Organoruthenaborane Chemistry. Part 7.* Preparation, Molecular Structure, and Nuclear Magnetic Resonance Properties of Eleven-vertex *closo*-Type Clusters: [2,4-Me$_2$-1-(pcym)-1,2,4-RuC$_2$B$_8$H$_8$], [2,3-Me$_2$-1-(pcym)-1,2,3-RuC$_2$B$_8$H$_8$], [1-(pcym)-1-RuB$_{10}$H$_{10}$]† and Some Related Species

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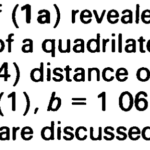
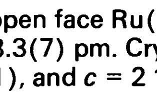
Reaction of [{Ru(pcym)Cl$_2$}$_2$] or [{Ru(hmb)Cl$_2$}$_2$] (pcym = *p*-cymene, 1-Me-4-Pr^{i}C$_6$H$_4$, hmb = hexamethylbenzene, C$_6$Me$_6$) with the *nido*-dicarbaborane 5,6-Me$_2$-5,6-C$_2$B$_8$H$_{10}$ in the presence of *N,N,N',N'*-tetramethylnaphthalene-1,8-diamine gave, respectively, the orange-yellow air-stable metalladicarbaborane [2,4-Me$_2$-1-(pcym)-1,2,4-RuC$_2$B$_8$H$_8$] (**1a**) or the corresponding yellow hmb derivative [2,4-Me$_2$-1-(hmb)-1,2,4-RuC$_2$B$_8$H$_8$] (**1b**), both of which were characterized by elemental analysis, mass spectrometry, and n.m.r. spectroscopy. A single-crystal *X*-ray diffraction analysis of (**1a**) revealed considerable distortion from idealized C_{2v} cluster symmetry due to the presence of a quadrilateral open face Ru(1)C(2)C(4)B(7) with an essentially non-bonding Ru(1)–C(4) distance of 268.3(7) pm. Crystals of (**1a**) are orthorhombic, space group $P2_12_12_1$, with a = 827.5(1), b = 1 066.0(1), and c = 2 154.4(2) pm, and Z = 4. Possible interpretations of the distortion are discussed. Thermal isomerization of (**1a**) at 400 °C gave a quantitative yield of the yellow symmetrical isomer [2,3-Me$_2$-1-(pcym)-*closo*-1,2,3-RuC$_2$B$_8$H$_8$] (**2a**) in which the 'distortion,' as revealed by a single-crystal *X*-ray study, manifests itself as a substantial lengthening of the distances from Ru(1) to each of the six directly bonded atoms in the η^6-dicarbaborane ligand. Crystals of (**2a**) are monoclinic, space group $P2_1/n$, with a = 879.7(1), b = 1 527.7(2), and c = 1 414.3(1) pm, β = 92.90(1)°, and Z = 4. N.m.r. data on (**2a**) are also reported. Further insight into the structure and bonding relations of eleven-vertex metalladicarbaborane clusters was obtained by the synthesis and characterization of the non-carbon-containing analogue [1-(pcym)-1-RuB$_{10}$H$_{10}$] (**3a**) and its (known) hmb congener [1-(hmb)-1-RuB$_{10}$H$_{10}$] (**3b**). Crystals of (**3a**) are orthorhombic, space group *Pbca*, with a = 787.8(1), b = 1 417.0(2), and c = 3 019.9(4) pm, and Z = 4. The {RuB$_{10}$} cluster is significantly more compact than its symmetrical dicarba analogue {RuC$_2$B$_8$}. Further compounds studied include the monomethylated dicarba derivatives [4-Me-1-(hmb)-1,2,4-RuC$_2$B$_8$H$_9$] (**4**), [3-Cl-4-Me-1-(hmb)-1,2,4-RuC$_2$B$_8$H$_8$] (**7**) and [2-Me-1-(hmb)-*closo*-1,2,3-RuC$_2$B$_8$H$_9$] (**8**).

In a preliminary note we reported that the ruthenadicarbaborane [2,4-Me$_2$-1-(pcym)-1,2,4-RuC$_2$B$_8$H$_8$] (**1a**)‡ exhibited an open cluster structure (I) rather than the previously expected closed structure (II).[1] Here we report more complete details of this work, together with (for comparison) the synthesis, structure, and n.m.r. properties of the symmetrical analogue [2,3-Me$_2$-1-(pcym)-1,2,3-RuC$_2$B$_8$H$_8$] [(**2a**), schematic structure (**III**)], and the related species [1-(pcym)-1-RuB$_{10}$H$_{10}$] [(**3a**), schematic structure (**IV**)],that does not contain the two skeletal carbon atoms in the cluster. For additional comparison the η^6-C$_6$Me$_6$ analogue of compound (**1a**), *viz.* [2,4-Me$_2$-1-(hmb)-1,2,4-RuC$_2$B$_8$H$_8$] (**1b**) is also reported, as are the *C*-monomethylated compound [4-Me-1-(hmb)-1,2,4-RuC$_2$B$_8$H$_9$] (**4**) and its isomer [2-Me-1-(hmb)-1,2,3-RuC$_2$B$_8$H$_9$] (**8**). The hmb analogue of (**3a**) *viz.* [1-(hmb)-1-RuB$_{10}$H$_{10}$] (**3b**), has been described previously.[2] Recent related ruthenadicarbaborane and ruthenaborane work is in refs. 3—11 and structures related to (**1**) have recently been described in refs. 12—14. The eleven- and ten-vertex numbering schemes used in this work are shown in (**V**) and (**VI**) respectively.



(**I**)



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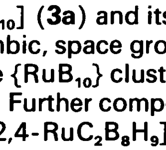
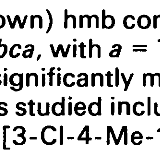


(**III**)



(**IV**)

Results and Discussion

Reaction between [{Ru(pcym)Cl$_2$}$_2$] and 5,6-Me$_2$-*nido*-5,6-C$_2$B$_8$H$_{10}$ in the presence of *N,N,N',N'*-tetramethylnaphtha-

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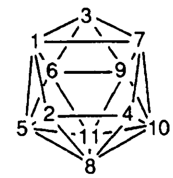
* Part 6 is ref. 2.

† 1-(η^6-*p*-cymene)-2,4-dimethyl-2,4-dicarba-1-ruthena-*closo*-undecaborane, 1-(η^6-*p*-cymene)-2,3-dimethyl-2,3-dicarba-1-ruthena-*closo*-undecaborane, and 1-(η^6-*p*-cymene)-1-ruthena-*closo*-undecaborane.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

‡ Throughout pcym denotes the η^6-ligand *p*-cymene (1-Me-4-Pr^{i}C$_6$H$_4$) and hmb denotes η^6-hexamethylbenzene (C$_6$Me$_6$).



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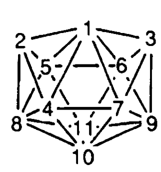

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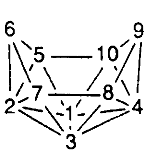

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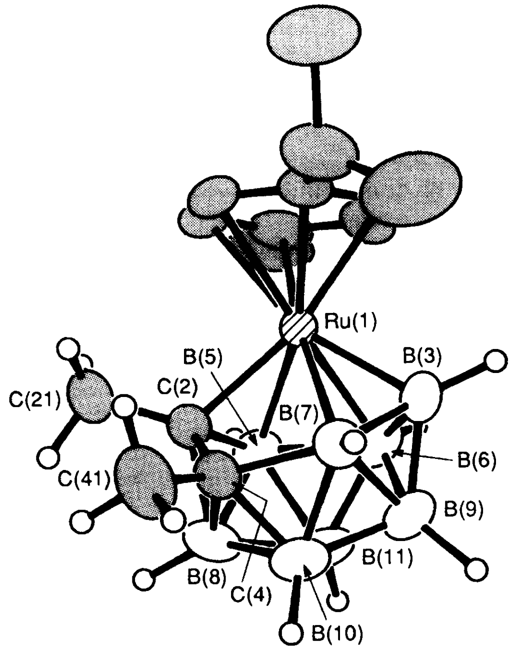


Figure 1. ORTEP drawing of the crystallographically determined molecular structure of [2,4-Me_2-1-(pcym)-1,2,4-$RuC_2B_8H_8$] (**1a**). The dihedral angle between the C_6(aryl) plane and the B(5)—B(7) plane is 7.35°. The C(4) atom is 31.6 pm below the B(5)—B(7) plane. The H atoms associated with the *p*-cymene ligand have been omitted for clarity; one of the arene ring C atoms is obscured in this projection, as is the H atom attached to B(6)

lene-1,8-diamine (tmnd) in dichloromethane solution for 2 h, followed by chromatographic separation, yielded (30%) a single orange-yellow air-stable metalladicarbaborane product, characterized as [2,4-Me_2-1-(pcym)-1,2,4-$RuC_2B_8H_8$] (**1a**). The reaction may be represented stoicheiometrically by equation (1). The reaction system using [{Ru(hmb)Cl_2}$_2$]

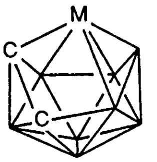
$$\tfrac{1}{2}[\{Ru(pcym)Cl_2\}_2] + Me_2C_2B_8H_{10} + 2tmnd \longrightarrow [Me_2(pcym)RuC_2B_8H_8] + 2[Htmnd]Cl \quad (1)$$

instead of the *p*-cymene derivative worked similarly, giving the analogous product [2,4-Me_2-1-(hmb)-1,2,4-$RuC_2B_8H_8$] (**1b**), but now in the somewhat lower yield of 10%. Compounds (**1a**) and (**1b**) were characterized by elemental analysis, mass spectrometry, and n.m.r. spectroscopy, together with [in the case of (**1a**)] a single-crystal *X*-ray diffraction analysis.

