Syntheses and Molecular Structures of Two Boride Cluster Anions: Octahedral $[Rh_2Ru_4(CO)_{16}B]^-$ and Double-prismatic $[Rh_3Ru_6(CO)_{23}B_2]^-$†

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The compounds $[N(PPh_3)_2][Rh_2Ru_4(CO)_{16}B]$ **1** and $[N(PPh_3)_2][Rh_3Ru_6(CO)_{23}B_2]$ **3** were isolated after treating $[N(PPh_3)_2][Ru_3(CO)_9BH_4]$ with $[\{Rh(CO)_2Cl\}_2]$ for 1 h. The neutral cluster $[Rh_2Ru_4H(CO)_{16}B]$ **2** was also isolated. The crystal structure of **1** has been determined: monoclinic, space group $P2_1/n$, $a = 16.370(5)$, $b = 10.330(3)$, $c = 33.532(9)$ Å, $\beta = 96.33(2)°$, $Z = 4$. The core of **1** is octahedral with the two rhodium atoms in a *trans* arrangement; the boron atom is sited at the centre of the octahedron. The crystal structure of **3** has also been determined: triclinic, space group $P\bar{1}$, $a = 10.666(2)$, $b = 17.540(4)$, $c = 18.658(3)$ Å, $\alpha = 91.06(2)$, $\beta = 104.15(2)$, $\gamma = 92.54(2)°$, $Z = 2$. The cluster core consists of two, face-sharing prisms with one square face capped by a rhodium carbonyl fragment; each prismatic cavity contains a boron atom and B–B separation is 1.80(2) Å. The structure of cluster **3** is novel both as far as the environment of the boron atoms and the geometry of the metal skeleton are concerned but it is related to a series of previously characterised carbido clusters.

The encapsulation of an atom of a p-block element within a transition-metal cage is now a familiar phenomenon.[1-6] For a p-block atom within a cage of six metal atoms the environments of both the octahedron and trigonal prism have been exemplified. For boron, octahedral borides,[1,2,7] including $[Ru_6H(CO)_{17}B]$,[8,9] $[Fe_4Rh_2(CO)_{16}B]^-$ [10-12] and $[Fe_3Rh_3H(CO)_{16}B]$,[12] have now been known for a few years. Recently, we showed with the structural characterisation of $[Ru_6H_2(CO)_{18}B]^-$ that a boron atom may also occupy a trigonal-prismatic cavity.[13,14] The formation in the *same* reaction pot of both the octahedral anion $[Ru_6(CO)_{17}B]^-$ and the trigonal-prismatic anion $[Ru_6H_2(CO)_{18}B]^-$ was a significant result.[13,14] Previously, a preference for a trigonal-prismatic M_6E cage in which M is a Group 8 metal atom had been observed when the interstitial atom, E, was relatively sterically demanding, for example E = P.[1,15,16] Here we present a second example of a reaction in which both octahedral and trigonal-prismatic boron-containing clusters are assembled in the same reaction although, as will be discussed, the origin of the octahedral species is not clear cut.

Experimental

General.—Fourier-transform NMR spectra were recorded on a Bruker WM 250 or AM 400 spectrometer: ^1H shifts are reported with respect to δ 0 for $SiMe_4$, ^{11}B with respect to δ 0 for $F_3B{\cdot}OEt_2$; all downfield chemical shifts are positive. Infrared spectra were recorded on a Perkin-Elmer FT 1710 spectrophotometer, FAB (fast atom bombardment) mass spectra on Kratos instruments; with 3-nitrobenzyl alcohol as matrix.

All reactions were carried out under argon by using standard Schlenk techniques. Solvents were dried over suitable reagents and freshly distilled under N_2 before use. Separations were carried out by thin-layer plate chromatography with Kieselgel 60-PF-254 (Merck). The compound $[\{Rh(CO)_2Cl\}_2]$ was used as received (Aldrich); $[N(PPh_3)_2][Ru_3(CO)_9BH_4]$[9] was prepared as previously described. Yields for **1** and **2** are based on a reactant:product ratio of 1:1 with respect to the Ru_3-starting cluster; that for **3** assumes a 2:1 ratio.

