Two Unusual *closo*-type Ruthenaboranes: Preparation, Molecular Structure, and Nuclear Magnetic Resonance Properties of $[1,1,1\text{-}(PPh_3)HCl\text{-}1\text{-}RuB_9H_7\text{-}3,5\text{-}(PPh_3)_2]$ and $[1,1\text{-}(PPh_3)_2\text{-}1\text{-}RuB_{10}H_8\text{-}2,5\text{-}(OEt)_2]$ *

Janet E. Crook, Margaret Elrington, Norman N. Greenwood, John D. Kennedy, Mark Thornton-Pett, and J. Derek Woollins
Department of Inorganic and Structural Chemistry, University of Leeds, Leeds LS2 9JT

Reaction of *arachno*-$[B_9H_{14}]^-$ with $[RuCl_2(PPh_3)_3]$ under mild conditions gives the orange 10-vertex ruthenadecaborane $[1,1,1\text{-}(PPh_3)HCl\text{-}1\text{-}RuB_9H_7\text{-}3,5\text{-}(PPh_3)_2]$ in *ca.* 40% yield. The molecular structure is based on an *'isocloso'* C_{3v} 1:3:3:3 RuB_9 stack with the nine-co-ordinate metal occupying the unique six-connected apical position. The electronic structure may be interpreted either on the basis of a 'PSEPT-deficient' $2n$-electron cluster with the metal having a straightforward 'conical' three-orbital contribution, or as a 'PSEPT-precise' $(2n + 2)$-electron cluster with the metal having a four-orbital involvement, also conical, with the cluster. Similar bonding considerations apply to the red 11-vertex ruthenaundecaborane $[1,1\text{-}(PPh_3)_2\text{-}1\text{-}RuB_{10}H_8\text{-}2,5\text{-}(OEt)_2]$ which is obtained in a yield of 80% from the reaction of $[RuCl_2(PPh_3)_3]$ with *closo*-$[B_{10}H_{10}]^{2-}$ in refluxing ethanolic chloroform. The molecular structure is based on that of a *closo*-type C_{2v} 1:2:4:2:2 RuB_{10} stack again with the metal occupying the unique six-connected apical position. Both compounds can be considered as having *'isocloso'* structures derived from the complete capping of the open face of an *arachno* geometry to give a completely closed deltahedral cluster.

Although several hundred polyhedral metallaboranes have been characterized,[1] the incidence of ruthenaboranes is, perhaps surprisingly,[2] low. We have very recently reported some polyhedral ruthenaborane chemistry in which relatively straightforward four-, five-, six-, and 10-vertex metallaborane clusters were formed.[2] Here we report the formation and identification of two further somewhat more novel ruthenaboranes. Some aspects of this and related work have appeared in various preliminary publications.[3–6]

Results and Discussion

Reaction between $[RuCl_2(PPh_3)_3]$ and the *arachno*-$[B_9H_{14}]^-$ anion in dichloromethane solution at ambient temperature yields an orange crystalline solid, somewhat air-sensitive, in an isolable yield of *ca.* 40%. The compound was identified by single-crystal *X*-ray diffraction analysis and multielement n.m.r. spectroscopy (see below). Although the reaction has an apparently straightforward stoicheiometry [equation (1)], the

$$[RuCl_2(PPh_3)_3] + [B_9H_{14}]^- \longrightarrow [(PPh_3)HClRuB_9H_7(PPh_3)_2] + 3\,H_2 + Cl^- \quad (1)$$

mechanism of formation is undoubtedly complex and probably involves free phosphine in the reaction system since phosphine–borane species such as $BH_3(PPh_3)$ and $B_9H_{13}(PPh_3)$ are also present as reaction products, and the elimination of three molecules of dihydrogen must in any event involve a series of reaction steps.[3,7–10] The product was isolated as a solvate containing $3CH_2Cl_2$.

In the initial work, the similarity of the cluster boron and proton n.m.r. spectroscopic data to those[9,10] for 10-vertex *'isocloso'* iridaboranes such as $[(PPh_3)(o\text{-}Ph_2PC_6H_4)HIrB_9H_8]$ (Tables 1 and 2, and Figure 1) suggested that the ruthenaborane was similarly an *isocloso* cluster compound, but now with two boron-bound PPh_3 ligands. In this regard, however, aspects of the ^{31}P coupling behaviour, and that of the high-field proton at $\delta(^1H)$ −7.83 p.p.m., were puzzling and introduced interpretational ambiguities.

A single-crystal *X*-ray diffraction analysis of $[(PPh_3)HClRuB_9H_7(PPh_3)_2]\cdot 3CH_2Cl_2$ was therefore undertaken. This confirmed the *isocloso* structure of the cluster (in the ideal case a C_{3v} 1:3:3:3 stack) and established the *exo*-polyhedral bonding geometry about the metal atom. In particular, all the hydrogen atoms, including that on the ruthenium atom, were located and refined.

A drawing of the molecular structure, with certain organyl atoms omitted for clarity, is given in Figure 2. Selected interatomic distances and angles are given in Tables 3 and 4 respectively. The 10-vertex *isocloso* structure is readily apparent from the closed 1:3:3:3 $RuB_3B_3B_3$ cluster structure which approximates closely to an idealized C_{3v} symmetry. The upper belt of three ruthenium-bound boron atoms B(2)B(4)B(6) (of which each has a cluster connectivity of four) is closer to the metal atom [209.0(11)—219.3(9) pm] than is the middle belt B(3)B(5)B(7) [235.3(9)—251.7(9) pm] of which each has a cluster connectivity of five. This is also observed in the *isocloso*-iridium species reported elsewhere.[3,9,10] The interatomic angles in the Ru–η^6-B(2)B(3)B(4)B(5)B(6)B(7) chair average *ca.* 106° [at B(2), B(4), and B(6)] and *ca.* 115.5° [at B(3), B(5), and B(7)]. There are no substituents on the B(2)B(4)B(6) upper belt, in contrast to the structurally-investigated iridium compound $[(PPh_3)(o\text{-}Ph_2PC_6H_4)HIrB_9H_8]$[3,9,10] which exhibits phenylene-to-cluster *ortho*-cycloboronation at B(2), but there are two phosphine substituents, PPh_3, on the second belt of boron atoms, at B(3) and B(5). All the other boron centres have *exo*-terminal hydrogen atoms bound to them, consistent with the n.m.r. properties (Table 1).

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* 1-Chloro-1-hydrido-1,3,5-tris(triphenylphosphine)-*isocloso*-1-ruthenadecaborane and 2,5-diethoxy-1,1-bis(triphenylphosphine)-*closo*-1-ruthenaundecaborane respectively.

Supplementary data available (No. SUP 56316, 6 pp.): H-atom coordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

PSEPT refers to 'polyhedral skeletal electron pair theories;' see, for example, D. M. P. Mingos, *Acc. Chem. Res.*, 1984, **17**, 311; K. Wade, *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 1.