A crystal of (**1a**) suitable for *X*-ray analysis was obtained from a chloroform solution under conditions of slow solvent evaporation. A drawing of the structure of the molecule is in Figure 1, and interatomic distances and angles are given in Tables 1 and 2 respectively. It can be seen from Figure 1 that there is considerable distortion of the eleven-vertex cluster [schematic structures (I) and (VII)] away from the idealized C_{2v} configuration (VIII) as exhibited,[15] for example, by the straightforward eleven-vertex *closo*-dicarbaborane 2,3-Me_2-*closo*-2,3-$C_2B_9H_9$ which it would be expected to resemble on the basis of the straightforward application of the Williams–Wade cluster-geometry[16] and electron-counting[17] rules. Indeed, just such a regular *closo*-1,2,4-geometry has previously been assumed for analogous MC_2B_8 compounds of cobalt,[18] iridium,[19,20] rhodium,[20] and ruthenium.[4,20] However, the overall similarities of the ^{11}B and ^1H n.m.r. shielding patterns for the above compounds (insofar as they have been reported) with those for compound (**1a**) (as listed in Table 3, below), may suggest that the more open structure is a general feature of this type of compound. This suggestion has very recently been reinforced by *X*-ray structural work on [1,1-$(PPh_3)_2$-1-H-1,2,4-$IrC_2B_8H_{10}$].[12]

Table 1. Interatomic distances (pm) for [2,4-Me_2-1-(pcym)-1,2,4-$RuC_2B_8H_8$] (**1a**) with estimated standard deviations (e.s.d.s) in parentheses

(*i*) Ruthenium–cluster distances			
Ru(1)–C(2)	212.4(6)	Ru(1)–B(3)	206.5(6)
Ru(1)–C(4)	268.3(7)	Ru(1)–B(5)	228.7(6)
Ru(1)–B(6)	228.9(6)	Ru(1)–B(7)	236.3(6)
(*ii*) Other ruthenium–cluster distances			
Ru(1)–C(5)	223.0(5)	Ru(1)–C(8)	226.2(5)
Ru(1)–C(6)	219.0(5)	Ru(1)–C(9)	230.1(5)
Ru(1)–C(7)	220.7(5)	Ru(1)–C(10)	228.5(5)
(*iii*) Other cluster distances among boron and carbon atoms			
C(2)–C(4)	148.5(7)	B(3)–B(7)	172.9(8)
C(2)–B(5)	162.6(8)	B(3)–B(6)	172.6(9)
C(2)–B(8)	172.0(9)	B(3)–B(9)	169.6(9)
C(4)–B(7)	176.2(8)	—	
C(4)–B(8)	175.1(9)	B(7)–B(9)	187.3(9)
C(4)–B(10)	167.2(9)	B(7)–B(10)	182.1(9)
B(5)–B(6)	182.5(9)	—	
B(5)–B(8)	180.0(9)	B(6)–B(9)	178.1(9)
B(5)–B(11)	181.4(9)	B(6)–B(11)	179.4(10)
B(8)–B(10)	174.3(9)	B(9)–B(10)	177.0(10)
B(8)–B(11)	170.2(11)	B(9)–B(11)	176.1(10)
B(10)–B(11)	177.3(10)	—	
(*iv*) Selected other distances			
C(2)–C(21)	150.8(8)	B(3)–H(3)	115(4)
C(4)–C(41)	150.5(8)	B(7)–H(7)	114(4)
B(5)–H(5)	108(5)	B(6)–H(6)	107(4)
B(8)–H(8)	122(6)	B(9)–H(9)	123(5)
B(10)–H(10)	121(5)	B(11)–H(11)	117(5)



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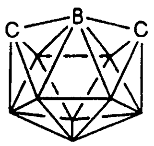


(VIII)

Specifically, the ruthenium–carbon distance Ru(1)–C(4) in (**1a**) (Figure 1) is essentially non-bonding at 268.3(7) pm [compared to Ru(1)–C(2) at 212.4(6) pm]; this thereby generates an open quadrilateral face Ru(1)C(2)C(4)B(7). The anomalous open face, together with the retention of a high metal-to-cluster connectivity, is reminiscent of the structures about the metal in the *isonido* ten-vertex iridacarbaborane [$(PPh_3)(PPh_2\overline{C_6H_4)IrC(OH)B}_8H_6(OMe)$] [schematic struc-

Table 2. Selected interatomic angles (°) for [2,4-Me_2-1-(pcym)-1,2,4-$RuC_2B_8H_8$] (**1a**) with e.s.d.s in parentheses

(*i*) About the ruthenium atom

C(4)–Ru(1)–C(2)	33.5(1)	C(5)–Ru(1)–C(2)	112.2(2)
C(5)–Ru(1)–C(4)	145.3(1)	C(6)–Ru(1)–C(2)	147.6(1)
C(6)–Ru(1)–C(4)	176.5(1)	C(7)–Ru(1)–C(2)	163.4(1)
C(7)–Ru(1)–C(4)	143.6(1)	C(8)–Ru(1)–C(2)	127.3(2)
C(8)–Ru(1)–C(4)	116.6(2)	C(9)–Ru(1)–C(2)	99.2(2)
C(9)–Ru(1)–C(4)	106.6(2)	C(10)–Ru(1)–C(2)	92.5(2)
C(10)–Ru(1)–C(4)	117.9(2)	B(3)–Ru(1)–C(2)	106.9(3)
B(3)–Ru(1)–C(4)	81.6(3)	B(3)–Ru(1)–C(5)	128.0(3)
B(3)–Ru(1)–C(6)	95.3(3)	B(3)–Ru(1)–C(7)	85.1(3)
B(3)–Ru(1)–C(8)	105.1(3)	B(3)–Ru(1)–C(9)	139.8(2)
B(3)–Ru(1)–C(10)	160.2(2)	B(7)–Ru(1)–C(2)	72.6(3)
B(7)–Ru(1)–C(4)	40.2(1)	B(7)–Ru(1)–C(5)	173.4(1)
B(7)–Ru(1)–C(6)	137.4(1)	B(7)–Ru(1)–C(7)	110.8(2)
B(7)–Ru(1)–C(8)	104.1(2)	B(7)–Ru(1)–C(9)	120.1(2)
B(7)–Ru(1)–C(10)	150.3(1)	B(7)–Ru(1)–B(3)	45.3(2)
B(6)–Ru(1)–C(7)	112.9(3)	B(6)–Ru(1)–C(8)	146.3(2)
B(6)–Ru(1)–C(9)	170.1(1)	B(6)–Ru(1)–C(10)	135.4(1)
B(6)–Ru(1)–B(3)	46.4(2)	B(6)–Ru(1)–B(7)	69.8(3)
B(5)–Ru(1)–C(2)	43.1(2)	B(5)–Ru(1)–C(4)	61.6(2)
B(5)–Ru(1)–C(5)	97.6(2)	B(5)–Ru(1)–C(6)	116.9(2)
B(5)–Ru(1)–C(7)	151.7(1)	B(5)–Ru(1)–C(8)	166.4(1)
B(5)–Ru(1)–C(9)	130.8(1)	B(5)–Ru(1)–C(10)	104.0(2)
B(5)–Ru(1)–B(3)	88.2(3)	B(5)–Ru(1)–B(7)	82.9(3)
B(5)–Ru(1)–B(6)	47.0(2)		

(*ii*) About the two cluster carbon atoms

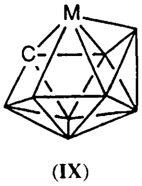
C(4)–C(2)–C(21)	119.8(5)	B(5)–C(2)–C(21)	124.1(5)
B(5)–C(2)–C(4)	111.2(4)	B(8)–C(2)–C(21)	116.9(4)
B(8)–C(2)–C(4)	65.7(4)	B(8)–C(2)–B(5)	65.0(4)
Ru(1)–C(2)–C(21)	120.8(4)	Ru(1)–C(2)–C(4)	94.4(3)
Ru(1)–C(2)–B(5)	73.8(3)	Ru(1)–C(2)–B(8)	121.0(4)
C(41)–C(4)–C(2)	120.0(5)	B(7)–C(4)–C(2)	110.0(4)
B(7)–C(4)–C(41)	115.4(5)	B(8)–C(4)–C(2)	63.6(4)
B(8)–C(4)–C(41)	125.4(5)	B(8)–C(4)–B(7)	111.8(4)
B(10)–C(4)–C(2)	114.3(5)	B(10)–C(4)–C(41)	119.7(5)
B(10)–C(4)–B(7)	64.0(4)	B(10)–C(4)–B(8)	61.2(4)
Ru(1)–C(4)–C(2)	52.1(3)	Ru(1)–C(4)–C(41)	130.8(3)
Ru(1)–C(4)–B(7)	60.1(3)	Ru(1)–C(4)–B(8)	95.9(3)
Ru(1)–C(4)–B(10)	192.2(4)		

(*iii*) Ruthenium–boron–boron and ruthenium–boron–carbon

Ru(1)–B(3)–B(7)	76.5(3)	Ru(1)–B(3)–B(6)	73.7(3)
Ru(1)–B(3)–B(9)	113.5(4)	Ru(1)–B(5)–C(2)	63.1(3)
Ru(1)–B(5)–B(6)	66.5(3)	Ru(1)–B(5)–B(8)	109.6(4)
Ru(1)–B(5)–B(11)	109.1(4)	Ru(1)–B(6)–B(3)	60.0(3)
Ru(1)–B(6)–B(5)	66.5(3)	Ru(1)–B(6)–B(9)	100.8(4)
Ru(1)–B(6)–B(11)	109.7(4)	Ru(1)–B(7)–B(3)	58.2(3)
Ru(1)–B(7)–B(9)	95.5(3)	Ru(1)–B(7)–B(10)	110.4(4)

(*iv*) Boron–boron–boron and boron–boron–carbon

B(6)–B(3)–B(7)	100.9(4)	B(6)–B(5)–C(2)	117.1(4)
B(5)–B(6)–B(3)	117.4(4)	B(3)–B(7)–C(4)	127.9(4)



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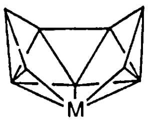

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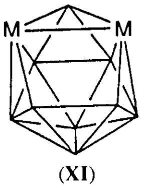
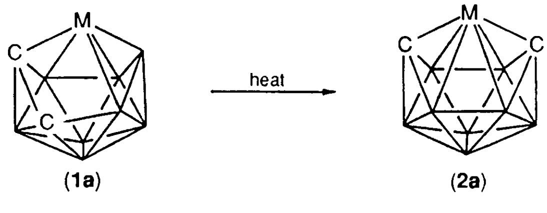


(XI)

ture (**IX**)],[21] and in the *isoarachno*-structured *nido*-type species [1-(hmb)-1-RuB_9H_{13}] [structure (**X**)].[22] It is thus of interest to speculate whether the eleven-vertex *isonido* configuration observed in (**1a**) arises from the localization of an electron pair in the C(2)–C(4) linkage, within the context of a 24-electron Wadian *closo* count, or as a result of a hyper-Wadian four-orbital metal-to-cluster contribution in which the metal contributes four rather than two electrons to the cluster bonding scheme, thereby engendering an effective 26-electron *nido* electron count and a more open structure. However, although the latter explanation has been invoked to account for anomalously *isocloso*-structured species[23–27] its applicability has been seriously questioned on circumstantial[28,29] and theoretical[30] grounds. Additionally, in the eleven-vertex 24-electron area, it has in any event been recently claimed[12–14] that open structures are, in fact, energetically very close to the conventional closed structures such as (**VIII**) and that, in particular, the *isonido*-type structure exhibited here by compounds (**1a**) and (**1b**) [structure (**I**) above], and typified elsewhere[13] by compounds such as [$(\eta^5$-$C_5Me_5)_2RhIrB_9H_{11}$] [structure (**XI**), *cf.* (**I**) above] that also have bridging hydrogen atoms associated with the open face, must be a particularly favoured alternative configuration.