Reaction of $[N(PPh_3)_2][Ru_3(CO)_9BH_4]$ *with* $[\{Rh(CO)_2Cl\}_2]$.—The compound $[\{Rh(CO)_2Cl\}_2]$ (39 mg, 0.1 mmol) was dissolved in CH_2Cl_2 (5 cm^3) and added to a solution of $[N(PPh_3)_2][Ru_3(CO)_9BH_4]$ (100 mg, 0.1 mmol) in CH_2Cl_2 (5 cm^3). The solution changed from orange-red to dark brown immediately. After stirring for 1 h the reaction mixture was filtered through a medium sinter and solvent was removed. Separation by TLC eluting first with hexane gave three yellow fractions, $[Ru_3(CO)_9BH_5]$,[17] $[Ru_3(CO)_9(B_2H_6)]$[18] and $[Ru_4H(CO)_{12}(BH_2)]$,[19,20] followed by red-brown $[Rh_2Ru_4H(CO)_{16}B]$ **2** (≈10% yield). Most material remained on the baseline and was separated by eluting again with CH_2Cl_2–hexane (2:1). Three fractions were collected. First, brown $[N(PPh_3)_2][Rh_2Ru_4(CO)_{16}B]$ **1**‡ (24 mg, 15% yield), secondly, a green fraction (5 mg) which remains unidentified, and thirdly red $[N(PPh_3)_2][Rh_3Ru_6(CO)_{23}B_2]$ **3** (16 mg, 15% yield).

Compound **2**: NMR ($CDCl_3$, 298 K), ^1H (400 MHz), δ −17.81 (s, Ru–H–Ru); ^{11}B (128 MHz), δ +191.4 (t, J_{RhB} = 26 Hz); IR (CH_2Cl_2, cm^{-1}) ν_{CO} 2081m, 2060vs, 2023m, 1718w and 1685w; FAB mass spectrum, *m/z* 1069 (P^+) with six CO losses (calc. for $^{12}C_{16}{}^1H_1{}^{11}B_1{}^{16}O_{16}{}^{103}Rh_2{}^{101}Ru_4$ 1070).

Compound **1**:‡ NMR ($CDCl_3$, 298 K), ^1H (400 MHz), δ 7.7–7.4 (m); ^{11}B (128 MHz), δ +193.4 (t, J_{RhB} = 26 Hz); IR (CH_2Cl_2, cm^{-1}) ν_{CO} 2081vw, 2026vs, 2009m and 1964w; FAB mass spectrum, *m/z* 1069 (P^-) with 11 CO losses observed (calc. for $^{12}C_{16}{}^{11}B_1{}^{16}O_{16}{}^{103}Rh_2{}^{101}Ru_4$ 1069).

Compound **3**: NMR (298 K), ^1H (400 MHz, $CDCl_3$), δ 7.7–7.4 (m); ^{11}B (128 MHz, CD_2Cl_2), δ +164.3 ($w_{\frac{1}{2}}$ ≈ 70) and +150.0 ($w_{\frac{1}{2}}$ ≈ 70 Hz) with relative integrals 1:1; IR (CH_2Cl_2, cm^{-1}) ν_{CO} 2085vw, 2048vs, 2028m, 2002w(sh) and 1806w(br); FAB mass spectrum, *m/z* 1580 (P^-) with 11 CO losses observed (calc. for $^{12}C_{23}{}^{11}B_2{}^{16}O_{23}{}^{103}Rh_3{}^{101}Ru_6$ 1581).