Table 1. Cluster proton and boron-11 n.m.r. data for the *isocloso* species $[(PPh_3)HClRuB_9H_7(PPh_3)_2]$[a] and $[(PPh_3)(o\text{-}Ph_2PC_6H_4)HIrB_9H_8]$[b]

	$[(PPh_3)HClRuB_9H_7(PPh_3)_2]$		$[(PPh_3)(o\text{-}Ph_2PC_6H_4)HIrB_9H_8]$	
Assignment[c]	$\delta(^{11}B)$[d]	$\delta(^{1}H)$[e]	$\delta(^{11}B)$[d]	$\delta(^{1}H)$[e]
2,4,6	$+78.1$[f]	$+8.56$[f]	$+99.7$	[g]
	$+76.5$[f]	$+8.02$[f]	$+92.5$	$+10.39$
	$+72.3$	$+7.68$	$+86.9$	$+10.04$
8,9,10	$+15.1$	$+3.49$	$+29.8$	$+5.39$
	$+12.8$	$+3.21$	$+25.6$	$+5.34$
	$+6.3$	$+2.34$	$+22.0$	$+5.15$
3,5,7	-15.3[h,i]	[j]	-9.6	$+1.63$
	-18.3[k]	[j]	-13.9	$+0.09$
	-20.1	$+0.61$	-16.0	-1.63
1	—	-7.83[h,l]	—	-11.79[m]

[a] This work; $CDCl_3$ solution at +21 °C. [b] From refs. 9 and 10; $CDCl_3$ solution at +21 °C. [c] See text. [d] In p.p.m. ±0.5 to high frequency (low field) of $BF_3(OEt_2)$–$CDCl_3$. [e] In p.p.m. ±0.05 to high frequency (low field) of $SiMe_4$–$CDCl_3$; ^{1}H resonances related to ^{11}B resonances by selective ^{1}H-$\{^{11}B\}$ spectroscopy. [f] Pairs of ^{11}B resonances too close to distinguish individual ^{1}H assignments in ^{1}H-$\{^{11}B\}$ experiments. [g] Site of cyclization; effective aromatic C-bonded substituent. [h] Selective sharpening of Ru(1)–^{1}H(terminal) at $\delta(^{1}H)$ −7.83 p.p.m. on irradiation at $\nu(^{11}B)$ corresponding to $\delta(^{11}B)$ −15.3 p.p.m.; this arises from (unresolved) coupling $^{2}J(^{11}B\text{–}Ru\text{–}^{1}H)$ (*trans*) $\leqslant$ *ca.* 20 Hz. [i] B(3), doublet, $^{1}J(^{31}P\text{–}^{11}B)$ (*exo*) *ca.* 110 Hz. [j] P-substituted site. [k] B(5), doublet structure arising from $^{1}J(^{31}P\text{–}^{11}B)$ (*exo*) not resolved because of overlap with resonance at $\delta(^{11}B)$ −20.1; estimated value *ca.* 120 Hz. [l] Doublet of doublets of doublets, arising from one coupling $^{2}J(^{31}P\text{–}Ru\text{–}^{1}H)$ (*cis*) and two couplings $^{3}J(^{31}P\text{–}B\text{–}Ru\text{–}^{1}H)$; values *ca.* 15, 20, and 25 Hz. [m] Doublet of doublets, $^{2}J(^{31}P\text{–}Ir\text{–}^{1}H)$ (*cis*) *ca.* 16 and 25 Hz.

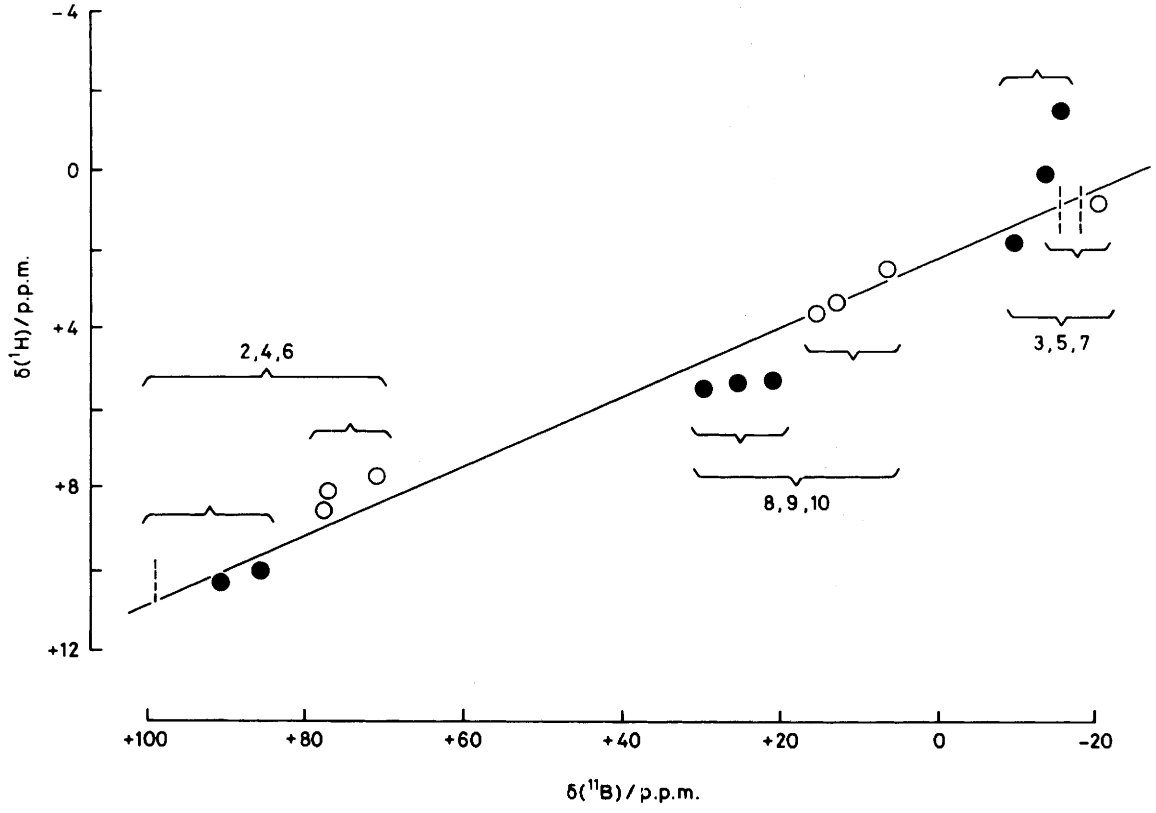


Figure 1. Proton *versus* boron-11 nuclear shielding correlation plot for $[(PPh_3)HClRuB_9H_7(PPh_3)_2]$ (○) (this work) and the *isocloso* iridium species $[(PPh_3)(o\text{-}Ph_2PC_6H_4)HIrB_9H_8]$ (●) (data from refs. 9 and 10). The line drawn has slope $\delta(^{11}B):\delta(^{1}H)$ of *ca.* 11 : 1. Note that for each compound the boron resonances are distinctively grouped into three groups of three, one group being at extreme low field; this is diagnostic for the 10-vertex *isocloso*-1-metallaborane structural type. The assignments are discussed in the text

The metal centre has three *exo*-polyhedral ligands, triphenylphosphine, chloride, and hydride, in an approximately trigonal array about the (idealized) cluster three-fold axis. Interestingly, as with the (constrained) exocyclic iridium compound $[(PPh_3)(o\text{-}Ph_2PC_6H_4)HIrB_9H_8]$,[3,9,10] the bonding vectors in this unconstrained compound are also in approximately eclipsed positions with respect to the nearer boron atoms B(2)B(4)B(6) in the upper belt of the nine-boron 3 : 3 : 3 stack. There is considerable variation in the ruthenium–boron distances within each of the three bands; this will presumably reflect the various *trans* effects of the three different *exo*-polyhedral ligands on the metal. For example, the distance Ru(1)–B(3) *trans* to Ru(1)–H(1) is some 10—15 pm longer than the distances to B(5) and B(7), which are *trans* to Ru(1)–Cl(1) and Ru(1)–P(1). Conversely, the two boron-bound phosphine ligands will also affect the symmetry of bonding electron density about the metal. In this regard it is of interest that, although the borane-to-metal bonding in the unconstrained iridium species $[(PMe_3)_2HIrB_9H_9]$ appears to be highly fluxional,[3,9,10] the ruthenaborane reported here exhibits no fluxionality in the metal-to-borane bonding mode at ambient temperatures. Presumably in the ruthenaborane the *exo*-polyhedral substituents produce strong electron-localizing effects which inhibit the dynamic metal-to-borane bonding flexibility required for facile fluxionality.