The measured n.m.r. properties of compounds (**1a**) and (**1b**) are given in Table 3. Assignments were made by [^{11}B–^{11}B]-COSY and [^1H–^1H]-COSY-{^{11}B} experiments, the ^{11}B and ^1H n.m.r. spectra being additionally interrelated by use of ^1H-{^{11}B(selective)} n.m.r. spectroscopy. Although a number of examples of this ostensibly *closo*-type of MC_2B_8 cluster have previously been examined by ^{11}B n.m.r. spectroscopy[4,18–20] the cluster-proton shieldings have not previously been reported and, as far as we are aware, no detailed assignments have previously been proposed. Despite this, it is nevertheless apparent that overall shielding patterns are very similar to those reported here, suggesting (as mentioned above) that all the clusters are similarly structured with a quadrilateral open face M(1)C(2)C(4)B(7).[12] In collaboration with others we hope to report more extensively on the n.m.r. features of open C_2B_8 ten-vertex clusters and their metallio derivatives at a later date.

The revelation of the unexpected open face for (**1a**) and (**1b**) engenders curiosity about the structures of the other possible isomers of these compounds that might, in principle, exist. Thermolysis is a well established route for the isomerization and modification of metalladicarbaboranes[31] and the high-yield isomerizations of the two cobaltadicarbaboranes [1-(η^5-C_5H_5)-1,2,4-$CoC_2B_8H_{10}$] and [1,3′-*commo*-Co-1,2,4-($CoC_2B_8H_{10}$)(3′,1′,2′-$CoC_2B_9H_{11}$)]$^-$ (of the then assumed *closo* eleven-vertex configuration) have been reported to occur at 150 °C in refluxing cyclo-octane.[32] The heating of [2,4-Me_2-1-(pycm)-1,2,4-$RuC_2B_8H_8$] (**1a**) for 1 h at 175 °C in hexadecane as the heat transfer medium produced no evidence of isomerization, but stronger heating at 400 °C in a sealed tube under nitrogen, until melting followed by sublimation occurred, did result in quantitative isomerization, with no significant decomposition, to give a yellow solid characterized as [2,3-Me_2-1-(pcym)-*closo*-1,2,3-$RuC_2B_8H_8$] (**2a**). This isomerization is in accord with those observed[32] in the cobaltadicarbaboranes mentioned above. Thus, the carbon atoms rearrange from the 2,4- to the 2,3-positions [equation (2)] and have thereby not only moved apart but also taken up positions of lowest



(**1a**) (**2a**) (2)

Table 3. Measured ^{11}B and ^{1}H n.m.r. data for [2,4-Me_2-1-(pcym)-1,2,4-$RuC_2B_8H_8$] (**1a**) and [2,4-Me_2-1-(hmb)-1,2,4-$RuC_2B_8H_8$] (**1b**)

	(**1a**)		(**1b**)		
Assignment ^{a}	$\delta(^{11}B)$/p.p.m.^{b,c} [$^{1}J(^{11}B-^{1}H)$/Hz]	$\delta(^{1}H)^{c,d}$	$\delta(^{11}B)$/p.p.m.^{b,c} [$^{1}J(^{11}B-^{1}H)$/Hz]	$\delta(^{1}H)^{c,e}$	Observed [$^{11}B-^{11}B$] two-dimensional COSY correlations ^{f,g}
3	+58.4 (1 B) [156]	+7.61 (1 H)	+61.5 (1 B) [152]	+7.07 (1 H)	5s, 6s, 9m
9	+9.6 (1 B) [142]	+3.79 (1 H)	+9.2 (1 B) [140]	+3.67 (1 H)	3m, 5w, 6m, 10s, 11s
7	+3.5 (1 B) [144]	+2.47 (1 H)	+2.8 (1 B) [143]	+2.19 (1 H)	6s, 8w, 11s
6	−5.2 (1 B) [140]	+1.20 (1 H)	−2.1 (1 B) [138]	+1.07 (1 H)	3s, 9m, 11s
10	−10.8 (1 B) [149]	+1.07 (1 H)	−11.0 (1 B) [148]	+0.96 (1 H)	5w, 8m, 9s, 11s
8	−11.9 (1 B) [160]	+1.73 (1 H)	−9.9 (1 B) [156]	+1.85 (1 H)	7w, 10m, 11s
11	−25.0 (1 B) [143]	+0.52 (1 H)	−25.7 (1 B) [142]	+0.41 (1 H)	6s, 7s, 8s, 9s, 10s
5	−37.2 (1 B) [149]	−2.07 (1 H)	−37.3 (1 B) [146]	−2.23 (1 H)	3s, 9w, 10w

[a] Assignment made on the basis of [$^{11}B-^{11}B$] two-dimensional COSY and [^{1}H-{^{11}B(selective)}] experiments, the [$^{11}B-^{11}B$] correlations for both compounds being essentially the same. [b] $CDCl_3$ solution at 297 K. [c] Relative intensities in parentheses. [d] $\delta(^{1}H)(MeC_6H_4Pr^{i})$: Me +1.94; C_6H_4 +5.61 (doublet of doublets), +5.63 (doublet of doublets), +5.74 (doublet of doublets), +5.93 (doublet of doublets) [$^{3}J(^{1}H-^{1}H)$(mean) 6.1 Hz; $^{n}J(^{1}H-^{1}H)$(mean) 1.4 Hz, *n* probably 4]; C*H*Me_2 +2.50 (heptet) [$^{3}J(^{1}H-^{1}H)$(mean) 6.9 Hz], CH*Me*$_2$ +1.08 (doublet) and +1.16 (doublet) [$^{3}J(^{1}H-^{1}H)$ 6.9 Hz]. [e] $\delta(^{1}H)(C_6Me_6)$ +2.13, $\delta(^{1}H)$ (C–Me) +1.52 and +2.40. [f] Measured with {^{1}H (broad-band) noise decoupling}. [g] s = Strong, m = medium, w = weak.

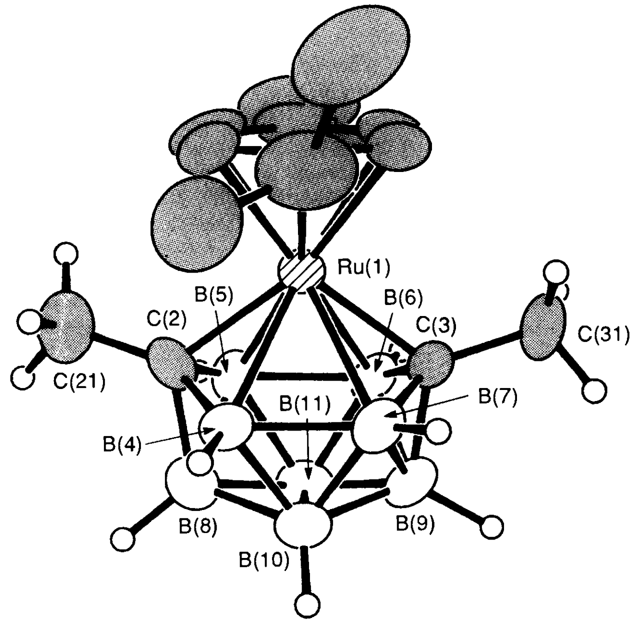


Figure 2. ORTEP drawing of the crystallographically determined molecular structure of [2,3-Me_2-1-(pcym)-1,2,3-$RuC_2B_8H_8$] (**2a**). The H atoms associated with the *p*-cymene ligand have been omitted for clarity. The arene ring C atom carrying the Pr^{i} substituent is obscured in this projection, as is the H atom attached to B(11)

Table 4. Interatomic distances (pm) for [2,3-Me_2-1-(pcym)-1,2,3-$RuC_2B_8H_8$] (**2a**) with e.s.d.s in parentheses

(*i*) Ruthenium–cluster distances			
Ru(1)–C(2)	210.7(9)	Ru(1)–C(3)	210.1(9)
Ru(1)–B(4)	239.4(10)	Ru(1)–B(5)	232.4(12)
Ru(1)–B(6)	239.9(10)	Ru(1)–B(7)	240.8(11)
(*ii*) Other ruthenium–carbon distances			
Ru(1)–C(4)	225.5(9)	Ru(1)–C(7)	226.6(10)
Ru(1)–C(5)	219.7(10)	Ru(1)–C(8)	221.5(11)
Ru(1)–C(6)	222.6(10)	Ru(1)–C(9)	220.4(10)
(*iii*) Other cluster distances among boron and carbon atoms			
C(2)–B(4)	159.7(16)	C(3)–B(7)	157.3(15)
C(2)–B(5)	155.6(16)	C(3)–B(6)	158.7(14)
C(2)–B(8)	167.8(14)	C(3)–B(9)	164.4(13)
B(4)–B(7)	191.2(15)	—	
B(4)–B(8)	183.7(16)	B(7)–B(9)	180.4(16)
B(4)–B(10)	179.5(14)	B(7)–B(10)	180.2(16)
B(5)–B(6)	192.3(15)	—	
B(5)–B(8)	178.5(17)	B(6)–B(9)	181.3(15)
B(5)–B(11)	181.9(15)	B(6)–B(11)	178.3(15)
B(8)–B(10)	175.9(17)	B(9)–B(10)	168.9(16)
B(8)–B(11)	177.7(15)	B(9)–B(11)	172.5(16)
B(10)–B(11)	181.8(18)	—	
(*iv*) Selected other distances			
C(2)–C(21)	148.7(13)	C(3)–C(31)	154.2(15)
B(4)–H(4)	128(4)	B(7)–H(7)	113(4)
B(5)–H(5)	95(4)	B(6)–H(6)	102(4)
B(8)–H(8)	119(3)	B(9)–H(9)	128(4)
B(10)–H(10)	109(3)	B(11)–H(11)	100(3)

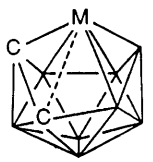
connectivity, consistent with the rules laid down by Hawthorne and co-workers.[32]

The isomerized compound (**2a**) was characterized by elemental analysis, mass spectrometry, n.m.r. spectroscopy, and a single-crystal *X*-ray diffraction analysis. Suitable crystals were grown by slow evaporation of a solution of (**2a**) in n-hexane–dichloromethane. A drawing of the structure of the molecule thus established is in Figure 2; interatomic distances and angles are in Tables 4 and 5 respectively. The measured n.m.r. properties of (**2a**) are in Table 6 and are consistent with the symmetrical *closo*-1,2,3-RuC_2B_8 cluster configuration. As with compounds of the 1,2,4-MC_2B_8 configuration exemplified by compounds (**1a**) and (**1b**), we hope to discuss the general n.m.r. shielding patterns in a more extensive series of these and related compounds elsewhere.

