suggests that the role of the B_3H_8 moiety in compound (**1**) is essentially that of a reducing agent during the formation of compound (**4**). This suggests other more general routes into both boron-containing and non-boron-containing arene–ruthenium cluster compounds using both boron–hydride and other hydridic reducing agents, and we would hope to report on this in the future.

Experimental

General.—The starting materials $[\{Ru(\eta^6\text{-}C_6Me_6)Cl_2\}_2]$,[32] $Tl[B_3H_8]$,[33] and $[NHEt_3]_2[B_{10}H_{10}]$ [34] were prepared according to literature methods. Reactions were carried out under an atmosphere of dry nitrogen, although manipulation and separation procedures were generally carried out in air. Preparative t.l.c. was carried out using silica gel G (Fluka,

Table 6. Elemental analyses

Compound	Analysis (%)* C	H	B	Cl
(**1**) $[(\eta^6\text{-}C_6Me_6)ClRuB_3H_8]$	43.4 (42.4)	7.7 (7.7)	8.6 (9.5)	10.3 (10.4)
(**2**) $[(\eta^6\text{-}C_6Me_6)RuB_9H_8(OEt)]$	40.1 (40.6)	7.1 (7.6)		
(**3**) $[(\eta^6\text{-}C_6Me_6)RuB_{10}H_9(OEt)]$	40.5 (39.5)	7.9 (7.6)		
(**4**) $[\{(\eta^6\text{-}C_6Me_6)_2Ru_2H_4\}RuB_{10}H_8(OEt)_2]$	39.6 (40.1)	6.9 (7.0)	12.9 (16.0)	

* Calculated values shown in parentheses.

Table 7. Non-hydrogen atomic co-ordinates (× 10^4) for compound (**4**) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Ru(1)	807.1(3)	2 415.4(2)	−301.5(2)
Ru(2)	1 170.4(4)	2 875.1(3)	−1 535.8(2)
Ru(3)	2 780.0(3)	1 803.7(2)	−829.9(2)
C(1)	50(4)	3 975(2)	−1 857(2)
C(2)	−482(4)	3 304(2)	−2 228(2)
C(3)	253(4)	2 834(2)	−2 560(2)
C(4)	1 520(4)	3 035(2)	−2 522(2)
C(5)	2 053(4)	3 706(2)	−2 151(2)
C(6)	1 318(4)	4 176(2)	−1 819(2)
C(7)	−769(9)	4 535(5)	−1 524(4)
C(8)	−1 900(6)	3 082(6)	−2 286(4)
C(9)	−316(8)	2 039(5)	−2 899(3)
C(10)	2 288(8)	2 521(5)	−2 916(4)
C(11)	3 431(6)	3 959(5)	−2 141(4)
C(12)	1 926(10)	4 867(5)	−1 369(4)
C(13)	3 663(3)	783(2)	−236(2)
C(14)	3 540(3)	550(2)	−879(2)
C(15)	4 062(3)	1 038(2)	−1 298(2)
C(16)	4 708(3)	1 760(2)	−1 073(2)
C(17)	4 831(3)	1 993(2)	−430(2)
C(18)	4 309(3)	1 504(2)	−11(2)
C(19)	3 135(6)	214(4)	235(3)
C(20)	2 685(7)	−183(4)	−1 161(4)
C(21)	4 036(7)	729(5)	−1 985(3)
C(22)	5 486(6)	2 226(5)	−1 502(4)
C(23)	5 279(6)	2 870(4)	−213(4)
C(24)	4 587(7)	1 736(5)	706(3)
B(2)	1 523(6)	3 090(3)	519(3)
B(3)	−898(6)	1 817(4)	−414(3)
B(4)	−30(6)	3 490(4)	240(3)
B(5)	−1 190(6)	2 872(4)	−205(3)
B(6)	64(6)	1 503(4)	355(3)
B(7)	1 207(7)	2 106(4)	813(3)
B(8)	488(7)	3 045(4)	1 046(3)
B(9)	−1 496(6)	2 000(4)	290(3)
B(10)	−1 119(6)	2 985(4)	637(3)
B(11)	−320(7)	2 086(4)	994(3)
O(2)	2 671(3)	3 487(2)	593(2)
C(2A)	2 779(8)	4 321(5)	557(7)
C(2B)	3 937(9)	4 698(5)	738(6)
O(3)	−1 531(3)	1 360(2)	−918(2)
C(3A)	−904(6)	837(4)	−1 291(3)
C(3B)	−1 859(8)	356(5)	−1 762(4)

Table 8. Cluster hydrogen atomic co-ordinates (× 10^4) for compound (**4**) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
H(1,2)	99(61)	2 751(38)	−1 058(31)
H(1,3)	1 700(46)	1 440(31)	−426(24)
H(2,3A)	2 261(47)	2 909(30)	−808(23)
H(2,3B)	1 757(55)	1 866(36)	−1 468(28)
H(4)	−33(43)	4 185(31)	100(22)
H(5)	−1 881(57)	3 197(35)	−646(30)
H(6)	204(45)	841(33)	312(23)
H(7)	2 076(42)	1 834(26)	1 101(21)
H(8)	793(44)	3 402(30)	1 485(24)
H(9)	−2 403(48)	1 683(30)	296(23)
H(10)	−1 845(49)	3 356(32)	801(25)
H(11)	−367(86)	1 719(59)	1 420(46)

type GF254) on plates of dimensions 200 × 200 × 1 mm, made in these laboratories from acetone slurries followed by drying in air at 80 °C. H.p.l.c. was performed on commercially available instrumentation using a prepacked silica column (16 × 250 mm, Lichrosorb Si 60) with a silica pre-column [5 × 60 mm, Kieselgel 60 (Fluka AG CH9470)], with detection by change in u.v. absorption of eluant, and using a flow rate of 10 cm^3 min^{-1}. Elemental analyses for new compounds are given in Table 6.