As mentioned above, the cage ^{11}B and proton n.m.r. parameters are consistent with the *isocloso*-metallaborane cluster type, and reference to the crystallographically established structure now retrospectively removes any ambiguity in the interpretation of the other n.m.r. properties. In particular, the hydride proton resonance at $\delta(^1H)$ −7.83 p.p.m. exhibits a weak *trans* coupling $^2J(^{11}B\text{–Ru–}^1H)$ to $^{11}B(3)$, and also a transoid coupling $^3J(^{31}P\text{–B–Ru–}^1H)$ to the cluster-bound phosphine on B(3) as well as the expected $^2J(^{31}P\text{–Ru–}^1H)$ (*cis*) to the metal-bound phosphine. The longer-range coupling $^3J(^{31}P\text{–B–Ru–}^1H)$ (transoid) through the metallaborane cage might at one time have been thought to be unusual, but now has increasing precedent in metallaborane chemistry,[8,11–14] and is in fact within a range reasonable for a vicinal phosphorus–proton coupling *via* a σ framework.

Table 2. Selected phosphorus-31[a] and proton[b] n.m.r. data for *isocloso*-$[(PPh_3)HClRuB_9H_7(PPh_3)_2]$

$\delta(^{31}P)[P(1)]$/p.p.m.	+49.0
$\delta(^{31}P)[P(2)]$/p.p.m.	*ca.* +10 [c]
$\delta(^{31}P)[P(3)]$/p.p.m.	*ca.* +10 [c]
$^3J[^{31}P(3)\text{–B–Ru–}^{31}P(1)]$(transoid)/Hz	12
$^1J[^{31}P(2)\text{–}^{11}B(3)]$/Hz	*ca.* 110
$^1J[^{31}P(3)\text{–}^{11}B(5)]$/Hz	*ca.* 120
$\delta(^1H)[Ru(1)]$/p.p.m.	−7.83
$^3J[^{31}P(2)\text{–B(3)–Ru–}^1H]$/Hz $^3J[^{31}P(3)\text{–B(5)–Ru–}^1H]$/Hz $^2J[^{31}P(1)\text{–Ru–}^1H]$/Hz	*ca.* 15, *ca.* 20, *ca.* 25

[a] In $CDCl_3$ solution at −50 °C. [b] In $CDCl_3$ solution at +21 °C. [c] Broad overlapping resonances.

It is of interest that the ^{11}B resonances (and, in view of the general parallel between the nuclear shieldings of boron and

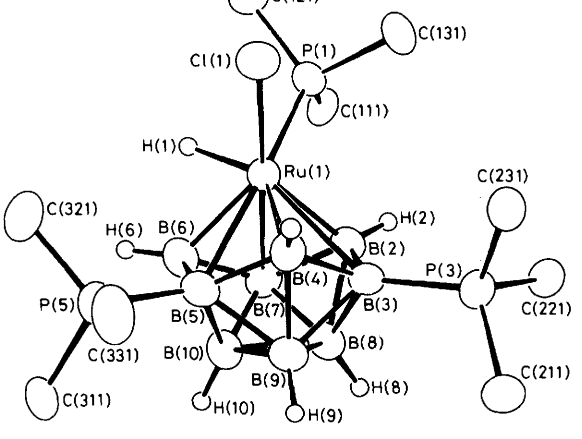


Figure 2. Molecular structure of $[1,1,1\text{-}(PPh_3)HCl\text{-}1\text{-}RuB_9H_7\text{-}3,5\text{-}(PPh_3)_2]$ as determined by *X*-ray diffraction analysis of a single crystal of its CH_2Cl_2 trisolvate. In this projection H(7) is obscured behind B(7) and only the *ipso*-C atoms of the nine phenyl rings are shown

Table 3. Interatomic distances (pm) for *isocloso*-$[(PPh_3)HClRuB_9H_7(PPh_3)_2]$

(*i*) About the ruthenium atom

Ru(1)–Cl(1)	245.6(4)	Ru(1)–H(1)	153(3)
Ru(1)–P(1)	235.4(4)		
Ru(1)–B(2)	209.1(9)	Ru(1)–B(3)	251.7(9)
Ru(1)–B(4)	219.3(9)	Ru(1)–B(5)	240.2(10)
Ru(1)–B(6)	209.0(11)	Ru(1)–B(7)	235.3(9)

(*ii*) Boron–boron

B(2)–B(3)	174.2(13)	B(5)–B(6)	177.1(14)
B(2)–B(7)	174.8(14)	B(6)–B(7)	173.4(14)
B(2)–B(8)	177.4(13)	B(6)–B(10)	177.5(10)
B(3)–B(4)	171.5(13)	B(4)–B(5)	171.0(14)
B(3)–B(8)	179.7(13)	B(5)–B(10)	180.2(13)
B(3)–B(9)	180.8(13)	B(5)–B(9)	179.5(12)
B(4)–B(9)	178.9(11)		
B(8)–B(9)	178.1(14)	B(9)–B(10)	179.6(14)
B(8)–B(10)	179.1(14)		

(*iii*) Boron–hydrogen

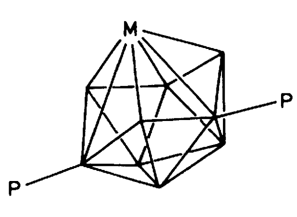
B(2)–H(2)	101(4)	B(6)–H(6)	109(3)
B(4)–H(4)	115(3)	B(7)–H(7)	112(3)
B(8)–H(8)	106(3)	B(10)–H(10)	106(2)
B(9)–H(9)	110(2)		

(*iv*) Phosphorus–carbon and phosphorus–boron

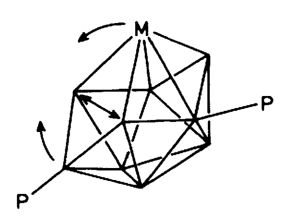
		P(2)–B(3)	189.5(10)	P(2)–B(5)	191.6(11)
P(1)–C(111)	182.8(6)	P(2)–C(211)	181.4(5)	P(3)–C(311)	179.9(6)
P(1)–C(121)	184.2(5)	P(2)–C(221)	179.7(6)	P(3)–C(321)	180.3(5)
P(1)–C(131)	183.3(7)	P(2)–C(231)	179.2(6)	P(3)–C(331)	179.4(7)

Table 4. Selected angles (°) between interatomic vectors for *isocloso*-$[(PPh_3)HClRuB_9H_7(PPh_3)_2]$