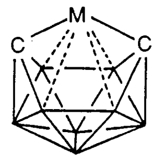
The symmetrical *closo*-1,2,3-RuC_2B_8 cluster of (**2a**) is apparent from Figure 2 although the disposition of the *p*-cymene ligand in the solid-state structure is inconsistent with the C_{2v} 'symmetry' observed by n.m.r. spectroscopy in solution; however, the essentially free rotation of the η^6-ligand in solution can reasonably be invoked to account for this. Within the cluster of (**2a**) [structure (**XIII**)] deviations from C_{2v} symmetry are generally within experimental error, with the possible exception of Ru(1)–B(5) which seems slightly shorter than the other Ru–B distances. However, there is some disorder of the *p*-cymene ligand, and the consequently high estimated standard deviations may well render such close comparison meaningless. In general, the Ru–B distances are somewhat longer by 10—20

Table 5. Selected interatomic angles (°) for [2,3-Me_2-1-(pcym)-1,2,3-$RuC_2B_8H_8$] (**2a**) with e.s.d.s in parentheses

(*i*) About the ruthenium atom			
C(3)–Ru(1)–C(2)	107.0(4)	B(4)–Ru(1)–C(2)	40.9(4)
B(4)–Ru(1)–C(3)	82.3(4)	B(5)–Ru(1)–C(2)	40.8(3)
B(5)–Ru(1)–C(3)	83.5(4)	B(5)–Ru(1)–B(4)	66.2(5)
B(6)–Ru(1)–C(2)	84.6(4)	B(6)–Ru(1)–C(3)	40.6(3)
B(6)–Ru(1)–B(4)	85.8(4)	B(6)–Ru(1)–B(5)	48.0(3)
B(7)–Ru(1)–C(2)	83.9(4)	B(7)–Ru(1)–C(3)	40.1(3)
B(7)–Ru(1)–B(4)	46.9(3)	B(7)–Ru(1)–B(5)	85.8(4)
B(7)–Ru(1)–B(6)	67.1(4)	C(4)–Ru(1)–C(2)	117.0(4)
C(4)–Ru(1)–C(3)	116.8(4)	C(4)–Ru(1)–B(4)	102.6(4)
C(4)–Ru(1)–B(5)	156.3(3)	C(4)–Ru(1)–B(6)	155.4(3)
C(4)–Ru(1)–B(7)	101.8(4)	C(5)–Ru(1)–C(2)	91.8(4)
C(5)–Ru(1)–C(3)	152.5(4)	C(5)–Ru(1)–B(4)	100.4(4)
C(5)–Ru(1)–B(5)	122.9(4)	C(5)–Ru(1)–B(6)	165.7(4)
C(5)–Ru(1)–B(7)	126.4(5)	C(6)–Ru(1)–C(2)	90.6(5)
C(6)–Ru(1)–C(3)	156.2(4)	C(6)–Ru(1)–B(4)	120.9(5)
C(6)–Ru(1)–B(5)	100.9(4)	C(6)–Ru(1)–B(6)	129.3(4)
C(6)–Ru(1)–B(7)	162.3(4)	C(7)–Ru(1)–C(2)	115.1(5)
C(7)–Ru(1)–C(3)	120.1(5)	C(7)–Ru(1)–B(4)	154.3(4)
C(7)–Ru(1)–B(5)	101.9(4)	C(7)–Ru(1)–B(6)	103.2(4)
C(7)–Ru(1)–B(7)	158.5(4)	C(8)–Ru(1)–C(2)	152.9(4)
C(8)–Ru(1)–C(3)	93.2(4)	C(8)–Ru(1)–B(4)	164.7(4)
C(8)–Ru(1)–B(5)	128.1(5)	C(8)–Ru(1)–B(6)	100.3(4)
C(8)–Ru(1)–B(7)	122.7(5)	C(9)–Ru(1)–C(2)	154.0(3)
C(9)–Ru(1)–C(3)	91.6(4)	C(9)–Ru(1)–B(4)	128.4(4)
C(9)–Ru(1)–B(5)	164.0(4)	C(9)–Ru(1)–B(6)	120.8(4)
C(9)–Ru(1)–B(7)	100.3(4)		
(*ii*) About the two cluster carbon atoms			
C(21)–C(2)–Ru(1)	124.6(7)	B(4)–C(2)–Ru(1)	79.2(5)
B(4)–C(2)–C(21)	126.6(9)	B(5)–C(2)–Ru(1)	77.1(6)
B(5)–C(2)–C(21)	121.5(9)	B(5)–C(2)–B(4)	109.6(7)
B(8)–C(2)–Ru(1)	117.6(7)	B(8)–C(2)–C(21)	117.6(8)
B(8)–C(2)–B(4)	68.2(7)	B(8)–C(2)–B(5)	66.9(7)
C(31)–C(3)–Ru(1)	123.8(6)	B(6)–C(3)–Ru(1)	79.9(5)
B(6)–C(3)–C(31)	121.5(8)	B(7)–C(3)–Ru(1)	80.5(5)
B(7)–C(3)–C(31)	121.5(8)	B(7)–C(3)–B(6)	114.4(8)
B(9)–C(3)–Ru(1)	118.4(6)	B(9)–C(3)–C(31)	117.8(7)
B(9)–C(3)–B(6)	68.3(7)	B(9)–C(3)–B(7)	68.1(7)
(*iii*) Boron–boron ruthenium and carbon–boron–ruthenium			
C(2)–B(4)–Ru(1)	59.8(5)	B(7)–B(4)–Ru(1)	66.9(5)
B(8)–B(4)–Ru(1)	99.3(6)	B(10)–B(4)–Ru(1)	104.4(6)
C(2)–B(5)–Ru(1)	62.1(5)	B(6)–B(5)–Ru(1)	68.0(5)
B(8)–B(5)–Ru(1)	103.6(7)	B(11)–B(5)–Ru(1)	107.2(6)
C(3)–B(6)–Ru(1)	59.5(4)	B(5)–B(6)–Ru(1)	63.9(5)
B(9)–B(6)–Ru(1)	99.0(6)	B(11)–B(6)–Ru(1)	105.4(6)
C(3)–B(7)–Ru(1)	59.4(5)	B(4)–B(7)–Ru(1)	66.2(5)
B(9)–B(7)–Ru(1)	99.0(6)	B(10)–B(7)–Ru(1)	103.6(6)
(*iv*) Boron–boron–boron and carbon–boron–boron			
B(7)–B(4)–C(2)	118.9(7)	B(6)–B(5)–C(2)	121.4(8)
B(5)–B(6)–C(3)	114.0(7)	B(4)–B(7)–C(3)	116.4(8)



(XII)



(XIII)

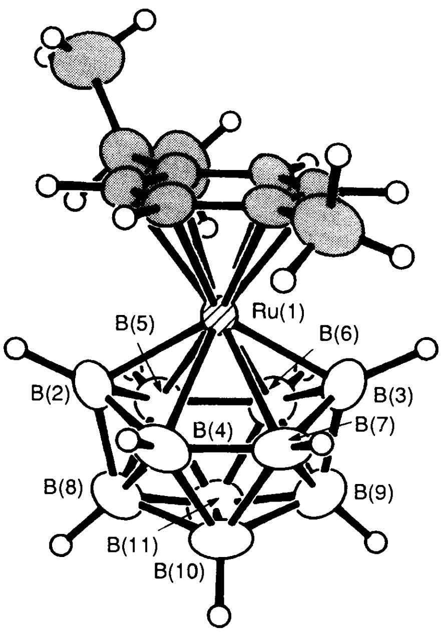


Figure 3. ORTEP drawing of the crystallographically determined molecular structure of [1-(pcym)-*isocloso*-1-$RuB_{10}H_{10}$] (**3a**). The H atom attached to B(11) is obscured in this projection, as is one of the methyl H atoms of the Pr^i group on the *p*-cymene ligand

pm than the corresponding ones in the asymmetric 1,2,4-analogue (**1a**) [structure (**XII**)], whereas the metal–carbon distances Ru(1)–C(2) and Ru(1)–C(3) at 210.7(9) and 210.1(9) respectively are both very similar to the Ru(1)–C(2) and Ru(1)–B(3) distances in (**1a**) at 212.4(6) and 206.5(6) pm respectively. The Ru–B distances in (**2a**), averaging at 238 pm are, in fact, at the high end of the range of Ru–B distances[2,4,5,7–9,11,22,25,26,33] reported for contiguous metallaborane cluster compounds. This suggests that any 'discomfort' that the closed RuC_2B_8 cluster has for its electronic constitution, as manifest by the asymmetric slippage and quadrilateral open face of the 1,2,4 compound (**1a**) [structure (**XII**), see also (**I**)], is manifest in the symmetrical 1,2,3 compound (**2a**) by an equal stretching of the four metal-boron contacts thereby maintaining an overall formal polar C_{2v} symmetry, *i.e.* a 'symmetrical elongation' rather than a 'slippage.'

Comparison of the preceding ruthenadicarbaundecaboranes with the non-carbon-containing eleven-vertex cluster species [1-(pcym)-1-$RuB_{10}H_{10}$] (**3a**) should also be of interest as this might be expected, by comparison with other species,[7,25,34–39] also to have an eleven-vertex cluster structure of formal C_{2v} symmetry, as in structure (**IV**) above. Now, however, the cluster has a formally *pileo* 22-electron count, and there is a question[27–30] as to whether the cluster actually does tolerate this hypo-Wadian count (as it is theoretically capable of doing without distortion from C_{2v} symmetry)[40] or whether a hyper-Wadian four-orbital cluster contribution[35,41] from the metal vertex must be invoked to engender the 24-electron count that is conventionally compatible with a *closo* eleven-vertex structure. Compound (**3a**) is previously unreported, although its hmb analogue (**3b**) has been prepared in 82% yield from the reaction in solution between [{Ru(hmb)Cl_2}$_2$] and *closo*-$[B_{10}H_{10}]^{2-}$ in accord with the stoicheiometry of equation (3).[2] The reaction

$$\tfrac{1}{2}[\{Ru(arene)Cl_2\}_2] + [B_{10}H_{10}]^{2-} \longrightarrow [(arene)RuB_{10}H_{10}] + 2Cl^- \qquad (3)$$

is now also found to work for the η^6 *p*-cymene derivative and affords (**3a**) in 87% yield, the constitution of the product being readily established by elemental analysis, mass spectrometry, and n.m.r. spectroscopy (Table 7), and confirmed by a single-crystal *X*-ray diffraction analysis.