Nuclear Magnetic Resonance Spectroscopy.—This was performed at 2.35 and/or 9.40 T on JEOL FX 100 and Bruker AM 400 instruments respectively. The techniques of $^1H\text{-}\{^{11}B\}$[35–37] and $[^{11}B\text{-}^{11}B]$-COSY[8,38–40] spectroscopy used were essentially as discussed elsewhere, other spectroscopy being straightforward. Chemical shifts $\delta(^1H)$ and $\delta(^{11}B)$ are given in p.p.m. to high frequency (low field) of Ξ100 MHz ($SiMe_4$) and Ξ32.083 971 MHz [nominally $BF_3(OEt)_2$ in $CDCl_3$][19] respectively.

Mass Spectrometry.—This was performed on an AEI (now KRATOS) MS30 instrument using the solid-sample introduction probe and 70 eV (*ca.* 112 × 10^{-19} J) electron-impact ionisation.

Preparation of $[(\eta^6\text{-}C_6Me_6)ClRuB_3H_8]$ (**1**).—$Tl[B_3H_8]$ (76 mg, 0.31 mmol) was added to a stirred, degassed solution of $[\{Ru(\eta^6\text{-}C_6Me_6)Cl_2\}_2]$ (100 mg, 0.15 mmol) in dichloromethane (50 cm^3). After 1 h the yellow reaction mixture was filtered over silica with CH_2Cl_2. The solvent was removed (rotary evaporator, 40 °C, water pump) to yield a yellow solid compound (**1**) (67 mg, 66%) identified as described in the text.

Reaction between $[(\eta^6\text{-}C_6Me_6)ClRuB_3H_8]$ (**1**) *and* $[NHEt_3]_2[B_{10}H_{10}]$.—Compound (**1**) (50 mg, 0.15 mmol) and $[NHEt_3]_2[B_{10}H_{10}]$ (97 mg, 0.3 mmol) were heated under reflux in dry degassed ethanol (35 cm^3) under an atmosphere of dry nitrogen gas, the initially yellow mixture giving a deep red solution. After 3 h the ethanol was removed under reduced pressure (rotary evaporator, 40 °C, water pump). The resulting red solid was dissolved in CH_2Cl_2 and applied to preparative t.l.c. plates. Elution with CH_2Cl_2–MeCN (9:1) gave two major bands, yellow [(**2**) + (**3**)] (R_f = 0.88) and red [(**4**)] (13 mg, 32%) (R_f = 0.65). Compounds (**2**) and (**3**) were separated by h.p.l.c. on silica, eluting with CH_2Cl_2–n-hexane (1:1) to give (**2**) (1 mg, 1.7%) (R_t, retention time = 16 min) and (**3**) (3 mg, 4.7%) (R_t = 17 min). Mass spectra: (**2**) *m*/*z* cut off 418, calc. for $[^{104}Ru^{12}C_{14}{}^1H_{31}{}^{11}B_9{}^{16}O]$ 418; (**3**) *m*/*z* cut off 430, calc. for $[^{104}Ru^{12}C_{14}{}^1H_{32}{}^{11}B_{10}{}^{16}O]$ 430.

X-Ray Crystallography.—A sample of compound (**4**) suitable for single-crystal diffraction analysis was obtained by the slow evaporation of a solution of the compound in acetonitrile.

All crystallographic measurements were made on a Nicolet *P3/F* diffractometer operating in the ω–2θ scan mode using graphite-monochromatised Mo-K_α radiation ($\lambda = 71.069$ pm) following a standard procedure described in detail elsewhere.[41] The data set was corrected for absorption empirically once the structure had been solved.[42] The structure was solved by direct methods and refined by full-matrix least squares using the SHELX program system.[43] All non-hydrogen atoms were assigned anisotropic thermal parameters. Methyl and methylene hydrogen atoms were included in calculated positions (C–H = 108 pm) and were assigned to an overall isotropic thermal parameter for each group. The borane- and ruthenium-attached hydrogen atoms were readily located in a Fourier difference map 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. Co-ordinates for non-hydrogen atoms and cluster hydrogen atoms are listed in Tables 7 and 8 respectively.

Crystal data. $C_{28}H_{58}B_{10}O_2Ru_3$, $M = 838.09$, monoclinic, $a = 1\,081.7(1)$, $b = 1\,622.6(3)$, $c = 2\,120.4(3)$ pm, $\beta = 102.07(1)^\circ$, $U = 3.639$ nm^3, $Z = 4$, space group $P2_1/c$, $D_c = 1.529$ g cm^{-3}, $\mu = 11.29$ cm^{-1}, $F(000) = 1\,696$.

Data collection. Scans running from 1° below $K_{\alpha 1}$ to 1° above $K_{\alpha 2}$, scan speeds 2.0—29.3° min^{-1}, $4.0 < 2\theta < 45.0^\circ$. 5 108 Data collected. 4 295 Observed $[I > 2.0\sigma(I)]$, $T = 290$ K.

Structure refinement. Number of parameters 458, weighting factor $g = 0.0004$, $R = 0.0344$, $R' = 0.0396$.

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