(*i*) About the ruthenium atom			
P(1)–Ru(1)–Cl(1)	82.3(2)	P(1)–Ru(1)–H(1)	80.1(12)
P(1)–Ru(1)–B(2)	85.5(3)	P(1)–Ru(1)–B(3)	116.2(3)
P(1)–Ru(1)–B(4)	145.4(2)	P(1)–Ru(1)–B(5)	170.7(2)
P(1)–Ru(1)–B(6)	125.0(3)	P(1)–Ru(1)–B(7)	102.7(3)
Cl(1)–Ru(1)–H(1)	91.9(10)		
Cl(1)–Ru(1)–B(2)	136.0(2)	Cl(1)–Ru(1)–B(3)	108.0(3)
Cl(1)–Ru(1)–B(4)	82.4(3)	Cl(1)–Ru(1)–B(5)	104.4(3)
Cl(1)–Ru(1)–B(6)	131.2(2)	Cl(1)–Ru(1)–B(7)	175.0(2)
H(1)–Ru(1)–B(2)	127.2(12)	H(1)–Ru(1)–B(3)	155.3(8)
H(1)–Ru(1)–B(4)	131.3(13)	H(1)–Ru(1)–B(5)	93.1(12)
H(1)–Ru(1)–B(6)	60.2(9)	H(1)–Ru(1)–B(7)	88.6(10)
B(2)–Ru(1)–B(3)	43.2(3)	B(5)–Ru(1)–B(6)	45.8(3)
B(2)–Ru(1)–B(4)	84.3(4)	B(4)–Ru(1)–B(6)	88.0(4)
B(2)–Ru(1)–B(5)	93.8(4)	B(3)–Ru(1)–B(6)	95.3(4)
B(2)–Ru(1)–B(6)	89.8(4)		
B(2)–Ru(1)–B(7)	45.8(3)	B(6)–Ru(1)–B(7)	45.4(3)
B(3)–Ru(1)–B(4)	42.0(3)	B(4)–Ru(1)–B(5)	43.4(3)
B(3)–Ru(1)–B(5)	68.4(4)		
B(3)–Ru(1)–B(7)	70.3(4)	B(5)–Ru(1)–B(7)	70.7(4)
B(4)–Ru(1)–B(7)	93.5(4)		
(*ii*) Boron–boron–boron			
B(3)–B(2)–B(7)	107.3(7)	B(5)–B(6)–B(7)	103.6(6)
B(2)–B(3)–B(4)	112.5(6)	B(4)–B(5)–B(6)	117.5(7)
B(3)–B(4)–B(5)	107.7(7)	B(6)–B(7)–B(2)	116.0(7)
(*iii*) Phosphorus–boron–boron			
P(2)–B(3)–B(2)	120.5(6)	P(3)–B(5)–B(6)	113.5(6)
P(2)–B(3)–B(4)	118.3(6)	P(3)–B(5)–B(4)	118.3(6)
P(2)–B(3)–B(8)	122.8(5)	P(3)–B(5)–B(10)	123.9(6)
P(2)–B(3)–B(8)	122.8(5)	P(3)–B(5)–B(10)	123.9(6)
P(2)–B(3)–B(9)	121.4(5)	P(3)–B(5)–B(9)	125.4(6)



(I)



(II)

directly bound *exo*-hydrogens,[15,16] the corresponding proton resonances) for the *isocloso*-ruthenium and -iridium species are distinctively grouped into three groups of three, with one of these groups at rather low field (Figure 1). This behaviour appears to be diagnostic of this *isocloso* 10-vertex metallaborane structural type,[14] which has no parallel in binary boron hydride chemistry. On the basis of the established substituent positions on the ruthenaborane and the iridaborane these three bands may be assigned (progressing from lower to higher shielding) to the (2,4,6), (8,9,10), and (3,5,7) positions respectively in the idealized C_{3v} stack (numbering as in Figure 2). This assignment of the extreme low-field resonances differs from that claimed[17] for the isohedral *'hypercloso'* ruthenacarboranes such as [1,1-$(PPh_3)_2$-1,2,4-$RuC_2B_7H_9$] in which they are ascribed to positions equivalent to B(3) in the ruthenaborane reported here. It may also be noted that the the boron atoms B(2)B(4)B(6) with extreme low-field shifts have the low cluster connectivity of four. In both the ruthenaborane and the iridaborane there is a reasonable correlation between the $\delta(^{11}B)$ *versus* $\delta(^{1}H)$ plot and a line of slope $\delta(^{11}B):\delta(^{1}H)$ of *ca.* 11:1, similar to that of *ca.* 12:1 observed for the smaller five- and six-vertex ruthenaboranes as reported elsewhere.[2]

The *isocloso* 10-vertex geometry (**I**) is related to that of the (hypothetical) straightforward *closo* species (**II**) by a diamond–square–diamond process involving the Ru(1)B(4)B(5)B(6) face-pair (numbering as in Figure 2).[6,9] This hypothetical species (**II**) would have the familiar bicapped square-antiprismatic geometry with the metal centre in an 18-electron d^6 ruthenium(II) configuration with a six-fold octahedral disposition of bonding orbitals. If this were the case, however, the neutral $RuH(PPh_3)Cl$ centre would contribute three orbitals, but no electrons, to the cluster bonding, and the cluster would thereby be deficient by two electrons for the $(2n + 2)$-electron Wade's-rule *closo* count.

The origins of the observed alternative *'isocloso'* geometry have at present two interpretations.[6,18] The first is that in which an unquantified 'distortion' of the otherwise expected bicapped square-antiprismatic structure is postulated in order to accommodate the two-electron deficiency.[17–19] The second, which we currently favour,[4,6,9,10] is that in which the electron deficiency is relieved by the utilization of two extra electrons from the metal valence-shell core. The $RuH(PPh_3)Cl$ centre thereby has a four-orbital two-electron involvement with the cluster within the constraints of an overall 18-electron ruthenium(IV) d^4 seven-orbital bonding configuration, and the resulting four-orbital metal involvement with the cluster generates the *isocloso* geometry.[6,9] In this latter interpretation, a reasonable view of the metal-to-borane bonding would in the first instance then involve three tangentially directed metal bonding orbitals directed along approximately 'octahedral' metal bonding axes, together with one centrally directed orbital along a 'capped octahedral' metal bonding axis.[9,10] There is now precedent for such overall seven(and eight)-orbital transition-metal bonding configurations in metallaborane chemistry,[20] *e.g.* in *nido*-MB_9 clusters (where M = Re;[14] W, Os, or Ir;[21] Mo[22]), in [(CO)-$(PPh_3)_2HIrB_3H_7$],[23] and in *nido*-$[(PMe_2Ph)_3H_2ReB_8H_{11}]$,[24] but so far these have retained a three-orbital metal involvement with the cluster and have four (or five) *exo*-polyhedral metal ligands.

Similar metal-to-borane bonding considerations, although perhaps with a greater geometrical ambiguity, apply to the second interesting polyhedral ruthenaborane that we report in this paper. This is a bright orange-red air-stable species $[(PPh_3)_2RuB_{10}H_8(OEt)_2]$ which is obtained in 80% yield from the reaction between $[RuCl_2(PPh_3)_3]$ and the *closo*-$[B_{10}H_{10}]^{2-}$ anion in ethanolic solution according to the idealized equation (2). The initial stages of the reaction are no

$$[RuCl_2(PPh_3)_3] + [B_{10}H_{10}]^{2-} + 2EtOH \longrightarrow [(PPh_3)_2RuB_{10}H_8(OEt)_2] + 2\,H_2 + PPh_3 + 2\,Cl^- \quad (2)$$

doubt related to the initial stages of reaction of species such as $[PtCl_2(PR_3)_2]$[25–28] or $[Ir(CO)Cl(PPh_3)_2]$[13,28–30] with *closo*-$[B_{10}H_{10}]^{2-}$ and alcohols under similar conditions, and presumably therefore involve initial formation of Ru–H–B linkages to the borane anion,[1] as observed, for example, in species such as $[(PPh_3)_2ClRuClRu(PPh_3)B_{10}H_8(OEt)_2]$[5] and $[Ru(B_{12}H_{12})(PPh_3)_3]$.[31] The ultimate reaction products are, however, quite different for the various metals.

The product [1,1-$(PPh_3)_2$-1-$RuB_{10}H_8$-2,5-$(OEt)_2$] was again characterized by single-crystal *X*-ray diffraction analysis, with all atoms located. The molecular structure, with certain organyl group atoms omitted for clarity, is shown in Figure 3. Selected interatomic distances and angles are in Tables 5 and 6 respectively.