Table 6. Measured ^{11}B and ^{1}H n.m.r. data for [2,3-Me_2-1-(pcym)-*closo*-1,2,3-$RuC_2B_8H_8$] (**2a**) and [2-Me-1-(hmb)-*closo*-1,2,3-$RuC_2B_9H_9$] (**8**)

	(**2a**)		(**8**)	
Tentative assignment[a]	$\delta(^{11}B)$/p.p.m. $[^1J(^{11}B-^1H)/Hz]^{b,c}$	$\delta(^1H)^{b,c,d}$	$\delta(^{11}B)$/p.p.m. $[^1J(^{11}B-^1H)/Hz]^{b,c}$	$\delta(^1H)^{b,c,e}$
4,7	−8.9 (4 B) [141]	+1.45 (4 H)	−9.8 (2 B) [*f*]	+1.11 (2 H)
5,6			−10.6 (2 B) [*f*]	+1.19 (2 H)
10,11	−24.6 (2 B) [139]	+0.20 (2 H)	−24.2 (2 B) [139]	+1.19 (2 H)
8	+12.4 (2 B) [154]	+3.08 (2 H)	+4.6 (1 B) [152]	+3.21[g] (2 H)
9			+13.9 (1 B) [152]	

[a] Assigned on the basis of [^1H-{^{11}B(selective)}] experiments. [b] CD_2Cl_2 solution at 297 K. [c] Relative intensities in parentheses. [d] $\delta(^1H)(MeC_6H_4Pr^i)$: Me +2.20; C_6H_4 +5.54 (doublet) and +5.58 (doublet) [$^3J(^1H-^1H)$ = 6.2 Hz]; C*H*Me_2 +2.69 (heptet) [$^3J(^1H-^1H)$ = 6.9 Hz]; CH*Me*$_2$ +1.22 (doublet) [$^3J(^1H-^1H)$ = 6.9 Hz]; $\delta(^1H)$(C–Me) +2.67. [e] $\delta(^1H)(C_6Me_6)$ +2.14; $\delta(^1H)$(C–Me) +2.56; $\delta(^1H)$(C–H) +2.47. [f] Accurate estimation precluded by overlap of ^{11}B resonances. [g] $^1H(8)$ and $^1H(9)$ resonances accidentally coincident.

***Table* 7.** Measured ^{11}B and ^{1}H n.m.r. data for [1-(pcym)-*isocloso*-1-$RuB_{10}H_{10}$] (**3a**)

Assignment[a]	$\delta(^{11}B)$/p.p.m.$[^1J(^{11}B-^1H)/Hz]^{b,c}$	$\delta(^1H)^{b,c,d}$
2,3	+107.4 (2 B) [168]	+11.05 (2 H)
10,11	+18.34 (2 B) [141]	+2.81 (2 H)
8,9	+12.51 (2 B) [142]	+4.21 (2 H)
4,5,6,7	+11.9 (4 B) [145]	+1.20 (4 H)

[a] Assignment made upon the basis of [^1H-{^{11}B(selective)}] n.m.r. spectroscopy and by comparison with the data for (**3b**) (ref. 2). [b] CD_2Cl_2 solution at 297 K. [c] Relative intensities in parentheses. [d] $\delta(^1H)(MeC_6H_4Pr^i)$: Me +2.02; C_6H_4 +6.48 (doublet) and +6.59 (doublet) [$^3J(^1H-^1H)$ = 6.8 Hz]; C*H*Me_2 +2.66 (heptet) [$^3J(^1H-^1H)$ *ca.* 7.0 Hz]; CH*Me*$_2$ +1.12 (doublet) [$^3J(^1H-^1H)$ *ca.* 7.0 Hz].

Table 8. Interatomic distances (pm) for [1-(pcym)-1-$RuB_{10}H_{10}$] (**3a**) with e.s.d.s in parentheses

(*i*) Ruthenium–boron

Ru(1)–B(2)	209.2(7)	Ru(1)–B(3)	210.3(7)
Ru(1)–B(4)	227.4(7)	Ru(1)–B(5)	228.4(7)
Ru(1)–B(6)	229.0(7)	Ru(1)–B(7)	228.1(7)

(*ii*) Ruthenium–carbon

Ru(1)–C(1)	232.7(4)	Ru(1)–C(4)	232.8(4)
Ru(1)–C(2)	233.1(4)	Ru(1)–C(5)	232.2(5)
Ru(1)–C(3)	233.2(5)	Ru(1)–C(6)	232.3(5)

(*iii*) Boron–boron

B(2)–B(4)	175.9(11)	B(3)–B(7)	176.5(10)
B(2)–B(5)	174.4(9)	B(3)–B(6)	175.6(10)
B(2)–B(8)	171.2(10)	B(3)–B(9)	169.0(11)
B(4)–B(7)	170.0(10)		
B(4)–B(8)	183.3(10)	B(7)–B(9)	183.3(10)
B(4)–B(10)	178.6(10)	B(7)–B(10)	177.2(10)
B(5)–B(6)	171.6(10)		
B(5)–B(8)	184.8(10)	B(6)–B(9)	182.8(11)
B(5)–B(11)	179.7(10)	B(6)–B(11)	179.2(11)
B(8)–B(10)	177.0(11)	B(9)–B(10)	176.5(11)
B(8)–B(11)	174.1(11)	B(9)–B(11)	178.5(11)
B(10)–B(11)	174.1(11)		

(*iv*) Boron-hydrogen

B(2)–H(2)	124(4)	B(3)–H(3)	129(5)
B(4)–H(4)	99(5)	B(7)–H(7)	113(5)
B(5)–H(5)	110(5)	B(6)–H(6)	128(5)
B(8)–H(8)	114(5)	B(9)–H(9)	115(6)
B(10)–H(10)	113(4)	B(11)–H(11)	116(4)

Crystals of (**3a**) suitable for *X*-ray analysis were obtained by cooling a solution of the compound in dichloromethane. A drawing of the molecular structure is in Figure 3 and listings of interatomic distances and angles are in Tables 8 and 9 respectively. As expected, the basic idealized C_{2v} cluster symmetry exhibited by (**2a**) (Figure 2 and Tables 4 and 5) is also shown by the non-carbon-containing cluster of (**3a**). However, there are subtle differences of detail, as the metal atom is held more compactly within the cluster {RuB_{10}} than it is within {RuC_2B_8}; for example the Ru(1)–C(2) and Ru(1)–C(3) distances in (**2a**) are essentially the same as the corresponding distances Ru(1)–B(2) and Ru(1)–B(3) in (**3a**), whereas a smaller covalent radius would be expected for carbon *versus* boron in equivalent bonding situations. More noticeably, the distances from Ru(1) to B(4)—B(7) in the {RuB_{10}} compound (**3a**) average at *ca.* 228(1) pm which is some 10 pm less than the corresponding distances in the {RuC_2B_8} compound (**2a**) which average 238(3) pm. These effects are also manifested in other dimensions, for example (*a*) the distances from Ru(1) to the mid-point of either the C(2)–C(3) or B(2)–B(3) vector differ by 25 pm, and (*b*) the distances from Ru(1) to the mean B(4)—B(7) plane in the two clusters differ by some 11 pm. Likewise, there are concomitant differences in interboron distances within the clusters, for example, the mean of the B(4)–B(7) and B(5)–B(6) distances in the metalladicarbaborane (**2a**) are more than 20 pm longer than in the {RuB_{10}} species (**3a**), *viz.* 191.8(15) *vs.* 170.8(10) pm. These all indicate that the binding in the metal-capped part of these *closo*-type structures is somewhat stronger for the {RuB_{10}} species (**3a**) with its formal *pileo* (22-electron) count than for the {RuC_2B_8} species (**2a**) which has a formal *closo* (24-electron) count. The ruthenium–carbon (arene) distances in (**3a**) [all > 232.2(5) pm] are also concomitantly appreciably longer than those in (**1a**) [219.0(5)–230.1(5) pm] and in (**2a**) [219.7(10)—226.6(10) pm]. It will be interesting to see theoretical considerations as to whether, in these clusters, the metal centres contribute four orbitals and four electrons to the cluster bonding[25,41] [so that (**3a**) and (**2a**) thereby achieve *closo* and *nido* electron counts respectively] or whether these features arise because of a limited applicability[12] of the simple Wadian cluster-electron counting formalism to the 22—26 electron eleven-vertex system.

As an extension of this work it was of interest to synthesize an analogue of [2,4-Me_2-1-(pcym)-1,2,4-$RuC_2B_8H_8$] (**1a**) in which the exopolyhedral substituents on the two cluster-carbon atoms differed, so that they were thereby effectively labelled. A sample of a suitable monomethylated starting dicarbaborane substrate *nido*-Me-5,6-$C_2B_8H_{11}$ was prepared by the action of propyne on *arachno*-$B_9H_{13}(OEt_2)$ in a minor extension of the published[42] synthesis of 5,6-$Me_2C_2B_8H_{10}$ from $B_9H_{13}(OEt_2)$ and but-2-yne. Although this gave a 90:10 mixture of the two

Table 9. Selected interatomic angles (°) for [1-(pcym)-1-RuB$_{10}$H$_{10}$] (**3a**) with e.s.d.s in parentheses

(*i*) About the ruthenium atom			
B(2)–Ru(1)–C(1)	129.3(3)	B(2)–Ru(1)–C(2)	157.1(2)
B(2)–Ru(1)–C(3)	134.1(2)	B(2)–Ru(1)–C(4)	100.5(3)
B(2)–Ru(1)–C(5)	83.8(3)	B(2)–Ru(1)–C(6)	96.7(3)
B(3)–Ru(1)–C(1)	98.7(3)	B(3)–Ru(1)–C(2)	82.6(3)
B(3)–Ru(1)–C(3)	96.3(3)	B(3)–Ru(1)–C(4)	129.2(3)
B(3)–Ru(1)–C(5)	156.1(2)	B(3)–Ru(1)–C(6)	132.4(2)
B(3)–Ru(1)–B(2)	120.1(3)	B(4)–Ru(1)–C(1)	109.5(3)
B(4)–Ru(1)–C(2)	139.4(2)	B(4)–Ru(1)–C(3)	171.2(2)
B(4)–Ru(1)–C(4)	142.4(2)	B(4)–Ru(1)–C(5)	111.4(3)
B(4)–Ru(1)–C(6)	97.8(3)	B(4)–Ru(1)–B(2)	47.3(2)
B(5)–Ru(1)–B(3)	88.2(3)	B(5)–Ru(1)–C(1)	172.8(2)
B(5)–Ru(1)–C(2)	145.9(2)	B(5)–Ru(1)–C(3)	115.1(3)
B(5)–Ru(1)–C(4)	100.5(3)	B(5)–Ru(1)–C(5)	110.2(3)
B(5)–Ru(1)–C(6)	138.6(2)	B(5)–Ru(1)–B(2)	46.7(2)
B(5)–Ru(1)–B(3)	88.3(3)	B(5)–Ru(1)–B(4)	72.4(3)
B(6)–Ru(1)–C(1)	141.8(2)	B(6)–Ru(1)–C(2)	112.2(3)
B(6)–Ru(1)–C(3)	100.2(3)	B(6)–Ru(1)–C(4)	112.6(3)
B(6)–Ru(1)–C(5)	142.4(2)	B(6)–Ru(1)–C(6)	173.9(2)
B(6)–Ru(1)–B(2)	87.8(3)	B(6)–Ru(1)–B(3)	46.9(2)
B(6)–Ru(1)–B(4)	88.3(3)	B(6)–Ru(1)–B(5)	44.1(2)
B(7)–Ru(1)–C(1)	97.2(2)	B(7)–Ru(1)–C(2)	107.9(2)
B(7)–Ru(1)–C(3)	137.4(2)	B(7)–Ru(1)–C(4)	170.1(1)
B(7)–Ru(1)–C(5)	143.6(2)	B(7)–Ru(1)–C(6)	112.0(3)
B(7)–Ru(1)–B(2)	88.2(3)	B(7)–Ru(1)–B(3)	47.3(2)
B(7)–Ru(1)–B(4)	43.8(2)	B(7)–Ru(1)–B(5)	88.9(3)
B(7)–Ru(1)–B(6)	72.1(3)		
(*ii*) Boron–boron–ruthenium			
B(4)–B(2)–Ru(1)	71.8(3)	B(5)–B(2)–Ru(1)	72.4(3)
B(8)–B(2)–Ru(1)	108.4(4)	B(6)–B(3)–Ru(1)	72.2(4)
B(7)–B(3)–Ru(1)	71.6(4)	B(9)–B(3)–Ru(1)	108.4(5)
B(2)–B(4)–Ru(1)	60.9(3)	B(7)–B(4)–Ru(1)	68.3(3)
B(8)–B(4)–Ru(1)	97.2(4)	B(10)–B(4)–Ru(1)	105.6(4)
B(2)–B(5)–Ru(1)	60.8(3)	B(6)–B(5)–Ru(1)	68.2(4)
B(8)–B(5)–Ru(1)	96.4(4)	B(11)–B(5)–Ru(1)	104.9(4)
B(3)–B(6)–Ru(1)	61.0(3)	B(5)–B(6)–Ru(1)	67.8(3)
B(7)–B(6)–Ru(1)	53.8(3)	B(9)–B(6)–Ru(1)	96.5(4)
B(3)–B(7)–Ru(1)	61.1(3)	B(4)–B(7)–Ru(1)	67.9(4)
B(6)–B(7)–Ru(1)	54.1(3)	B(9)–B(7)–Ru(1)	96.7(4)
B(10)–B(7)–Ru(1)	105.8(4)		
(*iii*) Boron–boron–boron			
B(5)–B(2)–B(4)	100.4(5)	B(7)–B(3)–B(6)	99.7(5)
B(7)–B(4)–B(2)	123.4(5)	B(6)–B(5)–B(2)	123.1(5)

possible *C*-monomethylated *nido*-5,6-C$_2$B$_8$ dicarbaboranes, we could not satisfactorily establish whether the 5- or the 6-methyl derivative was the major component. However, reaction of this mixture with [{Ru(hmb)Cl$_2$}$_2$] in the presence of tmnd in dichloromethane solution for 2.5 h [*cf.* equation (1)] followed by chromatographic separation afforded a pure metalladicarbaborane binary mixture in 54% yield; this could not be further separated chromatographically. The n.m.r. properties of the product (see Table 10) suggested that the major component was probably the 4-methylated derivative [4-Me-1-(hmb)-1,2,4-RuC$_2$B$_8$H$_9$] (**4**), though this was contaminated with about 10 mol % of the 2-methylated isomer (**5**). The predominance of the 4-methyl product (**4**) might be thought to imply that the starting dicarbaborane was principally the 5-methylated species 5-Me-*nido*-5,6-C$_2$B$_8$H$_{11}$ although it should be remembered that *nido*-5,6-dicarbaboranes can isomerize when deprotonated.[43]

A by-product in trace quantities (*ca.* 1 mg, < 1% yield) in the synthesis of (**4**) was identified by n.m.r. spectroscopy as the known ten-vertex non-carbon *nido*-6-metalladecaborane [6-(hmb)-*nido*-6-RuB$_9$H$_{13}$] (**6**). It is probable that this derived from trace *arachno*-nonaborane impurities in the *nido*-MeC$_2$B$_8$H$_{11}$ starting material rather than from any comproportionation process involving the C$_2$B$_8$ residue since compound (**6**) is known to be formed in high yield from the reaction of [{Ru(hmb)Cl$_2$}$_2$] with *arachno*-nonaboranes.[6] A fourth product was tentatively identified on the basis of its n.m.r. properties as the 3-chlorinated derivative of (**4**), *viz.* [3-Cl-4-Me-1-(hmb)-1,2,4-RuC$_2$B$_8$H$_8$] (**7**). This was formed from its non-chlorinated analogue (**4**) on standing in CDCl$_3$ solution for a few months, the 3 substituent being assumed to be chlorine since solvent chlorination of boron sites α to the metal atom has been noted in other metallaborane systems;[44,45] the trace quantities of (**7**) obtained, however, were too small to establish this unequivocally.

Thermolysis of the *C*-monomethylated 1,2,4-compound (**4**) under conditions similar to those used for the quantitative isomerization of the *C,C′*-dimethylated compound (**2a**) above gave [2-Me-1-(hmb)-*closo*-1,2,3-RuC$_2$B$_8$H$_9$] (**8**) as a yellow air-stable crystalline solid. In this case, in contrast to the conversion of (**1a**) to (**2a**), slight decomposition to give small quantities of intractable materials accompanied the rearrangement, but extraction of the residue gave (**8**) in good yield as the only product. The constitution of (**8**) readily followed from ^{11}B and ^{1}H-{^{11}B} n.m.r. spectroscopy of which the measured parameters are summarized along with those for the *C,C′*-dimethylated analogue (**2a**) in Table 6. Obviously, in this instance, the absence of a second *C*-methyl substituent did not affect the course of the isomerization.

In an attempt to extend these studies to the formation and thermolytic isomerization of the *C*-unsubstituted species [1-(pcym)-1,2,4-RuC$_2$B$_8$H$_{10}$] and its hmb analogue we found that reaction of acetylene and *arachno*-4-(OEt$_2$)B$_9$H$_{13}$ did not yield significant quantities of the desired unsubstituted *nido*-5,6-dicarbadecaborane substrate 5,6-C$_2$B$_8$H$_{12}$. Instead, when HC≡CH was used in place of MeC≡CH or MeC≡CMe in simple modifications of the literature procedure,[42] we found, interestingly, that *nido*-B$_6$H$_{10}$ was produced in modest yield (*ca.* 20%) as an apparently air-stable colourless liquid.

Experimental

General.—The organometallic starting materials [{Ru(hmb)-Cl$_2$}$_2$] and [{Ru(pcym)Cl$_2$}$_2$][46] together with [NEt$_3$H]$_2$[B$_{10}$-H$_{10}$][47] and the *nido*-dicarbaborane 5,6-Me$_2$-5,6-C$_2$B$_8$H$_{10}$[42] were prepared according to literature methods. The monomethylated derivative 5(or 6)-Me-5,6-C$_2$B$_8$H$_{11}$ was prepared by a similar route to the dimethyl analogue by use of propyne instead of but-2-yne. The corresponding anions [5,6-Me$_2$-5,6-C$_2$B$_8$H$_9$]$^-$ and [5(or 6)-Me-5,6-C$_2$B$_8$H$_{10}$]$^-$ were generated by bridge-hydrogen deprotonation of the neutral *nido*-dicarbaboranes using *N,N,N′,N′*-tetramethylnaphthalene-1,8-diamine (tmnd) in dichloromethane solution at room temperature. All reactions were carried out under an atmosphere of dry nitrogen, although subsequent manipulations were carried out in air. Preparative thin-layer chromatography (t.l.c.) was carried out using silica gel G (Fluka, type GF 254) as the stationary phase on plates of dimensions 200 × 200 × 1 mm, made on glass formers from acetone slurries followed by drying in air at 80 °C. Note that R_f values given are useful mainly as a guide since they vary somewhat with factors such as minor variations in plate preparation, laboratory humidity, and the amount of sample applied. Low resolution mass spectra were obtained using an AEI (now Kratos) MS30 instrument, and 70 eV (1.12 × 10^{-17}J) electron impact ionisation.

Nuclear Magnetic Resonance Spectroscopy.—N.m.r. spectroscopy was performed at 2.35 and 9.4 T using commercially

Table 10. Measured ^{11}B and ^{1}H n.m.r. data for [4-Me-1-(hmb)-1,2,4-$RuC_2B_8H_9$] (**4**) and [3-Cl-4-Me-1-(hmb)-1,2,4-$RuC_2B_8H_8$] (**7**)

	(**4**)[a]		(**7**)	
Assignment[b]	$\delta(^{11}B)$/p.p.m. $[^{1}J(^{11}B-^{1}H)/Hz]$[c,d]	$\delta(^{1}H)$[c,d,e]	$\delta(^{11}B)$/p.p.m. $[^{1}J(^{11}B-^{1}H)/Hz]$[c,d]	$\delta(^{1}H)$[c,d,f]
3	+62.3 (1 B) [151]	+7.14 (1 H)	+60.3 (1 B) *g*	*g*
9	+9.7 (1 B) [138]	+3.72 (1 H)	+11.1 (1 B) [147]	+3.80 (1 H)
7	+0.7 (1 B) [140]	+1.98 (1 H)	+0.7 (1 B) [145]	+2.05 (1 H)
6	−2.9 (1 B) [135]	+1.10 (1 H)	−4.2 (1 B) [141]	+1.46 (1 H)
10	−11.2 (1 B) [152]	+0.89 (1 H)	−10.5 (1 B) [155]	+1.08 (1 H)
8	−16.5 (1 B) [166]	+1.93 (1 H)	−17.6 (1 B) [168]	+1.79 (1 H)
11	−24.7 (1 B) [142]	+0.43 (1 H)	−28.3 (1 B) [143]	+0.33 (1 H)
5	−37.1 (1 B) [143]	−2.31 (1 H)	−39.1 (1 B) [148]	−2.01 (1 H)

[a] ^{11}B n.m.r. also showed *ca.* 10 mol % of a compound (**5**) tentatively identified as the 2-Me isomer of (**4**); $\delta(^{11}B)$ +63.4, *ca.* +10, +2.7, *ca.* −3.5, −12.5, −14.2, −26.0, and −42.2 p.p.m. (see text). [b] Assignment made on the basis of [^{11}B-^{11}B] two-dimensional COSY and ^{1}H-{^{11}B(selective)} experiments; [^{11}B–^{11}B] two-dimensional COSY correlations observed for compounds (**4**) and (**7**) are as shown for (**1a**) in Table 3. [c] $CDCl_3$ solution at 297 K. [d] Relative intensities in parentheses. [e] $\delta(^{1}H)(C_6Me_6)$ +2.12, $\delta(^{1}H)$(C–H) +3.73, $\delta(^{1}H)$(C–Me) +1.61. [f] $\delta(^{1}H)(C_6Me_6)$ +2.12, $\delta(^{1}H)$(C–H) +3.76, $\delta(^{1}H)$(C–Me) +1.69. [g] Identification of 3 substituent as Cl not unequivocally confirmed; a second possibility could in principle be OH.

available instrumentation, the general techniques and the techniques of [^{11}B–^{11}B]-COSY[48] and ^{1}H-{^{11}B}[49] spectroscopy being essentially as described and illustrated in other recent papers describing n.m.r. work in our laboratories.[50–53] Chemical shifts (δ) are given in p.p.m. positive to high frequency (low field) of Ξ 100 ($SiMe_4$) for ^{1}H, and Ξ 31.083 971 MHz (nominally $BF_3 \cdot OEt_2$ in $CDCl_3$) for ^{11}B, Ξ being defined as in ref. 54.