The 11-vertex cluster structure (octadecahedron) is seen to be that of a closed deltahedron corresponding to that reasonably supposed[32] for *closo*-$[B_{11}H_{11}]^{2-}$ {and established[33] for its

Table 5. Interatomic distances (pm) for *closo*-$[(PPh_3)_2RuB_{10}H_8(OEt)_2]$

(*i*) To the ruthenium atom			
Ru(1)–P(1)	253.2(4)	Ru(1)–P(2)	251.2(4)
Ru(1)–B(2)	205.3(8)	Ru(1)–B(5)	204.1(8)
Ru(1)–B(3)	235.7(8)	Ru(1)–B(6)	235.0(8)
Ru(1)–B(4)	240.2(8)	Ru(1)–B(7)	238.3(8)
(*ii*) Boron–boron			
B(2)–B(3)	184.6(10)	B(2)–B(7)	179.7(11)
B(2)–B(8)	175.7(10)	B(5)–B(10)	173.4(11)
B(3)–B(4)	168.4(10)	B(6)–B(7)	169.8(11)
B(3)–B(8)	184.7(11)	B(7)–B(8)	182.3(12)
B(3)–B(9)	177.9(10)	B(7)–B(11)	177.4(10)
B(4)–B(5)	175.1(10)	B(5)–B(6)	177.9(10)
B(4)–B(9)	177.9(11)	B(6)–B(11)	180.7(11)
B(4)–B(10)	181.5(11)	B(6)–B(10)	183.5(11)
B(8)–B(9)	175.8(11)	B(8)–B(11)	177.0(12)
B(9)–B(10)	176.4(12)	B(10)–B(11)	175.7(12)
B(9)–B(11)	176.8(12)		
(*iii*) Boron–hydrogen			
B(3)–H(3)	122(3)	B(7)–H(7)	118(2)
B(4)–H(4)	110(2)	B(6)–H(6)	105(3)
B(8)–H(8)	112(3)	B(10)–H(10)	100(2)
B(9)–H(9)	114(3)	B(11)–H(11)	122(2)
(*iv*) Others			
B(2)–O(2)	136.1(8)	B(5)–O(5)	136.8(8)
P(1)–C(111)	184.1(5)	P(2)–C(211)	185.4(4)
P(1)–C(121)	185.6(4)	P(2)–C(221)	185.4(4)
P(1)–C(131)	185.2(5)	P(2)–C(231)	184.2(5)

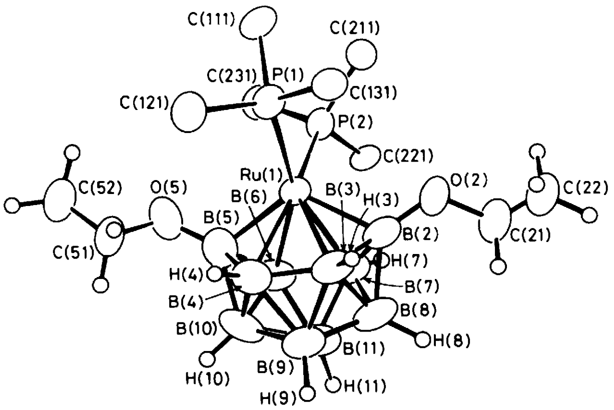


Figure 3. Molecular structure of $[1,1\text{-}(PPh_3)_2\text{-}1\text{-}RuB_{10}H_8\text{-}2,5\text{-}(OEt)_2]$ with the six phenyl rings (except their *ipso*-C atoms) omitted for clarity. In this projection H(6) is obscured behind the cluster and H(211) is behind C(21)

Figure 6. Selected angles (°) between interatomic vectors for *closo*-$[(PPh_3)_2RuB_{10}H_8(OEt)_2]$

(*i*) About the ruthenium atom			
P(1)–Ru(1)–P(2)	97.0(0.5)		
P(1)–Ru(1)–B(2)	112.3(3)	P(2)–Ru(1)–B(2)	99.5(3)
P(1)–Ru(1)–B(3)	94.6(2)	P(2)–Ru(1)–B(3)	148.3(1)
P(1)–Ru(1)–B(4)	93.9(2)	P(2)–Ru(1)–B(4)	163.8(1)
P(1)–Ru(1)–B(5)	108.5(3)	P(2)–Ru(1)–B(5)	119.0(3)
P(1)–Ru(1)–B(6)	155.5(2)	P(2)–Ru(1)–B(6)	94.7(3)
P(1)–Ru(1)–B(7)	159.4(2)	P(2)–Ru(1)–B(7)	88.2(2)
B(2)–Ru(1)–B(3)	48.9(2)	B(2)–Ru(1)–B(7)	47.1(2)
B(2)–Ru(1)–B(4)	87.4(3)	B(2)–Ru(1)–B(6)	86.7(3)
B(2)–Ru(1)–B(5)	118.4(3)		
B(3)–Ru(1)–B(4)	41.5(2)	B(6)–Ru(1)–B(7)	42.0(2)
B(3)–Ru(1)–B(5)	84.5(3)	B(5)–Ru(1)–B(7)	85.9(3)
B(3)–Ru(1)–B(6)	86.5(3)	B(4)–Ru(1)–B(7)	85.8(3)
B(3)–Ru(1)–B(7)	71.7(3)	B(4)–Ru(1)–B(6)	70.9(3)
B(4)–Ru(1)–B(5)	45.5(2)	B(5)–Ru(1)–B(6)	47.1(2)
(*ii*) Boron–boron–boron			
B(3)–B(2)–B(7)	99.2(5)	B(4)–B(5)–B(6)	102.6(5)
B(2)–B(3)–B(4)	121.8(5)	B(2)–B(7)–B(6)	120.2(5)
B(3)–B(4)–B(5)	119.3(5)	B(5)–B(6)–B(7)	120.9(5)
(*iii*) Others			
O(2)–B(2)–Ru(1)	120.6(5)	O(5)–B(5)–Ru(1)	115.6(5)
O(2)–B(2)–B(3)	130.1(5)	O(5)–B(5)–B(4)	128.8(6)
O(2)–B(2)–B(7)	129.9(6)	O(5)–B(5)–B(6)	128.6(6)
O(2)–B(2)–B(8)	129.7(6)	O(5)–B(5)–B(110)	132.5(5)
B(2)–O(2)–C(21)	121.1(6)	B(5)–O(5)–C(21)	118.8(6)
O(2)–C(21)–C(22)	114.2(8)	O(5)–C(21)–C(22)	110.7(7)

Table 7. Selected n.m.r. data for $[(PPh_3)_2RuB_{10}H_8(OEt)_2]$ in CD_2Cl_2 solution at +21 °C[a]

Assignment	$\delta(^{11}B)$/p.p.m.[b]	$\delta(^1H)$/p.p.m.[c]
2,5	+89.9 (2 B)	*d*
	+7.4 (6 B)[e]	+3.37 (2 H), +1.77 (4 H)
	+3.0 (2 B)	+1.73 (2 H)

[a] $\delta(^{31}P)$ +19.2 p.p.m. to high frequency (low field) of 85% H_3PO_4; $CDCl_3$ solution at −50 °C. [b] ±0.5 p.p.m. to high frequency (low field) of $BF_3(OEt_2)$–$CDCl_3$. [c] ±0.05 p.p.m. to high frequency (low field) of $SiMe_4$–$CDCl_3$; ^1H resonances related to ^{11}B resonances of directly-bound atoms by selective $^1H\text{-}\{^{11}B\}$ spectroscopy. [d] Ethoxy substituted positions B(2) and B(5); OEt group has $\delta(^1H)$ +1.74 (triplet) and +4.58 p.p.m. (quartet), $^3J(^1H\text{-}^1H)$ *ca.* 7 Hz ($CDCl_3$ solution). [e] Two accidentally coincident resonances, 2 B + 4 B.