Reaction of [{Ru(pcym)Cl_2}$_2$] *with* [Htmnd][5,6-Me_2-5,6-$C_2B_8H_9$].—A sample of tmnd, also known as 'proton sponge' (183 mg, 0.806 mmol), was added to a degassed solution of 5,6-$Me_2C_2B_8H_{10}$ (61 mg, 0.403 mmol) in dichloromethane (40 cm^3) and stirred for 10 min at room temperature to generate a yellow solution of [Htmnd][5,6-$Me_2C_2B_8H_9$]. The compound [{Ru(pcym)Cl_2}$_2$] (123 mg, 0.20 mmol) was then added and the solution stirred for a further 2 h during which time the initially red-brown solution changed to yellow. The reaction mixture was filtered over silica (type GF 254) with CH_2Cl_2. The solvent was removed (rotary evaporator, 40 °C, water pump) to yield an orange-yellow solid identified as [2,4-Me_2-1-(pcym)-'*isonido*'-1,2,4-$RuC_2B_8H_8$)] (**1a**) (46 mg, 29.9%) [Found: C, 44.9; H 6.9. $C_{14}H_{28}B_8Ru$ requires C, 43.9; H, 7.3%; *m*/*z*(max.) 388; $^{12}C_{14}{}^{1}H_{28}{}^{11}B_8{}^{104}Ru$ requires 388]. Crystals suitable for a single-crystal *X*-ray diffraction analysis were grown by slow evaporation of a $CHCl_3$ solution. Washing the silica with MeCN gave a small amount of a blue compound which was found by ^{11}B n.m.r. spectroscopy to contain no boron. This was not characterized further.

Reaction of [{Ru(hmb)Cl_2}$_2$] *with* [Htmnd][5,6-Me_2-5,6-$C_2B_8H_9$].—A sample of tmnd (150 mg, 0.70 mmol) was added to a degassed solution of 5,6-$Me_2C_2B_8H_{10}$ (50 mg, 0.33 mmol) in dichloromethane (40 cm^3) and stirred for 10 min at room temperature to generate a yellow solution of [Htmnd][5,6-$Me_2C_2B_8H_9$]. The compound [{Ru(hmb)Cl_2}$_2$] (110 mg, 0.165 mmol) was added and the resulting solution stirred for a further 2.5 h, during which time the initially red solution changed to yellow. The reaction mixture was filtered over silica (type GF 254) with CH_2Cl_2. The solvent was reduced to a volume of *ca.* 5 cm^3 (rotary evaporator, 40 °C, water pump), and applied to preparative t.l.c. plates, which were then developed with n-hexane–CH_2Cl_2 (40:60) as the liquid phase. This gave one major band, which was isolated as a yellow crystalline solid, identified as [2,4-Me_2-1-(hmb)-'*isonido*'-1,2,4-$RuC_2B_8H_8$] (**1b**) (13 mg, 9.6%) (R_f = 0.45) [Found: C, 46.2; H, 7.8; B, 20.3. $C_{16}H_{32}B_8Ru$ requires C, 46.6; H, 7.8; B 21.0%; *m*/*z*(max.) 416; $^{12}C_{16}{}^{1}H_{32}{}^{11}B_8{}^{104}Ru$ requires 416]. Several other minor yellow bands were present, which were found by ^{11}B n.m.r. spectroscopy to be very weak in boron content and to contain several compounds. These were not characterized due to their small yields.

Thermolysis of [2,4-Me_2-1-(pcym)-'*isonido*'-1,2,4-$RuC_2B_8H_8$], (**1a**).—A sample of (**1a**) in the bottom of a n.m.r. tube (5 mm outside diameter) was heated under nitrogen to 400 °C, whereupon the orange solid melted, boiled and condensed as a yellow solid at the top of the tube; t.l.c. in CH_2Cl_2 indicated the reaction to have proceeded quantitatively to give [2,3-Me_2-1-(pcym)-*closo*-1,2,3-$RuC_2B_8H_8$] (**2a**) as the sole product [Found: C, 41.1; H, 6.5. $C_{14}H_{28}B_8Ru \cdot 0.5\ CH_2Cl_2$ requires C, 40.9; H, 6.9%; *m*/*z*(max.) 388, $^{12}C_{14}{}^{1}H_{28}{}^{11}B_8{}^{104}Ru$ requires 388]. Crystals suitable for a single-crystal *X*-ray analysis were grown by slow evaporation of an n-hexane–CH_2Cl_2 solution.

Reaction of [{Ru(pcym)Cl_2}$_2$] *with* $[NEt_3H]_2[B_{10}H_{10}]$.—The compound [{Ru(pcym)Cl_2}$_2$] (200 mg, 0.327 mmol) and $[NEt_3H]_2[B_{10}H_{10}]$ (408 mg, 1.265 mmol) were stirred together in dichloromethane (40 cm^3) for 20 min, during which time the initially brown solution changed to orange. The solution was then filtered over silica with CH_2Cl_2 to remove unreacted $[NEt_3H]_2[B_{10}H_{10}]$. The solvent was removed (rotary evaporator, 40 °C, water pump) to yield an orange crystalline solid identified as [1-(pcym)-*isocloso*-1-$RuB_{10}H_{10}$] (**3a**) (202 mg, 87.4%) [Found: C, 33.6; H, 6.8; B, 29.9. $C_{10}H_{24}B_{10}Ru$ requires C, 34.0; H, 6.8; B, 30.6%; *m*/*z*(max.) 358; $^{12}C_{10}{}^{1}H_{24}{}^{11}B_{10}{}^{104}Ru$ requires 358]. Crystals of (**3a**) suitable for a single-crystal *X*-ray diffraction analysis were grown by slow cooling of a hot dichloromethane solution.

Reaction of [{Ru(hmb)Cl_2}$_2$] *with* [Htmnd][5(or 6)-Me-5,6-$C_2B_8H_{10}$].—A sample of tmnd (204 mg, 0.952 mmol) was added to a degassed solution of 5(or 6)-Me-5,6-$C_2B_8H_{11}$ (65 mg, 0.475 mmol) in dichloromethane (20 cm^3), and the resulting mixture stirred at room temperature for 5 min to give a yellow solution of [Htmnd][5(or 6)-Me-5,6-$C_2B_8H_{10}$]. The compound [{Ru(hmb)Cl_2}$_2$] (100 mg, 0.15 mmol) was then added, and the solution stirred for a further 2.5 h, during which time the initially red solution changed to orange. The reaction mixture was filtered over silica with CH_2Cl_2 to remove chromatographically immobile components. The solvent was reduced to *ca.* 5 cm^3 (rotary evaporator, 40 °C, water pump) and the liquid residue

Table 11. Measured ^{11}B and ^{1}H n.m.r. data for [9-X-5-(hmb)-*nido*-5-RuB_9H_{12}] (**9**)[a] in $CDCl_3$ solution at 297 K

Assignment[b]	δ(^{11}B)/p.p.m.[c] [^1J(^{11}B–^1H)/Hz]	δ(^1H)[c,d]	Observed [^{11}B–^{11}B] two-dimensional COSY correlations[e]
6	+24.4 (1 B)[f]	+4.44 (1 H)	2w
1	+18.0 (1 B) [130]	+3.45 (1 H)	2s, 3m, 4w, 10s
8	−10.2 (1 B)[f]	+2.28 (2 H)	3w, 4w(?)
3	+1.5 (1 B) [134]		1m, 2w, 4m, 7w(?), 8w
10	−17.4 (1 B) [132]	+1.70 (1 H)	1s, 4w
9	+20.1 (1 B)[g]		4s
2	−23.6 (1 B) [136]	−0.09 (1 H)	1s, 3w, 6w, 7w
7	+5.8 (1 B) [124]	+3.80 (1 H)	2w, 3w(?)
4	−36.4 (1 B) [139]	+0.94 (1 H)	1w, 3m, 8w(?), 9s, 10w
H (5,6)		−14.68 (1 H)	
H (6,7)		−2.43 (1 H)	
H (8,9)		−1.31 (1 H)	
H (9,10)		−0.94 (1 H)	

[a] The identity of the substituent is uncertain (see text). [b] Assignments based on [^{11}B–^{11}B] COSY and ^1H{^{11}B(selective)} experiments. [c] Relative intensities in parentheses. [d] δ(^1H)(C_6Me_6) +2.16. [e] Measured under conditions of {^1H(broad-band noise)} decoupling; s = strong, m = medium, w = weak. [f] Unresolved. [g] Site of substituent X.