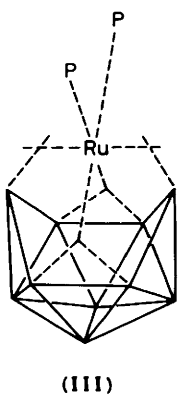
close relations such as $[B_{11}H_{10}(SMe_2)]^-$}. In gross geometric terms it is derived from the complete capping of the characteristic C_{2v} open 10-vertex *nido*-decaboranyl cluster shape with the metal atom to produce an MB_{10} 1:2:4:2:2 stack also of idealized C_{2v} symmetry (as such the effective borane ligand exhibits an η^6 boat co-ordination to the metal centre, as compared to the η^6 chair in the 10-vertex species discussed above). It is however evident that a straightforward *nido* character for the 10-boron subcluster does not obtain in the metallaborane; for example, the diagnostically long[34] B(5)–B(10) and B(7)–B(8) distances of *ca.* 200 pm of *nido*-decaborane are not apparent [their corresponding distances B(3)–B(4) and B(6)–B(7) in the metallaborane average at *ca.* 169 pm and are if anything *shorter* than average]. Moreover the ^{11}B nuclear shielding properties (Table 7) are dramatically different from those[16] of *nido*-decaborane, indicating widely different cluster electronic structures. In particular the resonances corresponding to B(2) and B(5) (of cluster connectivity four) are at extremely low field, with the other resonances grouped closely together at intermediate field. Preliminary results on analogous iron,[35] osmium,[36] and rhodium[37] compounds, and on $[(PPh_3)_2IrHB_{10}H_8(OEt)_2]$,[38] show that this n.m.r. shielding behaviour is probably diagnostic of this metallaborane structural type.[16]

The distances from the metal atom to these two low-connected boron atoms B(2) and B(5) at *ca.* 204 pm are some 30 pm shorter than those to the other atoms (of higher connectivity) in the η^6 boat. Previously reported ruthenium-to-boron distances in polyhedral metallaboranes are in the range 226—231 pm,[2] and this, together with the data reported in Table 2 above for the 10-vertex *isocloso*-ruthenaborane suggest that these distances [Ru(1)–B(2) and Ru(1)–B(5)] may be quite short for a polyhedral species, perhaps suggesting strong contributions from localized two-centre bonding along these two vectors.

The two metal-bound *exo*-polyhedral phosphine ligands are approximately digonally disposed about the formal C_2 cluster axis, with the ruthenium–phosphorus vectors approximately *trans* to the mid-points of B(3)–B(4) and B(6)–B(7), so that the 13-atom P_2RuB_{10} unit also approximates to C_{2v} symmetry. Interestingly, the ruthenium–phosphorus bond lengths at *ca.* 252 pm are some 15—20 pm longer than those found for the other structurally characterized ruthenaboranes (ref. 2 and Table 3) which also have PPh_3 ligands. This perhaps reflects a strong *trans* influence of the metal-to-borane bonding involving B(3)B(4) and B(6)B(7), although it should be emphasized that comparison data[1] are limited.

As mentioned above, the metallaborane cluster bonding is at present open to two interpretations.[6,18] In the first of these, if the 16-electron $Ru(PPh_3)_2$ metal centre has a two-electron three-orbital 'conical' contribution to the cluster electronic structure, like the unique BH unit in $[B_{11}H_{11}]^{2-}$, then this implies an overall 2*n* cluster electron count, *i.e.* two electrons deficient for a straightforward *closo* electron configuration, and the cluster is therefore a 'PSEPT-deficient' 2*n*-electron *closo* cluster. In this context it should be noted that the C_{2v} 11-vertex *closo* geometry may well be compatible with electron counts of 2*n* and (2*n* + 4) as well as (2*n* + 2)[39] (though appropriate detailed molecular orbital treatments have not in fact been done for the 11-vertex cluster itself). An additional factor which could be invoked to support this interpretation is that the alkoxy substituents on B(2) and B(5) may play some part either in relieving this two-electron deficiency or in perturbing the energy levels to ensure 2*n*-electron compatibility. We also note that the 11-vertex dihydroxydicarbaborane $Me_2C_2B_9H_6(OH)_2Br$,[40] which is formally *closo* with a (2*n* + 2) electron count, exhibits considerable distortion towards *nido* {although this would seem to counter the suggestion that the 11-vertex *closo* cluster might readily accommodate electron counts other than (2*n* + 2) without appreciable distortion; furthermore, recent results in iron[35] and rhodium[41] chemistry indicate that this structural type is stable *without* electronegative substituents, for example in $[(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,6)FeB_{10}H_{10}]$ and $[(\eta^5\text{-}C_5Me_5)RhB_{10}H_{10}]$}.

The second interpretation,[4] again which we currently favour,[6] is that the RuB_{10} cluster does in fact have a formal (2*n* + 2)-electron count, and that this is achieved by the metal centre contributing two additional electrons to the cluster structure, thus implying a four-orbital four-electron contribution from the neutral $Ru(PPh_3)_2$ moiety within an overall 16-electron six-bonding orbital ruthenium(IV) d^4 configuration. In this model the disposition of the two *exo*-polyhedral phosphine ligands on the metal, together with the short distances to B(2) and B(5), suggest an essentially octahedral distribution of the six metal bonding orbitals, with four two-electron two-centre bonds to B(2), B(5), P(1), and P(2), together with multicentre bonding involving B(3)B(4) and B(6)B(7) [schematic structure (III)].



(III)

In these terms the 11-vertex species is perceived to be an 11-vertex analogue of the 10-vertex *isocloso*-species $[(PPh_3)HClRuB_9H_7(PPh_3)_2]$ (discussed above) and also of the 10-vertex iridaborane analogues described elsewhere.[3,6,9,10] The geometry of these latter 10-vertex species can be regarded as derived by the complete capping of an open *arachno* geometry by a metal atom which contributes four orbitals to the cluster bonding scheme. A similar interpretation can also be offered for the 11-vertex compound reported here, since the gross geometry of the 10-boron subcluster is also that of an *arachno*- as well as a *nido*-decaboranyl species;[4] furthermore it seems that the *isocloso* nine-vertex species such as $[(PMe_3)_2HIrB_8H_7Cl]$[9,42,43] also fall into this category, as they similarly derive from the complete capping of the eight-vertex *arachno* geometry in an 'inverted boat' η^6 borane-to-metal ligation.

In general, therefore, a new family of *isocloso* structures may be categorized as being generated by the capping of an *arachno* geometry (although not of formal *arachno* electronic structure) with a metal centre which contributes four orbitals to the cluster bonding scheme.[4,6] Straightforward *closo* geometries are generally derived by the capping of a *nido* geometry by a three-orbital contributor. This approach to the rationalization of the *isocloso* geometries has some similarities to the treatment used by Nishimura,[44] but as far as we can tell[18] differs somewhat from the '*hypercloso*' concepts put forward to account for these types of geometry in 10-vertex metalladicarbaborane chemistry.[17–19]

Experimental

General.—The starting compounds $[RuCl_2(PPh_3)_3]$,[45] $[NEt_4][B_9H_{14}]$,[46,47] and $[NEt_3H]_2[B_{10}H_{10}]$[48] were prepared by previously published methods. Reactions were carried out under dry nitrogen in oxygen-free solvents, but subsequent manipulations and separations were generally carried out in air. Chromatography was by preparative thin-layer (t.l.c.) using Kieselgel GF254 (Fluka) on plates of dimensions 20 cm × 20 cm × *ca.* 1 mm, made in the laboratory as required.

100-MHz Proton, 40-MHz ^{31}P, and 32-MHz ^{11}B n.m.r. spectra were measured on a JEOL FX-100 instrument (Leeds) and 115- or 128-MHz ^{11}B on Bruker WH instruments (S.E.R.C. services, Universities of Edinburgh and Sheffield). Selective $^1H\text{-}\{^{11}B\}$ double-resonance spectroscopy was performed as described previously;[49,50] irradiation levels $\gamma B_2(^{11}B)/2\pi$, estimated by off-resonance residual splittings,[51] being of the order of 700 Hz for these experiments. Lower temperatures were used for the ^{31}P measurements to maximise the effects of 'thermal decoupling' of the couplings $^2J(^{11}B\text{–}Ru\text{–}^{31}P)$.[52] Proton, ^{31}P, and ^{11}B chemical shifts are quoted to low field (high frequency) of Ξ 100 ($SiMe_4$), Ξ 40.480 730 (85% H_3PO_4), and Ξ 32.083 971 MHz [$BF_3(OEt_2)$ in $CDCl_3$][16] respectively.

Preparation of $[(PPh_3)HClRuB_9H_7(PPh_3)_2]$.—$[NEt_4][B_9H_{14}]$ (0.48 g, 2 mmol) and $[RuCl_2(PPh_3)_3]$ (0.46 g, 0.5 mmol) were stirred together in CH_2Cl_2 (20 cm^3) for 4 d at room temperature. The resulting dark brown solution was reduced in volume and chromatographed twice (t.l.c.) using CH_2Cl_2–light petroleum (b.p. 60—80 °C) (4:1) as the eluant to give an orange compound at R_f 0.3, identified as $[(PPh_3)HClRuB_9H_7(PPh_3)_2]$ as described in the text. Smaller quantities of what appear from n.m.r. spectroscopy to be additional novel species (which we hope to report on later) were present at R_f 0.1 and 0.5, and colourless $BH_3(PPh_3)$ and $B_9H_{13}(PPh_3)$ were also identified.

The title compound was slightly air-sensitive, particularly in solution, and was recrystallized from CH_2Cl_2 under N_2 to give orange crystals (205 mg, 39% yield). N.m.r. studies were carried out in sealed tubes, and the results are presented in Tables 1 and 2 and Figure 1.

Preparation of $[(PPh_3)_2RuB_{10}H_8(OEt)_2]$.—$[NEt_3H]_2[B_{10}H_{10}]$ (0.13 g, 0.4 mmol) and $[RuCl_2(PPh_3)_3]$ (0.38 g, 0.4 mmol) were dissolved in EtOH (*ca.* 70 cm^3) and heated under reflux for 3 h under N_2. The bright red solution formed was reduced in volume and chromatographed using CH_2Cl_2–light petroleum (b.p. 60—80 °C) (4 : 1) as the eluting medium to give a bright orange compound at R_f 0.8, identified as $[(PPh_3)_2RuB_{10}H_8(OEt)_2]$ as described in the text [Found: C, 56.1; H, 5.85; B, 13.1; P, 7.7. Calc. for $C_{40}H_{48}B_{10}O_2P_2Ru$: C, 57.8; H, 5.8; B, 13.0; P, 7.5%]. The product was recrystallized from CH_2Cl_2–n-pentane to give deep red crystals (268 mg, 80% yield).

Traces of other products were formed in the reaction but have not yet been unambiguously identified: one is probably the diruthenium species $[(PPh_3)_2ClRuClRu(PPh_3)B_{10}H_8(OEt)_2]$ described in a preliminary note elsewhere.[5]

X-*Ray Studies*.—Intensity data for both compounds were collected on a Syntex $P2_1$ diffractometer operating in the ω–2θ scan mode, using graphite-monochromatised Mo-K_α radiation (λ = 71.069 pm), and following a procedure described elsewhere in detail.[53] Dimunition of an intensity control reflection during data collection indicated that the compound $[(PPh_3)HClRuB_9H_7(PPh_3)_2]$ underwent slight decay and so the data set was corrected for this. Both structures were solved by the Patterson method, developed by Fourier difference, and refined by blocked full-matrix least squares using the SHELX program system.[54] For $[(PPh_3)HClRuB_9H_7(PPh_3)_2]$ three highly disordered CH_2Cl_2 molecules were located and these were treated in terms of interlocking CCl_2 triangles with a common overall thermal parameter which summed up to an occupancy of one for each CH_2Cl_2 molecule. For both compounds all non-hydrogen atoms (except the solvent molecules in the RuB_9 compound) were refined with anisotropic thermal parameters, phenyl groups being included in the refinement as rigid bodies with regular hexagonal geometry (C–C = 139.5 pm). For the RuB_9 compound the phenyl hydrogen atoms were included in calculated positions (C–H = 108 pm) and were assigned an

Table 8. Atom co-ordinates (× 10^4) for $[(PPh_3)HClRuB_9H_7(PPh_3)_2]\cdot3CH_2Cl_2$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Ru(1)	1 291(0.5)	2 477(0.5)	2 161(0.5)
P(1)	2 598(1)	2 050(1)	3 628(2)
P(2)	−1 870(1)	1 496(1)	1 252(2)
P(3)	103(2)	3 678(1)	344(2)
Cl(1)	1 379(2)	3 077(1)	4 242(2)
B(2)	538(6)	1 645(3)	1 053(6)
B(3)	−699(6)	1 913(3)	944(6)
B(4)	−455(6)	2 643(3)	1 433(7)
B(5)	161(6)	2 905(3)	475(7)
B(6)	1 446(4)	2 689(4)	490(7)
B(7)	1 105(6)	1 952(4)	70(7)
B(8)	−403(6)	1 704(3)	−519(7)
B(9)	−1 021(6)	2 321(4)	−306(7)
B(10)	149(6)	2 342(3)	−839(7)
C(111)	3 206(3)	1 492(2)	2 904(3)
C(112)	3 379(3)	990(2)	3 326(3)
C(113)	3 910(3)	604(2)	2 762(3)
C(114)	4 267(3)	720(2)	1 774(3)
C(115)	4 093(3)	1 222(2)	1 351(3)
C(116)	3 563(3)	1 607(2)	1 916(3)
C(121)	3 934(3)	2 511(2)	4 829(3)
C(122)	4 713(3)	2 267(2)	5 716(3)
C(123)	5 769(3)	2 590(2)	6 582(3)
C(124)	6 046(3)	3 157(2)	6 563(3)
C(125)	5 268(3)	3 402(2)	5 676(3)
C(126)	4 211(3)	3 078(2)	4 810(3)
C(131)	2 031(3)	1 754(2)	4 713(3)
C(132)	2 257(3)	2 078(2)	5 981(3)
C(133)	1 756(3)	1 875(2)	6 777(3)
C(134)	1 029(3)	1 348(2)	6 304(3)
C(135)	804(3)	1 023(2)	5 036(3)
C(136)	1 305(3)	1 227(2)	4 240(3)
C(211)	−3 275(3)	1 449(2)	−2(3)
C(212)	−3 930(3)	922(2)	−777(3)
C(213)	−5 020(3)	892(2)	−1 714(3)
C(214)	−5 455(3)	1 390(2)	−1 877(3)
C(215)	−4 801(3)	1 917(2)	−1 102(3)
C(216)	−3 711(3)	1 947(2)	−165(3)
C(221)	−1 705(3)	772(1)	1 289(4)
C(222)	−1 919(3)	524(1)	2 230(4)
C(223)	−1 832(3)	−46(1)	2 210(4)
C(224)	−1 531(3)	−367(1)	1 248(4)
C(225)	−1 317(3)	−118(1)	307(4)
C(226)	−1 404(3)	451(1)	327(4)
C(231)	−1 965(3)	1 818(2)	2 785(3)
C(232)	−957(3)	2 053(2)	3 882(3)
C(233)	−995(3)	2 281(2)	5 109(3)
C(234)	−2 041(3)	2 274(2)	5 239(3)
C(235)	−3 049(3)	2 038(2)	4 142(3)
C(236)	−3 011(3)	1 810(2)	2 915(3)
C(311)	−166(3)	3 779(2)	−1 295(3)
C(312)	498(3)	3 558(2)	−1 959(3)
C(313)	321(3)	3 636(2)	−3 223(3)
C(314)	−520(3)	3 935(2)	−3 822(3)
C(315)	−1 184(3)	4 155(2)	−3 158(3)
C(316)	−1 007(3)	4 077(2)	−1 894(3)
C(321)	1 419(3)	4 152(2)	1 418(4)
C(322)	1 876(3)	4 129(2)	2 746(4)
C(323)	2 908(3)	4 477(2)	3 605(4)
C(324)	3 483(3)	4 848(2)	3 136(4)
C(325)	3 025(3)	4 871(2)	1 809(4)
C(326)	1 994(3)	4 523(2)	950(4)
C(331)	−1 012(3)	3 946(2)	757(4)
C(332)	−826(3)	4 486(2)	1 576(4)
C(333)	−1 731(3)	4 697(2)	1 805(4)
C(334)	−2 822(3)	4 368(2)	1 215(4)
C(335)	−3 008(3)	3 828(2)	396(4)
C(336)	−2 103(3)	3 167(2)	167(4)
C(1S)	6 387(10)	6 271(6)	2 451(11)
Cl(1a)	6 419(7)	6 523(3)	1 217(7)
Cl(1b)	6 330(13)	6 166(9)	972(14)
Cl(1c)	6 399(15)	6 724(9)	1 272(16)
Cl(2a)	5 891(6)	5 578(3)	2 281(7)
Cl(2b)	5 819(13)	5 599(8)	1 469(14)
Cl(2c)	6 248(13)	5 537(9)	2 895(14)
C(2S)	7 628(10)	893(6)	5 812(11)
Cl(3a)	6 466(5)	973(3)	6 330(5)
Cl(3b)	6 240(10)	719(6)	5 239(12)
Cl(3c)	6 562(16)	403(11)	4 764(16)
Cl(4a)	8 095(6)	298(4)	5 753(7)
Cl(4b)	7 427(11)	167(6)	5 063(12)
Cl(4c)	8 551(11)	311(7)	6 361(12)
C(3S)	6 629(12)	3 374(7)	3 171(13)
Cl(5a)	5 353(8)	3 031(5)	2 034(8)
Cl(5b)	4 806(15)	3 380(10)	2 030(16)
Cl(5c)	4 937(13)	3 012(9)	1 597(14)
Cl(6a)	5 937(9)	4 140(5)	3 577(10)
Cl(6b)	6 586(9)	4 139(5)	3 750(10)
Cl(6c)	5 189(16)	3 887(12)	2 767(17)