Table 12. Crystallographic data for compounds (**1a**), (**2a**) and (**3a**)

Crystal data	(**1a**)	(**2a**)	(**3a**)
Formula	$C_{14}H_{28}B_8Ru$	$C_{14}H_{28}B_8Ru$	$C_{10}H_{24}B_{10}Ru$
M	383.93	383.93	353.48
System	Orthorhombic	Monoclinic	Orthorhombic
a/pm	827.5(1)	879.7(1)	787.8(1)
b/pm	1 066.0(1)	1 527.7(2)	1 417.0(2)
c/pm	2 154.4(2)	1 414.3(1)	3 019.9(4)
β/°	—	92.90(1)	—
U/nm^{-3}	1.9004(3)	1.9006(3)	3.3639(7)
Z	4	4	4
Space group	$P2_12_12_1$	$P2_1/n$	*Pbca*
D_c/g cm^{-3}	1.34	1.34	1.395
μ/cm^{-1}	7.27	7.27	4.08
F(000)	784	784	712
Data collection			
Scan type	ω—2θ	ω	ω
Scan width (° + α-doublet splitting)	2.0	1.0	1.0
Scan speed/° min^{-1}	2.0—29.3	2.0—29.3	2.0—29.3
$2\theta_{min., max.}$/°	4.0, 50.0	4.0, 50.0	4.0, 50.0
Total data collected	2 066	3 797	3 485
No. observed [$I > 2.0\sigma(I)$]	1 890	3 382	2 397
Refinement			
g	0.0002	0.0002	0.0003
R	0.0232	0.0677	0.0355
R′	0.0259	0.0802	0.0372
No. of parameters	244	274	228

applied to preparative t.l.c. plates. Elution with n-hexane–CH_2Cl_2 (30:70) gave one major and two minor orange-yellow bands. These were [6-(hmb)-*nido*-6-RuB_9H_{13}] (**6**) (R_f = 0.70) (2 mg, *ca.* 1%) (identified by n.m.r. spectroscopy) (*cf.* ref. 7), [4-Me-1-(hmb)-1,2,4-$RuC_2B_8H_9$] (**4**) (R_f = 0.65) (65 mg, 54.3%) [Found: C, 43.6; H, 7.0. $C_{15}H_{30}B_8Ru$·0.5CH_2Cl_2 requires C, 42.3; H, 7.1%; *m*/*z*(max.) 403; $^{12}C_{15}{}^1H_{30}{}^{11}B_8{}^{104}Ru$ requires 402], and a compound (R_f = 0.50) tentatively identified as a 9-substituted *nido*-5-ruthenadecaborane, [9-X-5-(hmb)-*nido*-5-RuB_9H_{12}] (**9**) (*ca.* 1 mg, < 1%) (n.m.r. properties summarized in Table 11). Several other yellow bands were also revealed by chromatography but were not present in sufficient amounts to permit characterization. Although all the compounds isolated were air-stable, compound (**4**) reacted slowly in $CDCl_3$ solution over a period of several weeks to give a compound formulated as [3-Cl-4-Me-1-(hmb)-1,2,4-$RuC_2B_8H_8$] (**7**) as the major reaction product.

Thermolysis of [4-Me-1-(hmb)-'*isonido*'-1,2,4-$RuC_2B_8H_9$] (**4**).—Under conditions identical to those described above for compound (**1a**) a sample of (**4**) was thermolysed. The reaction proceeded with slight decomposition. T.l.c., eluting with CH_2Cl_2, indicated a single yellow product (R_f = 0.70). The residue from the reaction was dissolved in CH_2Cl_2, filtered over silica with CH_2Cl_2, and the solvent was removed (rotary evaporator, 40 °C, water pump) to give [2-Me-1-(hmb)-*closo*-1,2,3-$RuC_2B_8H_9$] (**8**) as a yellow, air-stable, crystalline solid which was characterized by n.m.r. spectroscopy.

Table 13. Atomic co-ordinates (× 10^4) for compound (**1a**)

Atom	*x*	*y*	*z*
Ru(1)	3 618.1(3)	−1 067.3(2)	3 566.4(1)
C(2)	3 487(5)	−158(4)	4 443(2)
C(21)	2 091(7)	−396(6)	4 876(2)
C(4)	3 743(5)	1 117(4)	4 183(2)
C(41)	2 481(8)	2 118(5)	4 275(3)
C(5)	2 980(4)	−3 096(2)	3 627(1)
C(6)	3 672(4)	−2 837(2)	3 051(1)
C(7)	2 992(4)	−1 927(2)	2 666(1)
C(8)	1 618(4)	−1 275(2)	2 858(1)
C(9)	925(4)	−1 533(2)	3 434(1)
C(10)	1 606(4)	−2 444(2)	3 819(1)
C(51)	3 735(12)	−4 138(5)	4 031(3)
C(81)	759(7)	342(5)	2 416(3)
C(82)	−557(8)	−1 052(7)	2 061(4)
C(83)	1 818(10)	353(8)	1 999(4)
B(3)	5 511(6)	−254(4)	3 089(2)
B(5)	5 159(6)	−959(5)	4 446(2)
B(6)	6 347(5)	−967(5)	3 732(3)
B(7)	4 546(6)	1 011(4)	3 428(2)
B(8)	5 131(8)	618(5)	4 745(2)
B(9)	6 736(6)	631(5)	3 543(3)
B(10)	5 683(7)	1 524(5)	4 105(3)
B(11)	6 775(6)	165(5)	4 327(3)
H(3)	5 872(55)	− 514(41)	2 589(20)
H(7)	4 129(55)	1 827(41)	3 124(19)
H(6)	7 103(51)	−1 776(39)	3 698(17)
H(5)	5 268(63)	−1 791(48)	4 729(21)
H(8)	4 953(71)	785(53)	5 301(26)
H(9)	7 845(62)	1 279(48)	3 338(23)
H(10)	6 010(70)	2 599(48)	4 234(25)
H(11)	7 983(57)	58(45)	4 602(21)

Table 14. Atomic co-ordinates (× 10^4) for compound (**2a**)

Atom	*x*	*y*	*z*
Ru(1)	2 944.2(6)	2 023.9(4)	1 832.6(4)
C(2)	1 114(9)	2 554(6)	2 549(6)
C(21)	1 280(12)	3 147(7)	3 380(7)
C(3)	2 000(8)	1 298(5)	687(5)
C(31)	2 953(11)	791(6)	−16(6)
B(4)	701(9)	1 538(7)	2 566(5)
B(5)	838(11)	2 916(6)	1 526(7)
B(6)	1 318(10)	2 234(6)	438(6)
B(7)	1 225(11)	821(7)	1 524(7)
B(8)	−653(11)	2 362(8)	2 093(7)
B(9)	136(11)	1 269(6)	523(7)
B(10)	−630(11)	1 309(8)	1 593(7)
B(11)	−568(10)	2 273(7)	843(7)
C(4)	4 823(8)	1 381(6)	2 727(6)
C(5)	4 503(10)	2 185(7)	3 084(6)
C(6)	4 544(11)	2 959(6)	2 565(8)
C(7)	4 894(10)	2 959(6)	1 615(8)
C(8)	5 205(10)	2 107(7)	1 217(7)
C(9)	5 147(8)	1 347(6)	1 757(6)
C(41)	4 787(12)	542(7)	3 315(8)
C(42)	3 858(19)	614(12)	4 151(11)
C(43)	6 389(21)	212(13)	3 481(14)
C(71)	5 079(13)	3 751(8)	1 012(11)
C(72)	6 449(18)	4 283(13)	1 354(20)
C(73)	3 787(21)	4 357(16)	781(21)
C(74)	4 432(25)	3 927(22)	38(13)
H(4)	456(26)	959(24)	3 194(24)
H(5)	594(27)	3 520(25)	1 484(25)
H(6)	1 634(27)	2 592(25)	−122(25)
H(7)	1 561(26)	109(24)	1 530(24)
H(8)	−1 648(26)	2 448(24)	2 625(24)
H(9)	−283(27)	837(24)	−214(24)
H(10)	−1 593(27)	877(24)	1 668(24)
H(11)	−1 277(27)	2 563(25)	373(25)

Table 15. Atomic co-ordinates (× 10^4) for compound (**3a**)

Atom	*x*	*y*	*z*
Ru(1)	528.8(3)	699.4(2)	1 365.3(1)
C(1)	1 691(3)	1 943(2)	1 766(1)
C(2)	3 038(3)	1 397(2)	1 611(1)
C(3)	3 216(3)	1 230(2)	1 158(1)
C(4)	2 047(3)	1 610(2)	861(1)
C(5)	700(3)	2 157(2)	1 016(1)
C(6)	522(3)	2 324(2)	1 469(1)
C(11)	1 504(7)	2 149(4)	2 263(1)
C(41)	2 216(6)	1 469(4)	353(1)
C(42)	3 337(9)	660(5)	226(2)
C(43)	2 812(10)	2 416(6)	151(2)
B(2)	−1 818(6)	615(4)	1 044(2)
B(3)	1 374(8)	−424(4)	1 764(2)
B(4)	−2 147(6)	406(4)	1 612(2)
B(5)	−658(7)	−388(4)	901(2)
B(6)	834(8)	−887(4)	1 243(2)
B(7)	−658(7)	80(4)	1 949(2)
B(8)	−2 745(7)	−439(4)	1 179(2)
B(9)	−130(9)	−1 275(4)	1 762(2)
B(10)	−2 219(8)	834(4)	1 718(2)
B(11)	−1 284(9)	−1 347(4)	1 255(2)
H(2)	−2 390(54)	1 245(30)	801(13)
H(3)	2 825(58)	−470(30)	1 963(15)
H(4)	−2 744(69)	972(35)	1 719(17)
H(5)	−282(61)	−428(34)	551(18)
H(6)	2 128(59)	−1 254(33)	1 053(15)
H(7)	−539(50)	269(34)	2 282(16)
H(8)	−4 039(61)	−644(29)	1 045(17)
H(9)	67(67)	−1 970(39)	1 951(18)
H(10)	−3 293(54)	−1 163(29)	1 909(14)
H(11)	−1 546(51)	−2 091(28)	1 114(12)

X-*Ray Crystallography*.—All crystallographic measurements were made on a Nicolet P3/F diffractometer operating in either the ω—2θ scan mode for (**1a**) or the ω scan mode for (**2a**) and (**3a**) using graphite-monochromatised Mo-K_α radiation (λ = 71.069 pm) following a standard procedure.[55] All three data sets were corrected for absorption empirically once their respective structures had been determined.[56] All three compounds were solved *via* standard heavy-atom methods and were refined by full-matrix least squares using the SHELX program system.[57] For the three compounds all non-hydrogen atoms were assigned anisotropic thermal parameters; phenyl rings were treated as rigid bodies with idealized hexagonal symmetry (C–C 139.5 pm) for (**1a**) and (**3a**) but not for (**2a**) where disorder was found between the isopropyl and methyl substituents of the *p*-cymene ligand. All methyl, methylene and phenyl hydrogen atoms were included in calculated positions [except for the hydrogen atoms associated with the disordered *p*-cymene ligand in (**2a**) which were not included] and these were assigned to an overall isotropic thermal parameter. In all three cases boron-associated hydrogen atoms were located in Fourier difference syntheses and were freely refined with individual isotropic thermal parameters. The weighting scheme $w = [\sigma^2(F_o) + g(F_o)^2]^{-1}$ was used in all three cases where the parameter *g* was included in the refinement in order to obtain satisfactory agreement analyses. All relevant crystal data, data collection and structure refinement parameters are listed in Table 12. Atomic co-ordinates for (**1a**)—(**3a**) are listed in Tables 13—15 respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters and remaining bond lengths and angles.

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