Table 9. Atom co-ordinates (× 10^4) for [$(PPh_3)_2RuB_{10}H_8(OEt)_2$] with e.s.d.s in parentheses

Atom	x	y	z
Ru(1)	2 010(0.3)	1 332(0.1)	2 251(0.2)
P(1)	3 471(1)	1 739(1)	1 355(1)
P(2)	3 059(1)	645(1)	3 296(1)
B(2)	1 546(4)	1 880(3)	3 293(4)
B(3)	1 023(4)	2 176(3)	2 133(4)
B(4)	710(4)	1 753(3)	1 178(4)
B(5)	932(4)	1 014(3)	1 267(4)
B(6)	460(4)	843(3)	2 404(4)
B(7)	715(4)	1 271(3)	3 377(4)
B(8)	218(5)	1 990(3)	3 132(5)
B(9)	−277(5)	1 963(3)	1 927(5)
B(10)	−286(5)	1 255(3)	1 480(5)
B(11)	−467(4)	1 378(3)	2 704(5)
O(2)	2 237(3)	2 106(2)	3 962(2)
C(21)	1 923(6)	2 343(4)	4 820(5)
C(22)	2 540(8)	2 767(5)	5 190(7)
O(5)	1 289(3)	649(2)	596(2)
C(51)	972(6)	733(3)	−396(4)
C(52)	1 463(6)	329(2)	−993(5)
C(111)	4 688(2)	1 342(1)	1 471(2)
C(112)	5 599(2)	1 606(1)	1 806(2)
C(113)	6 509(2)	1 293(1)	1 874(2)
C(114)	6 508(2)	716(1)	1 607(2)
C(115)	5 597(2)	453(1)	1 272(2)
C(116)	4 687(2)	766(1)	1 204(2)
C(121)	3 218(2)	1 730(1)	30(2)
C(122)	3 704(2)	1 444(1)	−619(2)
C(123)	3 473(2)	1 503(1)	−1 608(2)
C(124)	2 755(2)	1 908(1)	−1 947(2)
C(125)	2 269(2)	2 255(1)	−1 298(2)
C(126)	2 500(2)	2 196(1)	−310(2)
C(131)	3 877(2)	2 482(1)	1 646(2)
C(132)	4 315(2)	2 822(1)	956(2)
C(133)	4 668(2)	3 371(1)	1 198(2)
C(134)	4 584(2)	3 580(1)	2 130(2)
C(135)	4 147(2)	3 240(1)	2 820(2)
C(136)	3 794(2)	2 691(1)	2 578(2)
C(211)	4 338(2)	912(1)	3 742(2)
C(212)	5 231(2)	588(1)	3 716(2)
C(213)	6 157(2)	807(1)	4 110(2)
C(214)	6 190(2)	1 380(1)	4 529(2)
C(215)	5 296(2)	1 647(1)	4 555(2)
C(216)	4 370(2)	1 455(1)	4 161(2)
C(221)	2 491(2)	421(1)	4 424(2)
C(222)	1 767(2)	−19(1)	4 370(2)
C(223)	1 269(2)	−176(1)	5 188(2)
C(224)	1 496(2)	106(1)	6 060(2)
C(225)	2 219(2)	546(1)	6 115(2)
C(226)	2 717(2)	703(1)	5 297(2)
C(231)	3 257(2)	−63(1)	2 754(2)
C(232)	2 886(2)	−173(1)	1 810(2)
C(233)	3 050(2)	−707(1)	1 395(2)
C(234)	3 585(2)	−1 131(1)	1 925(2)
C(235)	3 956(2)	−1 021(1)	2 869(2)
C(236)	3 792(2)	−487(1)	3 284(2)

overall isotropic thermal parameter for each group while all other hydrogens (including that terminally attached to the ruthenium atom) were located experimentally and refined with isotropic thermal parameters. For [$(PPh_3)_2RuB_{10}H_8(OEt)_2$] the phenyl and borane-cluster hydrogen atoms were treated in a similar fashion to those of the RuB_9 compound, while the hydrogen atoms on the ethoxy groups were included in calculated positions (as permitted by AFIX routines in the SHELX program) with an overall isotropic thermal parameter for each group. Both sets of data were weighted to give acceptable agreement analyses. Final atomic co-ordinates and their standard deviations are given in Tables 8 and 9.

Crystal Data for [$(PPh_3)HClRuB_9H_7(PPh_3)_2$].—$C_{54}H_{53}B_9ClP_3Ru\cdot3CH_2Cl_2$, M = 1 382.57, triclinic, a = 1 278.9(7), b = 2 428.2(12), c = 1 113.3(4) pm, α = 100.72(3), β = 111.03(3), γ = 95.62(4)°, U = 3.120 nm^3, Z = 2, space group $P\bar{1}$, D_c = 1.37 g cm^{-3}, μ = 3.50 cm^{-1}, F(000) = 1 055.

Data collection. Scans running from 1° below $K_{\alpha1}$ to 1° above $K_{\alpha2}$, scan speeds 2.0—29.3° min^{-1}, $4.0 < 2\theta < 45.0°$. 8 187 Unique data, 6 053 observed [$I > 2\sigma(I)$], T = 290 K.

Structure refinement. Number of parameters = 607, weighting factor g = 0.000 15, R = 0.0601, R' = 0.0556.

Crystal Data for [$(PPh_3)_2RuB_{10}H_8(OEt)_2$].—$C_{40}H_{48}B_{10}O_2P_2Ru$, M = 831.94, monoclinic, a = 1 309.0(4), b = 2 333.5(4), c = 1 390.2(4) pm, β = 93.63(2)°, U = 4.238 nm^3, Z = 4, space group $P2_1/n$ (= $P2_1/c$, no. 14), D_c = 1.304 g cm^{-3}, μ = 4.17 cm^{-1}, F(000) = 1 712.

Data collection. Parameters as above. 5 033 Unique data, 4 459 observed.

Structure refinement. Number of parameters = 470, weighting factor g = 0.000 25, R = 0.0396, R' = 0.0408.

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