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

‡ We first observed compound **1** as the major product in the reaction of $[N(PPh_3)_2][Ru_4H(CO)_{12}(BH_2)]$ with $[\{Rh(CO)_2Cl\}_2]$.[21]

Crystal Structure Determinations.—Crystallographic data for compounds **1** and **3** are collected in Table 1. Crystals of both were mounted on glass fibres with epoxy cement. Preliminary photographic data showed $2/m$ and $\bar{1}$ Laue symmetry for **1** and **3** respectively. Systematic absences in the diffraction data uniquely identified the space group for **1**, while for **3** the results of refinement indicated a preference for the centrosymmetric alternative. Semiempirical corrections for absorption were applied to the data. The structures were solved by direct methods.

For compound **1**, a difference map prepared after all non-hydrogen atoms had been located showed the presence of a two-site disordered M_6 core structure. The six highest peaks in an intermediate Fourier-difference synthesis formed a second octahedral cluster and was interpreted as the core of the minor, disordered orientation of the main structure. Occupancies were refined with all atoms of each cluster tied to a common variable and the sum of the occupanices for the two was fixed at unity. The refined occupancy ratio was 0.893:0.107. None of the CO ligands was located in the minority core. Consequently, for the minority core, the location of the Rh atoms could not be determined and all of the minority metal atom positions were refined with ruthenium scattering factors.

All non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were assigned idealised positions. All computations used the SHELXTL-PC software.[22] Atomic coordinates for the anions of **1** and **3** are given in Tables 2 and 4, respectively.

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

Results and Discussion

The triruthenaborane cluster $[Ru_3(CO)_9BH_5]$ and its conjugate base $[Ru_3(CO)_9BH_4]^-$ are suitable precursors for heterometallic boron-containing clusters and we have reported the formation of several clusters with Ru_3MB butterfly frameworks (M = Mo,[18] W,[18] Fe[9] or Rh[23]). In solution, $[Ru_3(CO)_9BH_5]$ and $[Ru_3(CO)_9BH_4]^-$ undergo spontaneous cluster assembly to form tetra- and hexa-nuclear boron-containing clusters,[9,24] although, interestingly, a reaction aimed at introducing a $Ru(\eta\text{-}C_5Me_5)$ unit resulted in the formation of an unusual spiked-butterfly cluster, $[Ru_5H_2(CO)_{13}(\eta\text{-}C_5Me_5)(BH_2)]$.[24]

The compound $[N(PPh_3)_2][Ru_3(CO)_9BH_4]$ reacts readily with $[\{Rh(CO)_2Cl\}_2]$. The ^{11}B NMR spectrum of the crude mixture ($CDCl_3$) shows the presence of $[Ru_3(CO)_9BH_5]$[17] (two isomers,* δ +6.3 and +24.4), $[Ru_3(CO)_9(B_2H_6)]$[18] (δ +17.0), $[Ru_4H(CO)_{12}(BH_2)]$[19,20] (δ +109.9), as well as new resonances at δ +191.4, +193.4, +164.3 and +150.0. The ^{11}B NMR chemical shift is a sensitive probe into the environment of the boron atom with respect to the transition-metal framework.[25,26] From the wide range of ruthenium clusters now characterised[2,8,9,14,17–21,23,24] it is possible to assess that each of the new resonances is in a part of the NMR spectrum characteristic of a transition-metal-encapsulated boron atom. A chemical shift in the region δ +190 to +200 suggests that the boron atom is interacting with six metal atoms, either within an octahedral or trigonal-prismatic cage.[8,9,14] A further feature characteristic of such resonances is their narrow linewidth, typically $w_{\frac{1}{2}} \leqslant 20$ Hz. The shifts at δ +164.3 and +150.0 were less easily recognised, and in addition these resonances were both relatively broad with $w_{\frac{1}{2}} \approx 70$ Hz.

Chromatographic separation of the products indicated that both neutral and anionic clusters were present. Initial elution with hexane separated the known clusters $[Ru_3(CO)_9BH_5]$, $[Ru_3(CO)_9(B_2H_6)]$ and $[Ru_4H(CO)_{12}(BH_2)]$ as well as one other product **2** (^{11}B δ +191.4) whilst further elution with a more polar solvent system separated three compounds: brown **1** (^{11}B δ +193.4), a green non-boron-containing fraction, and red **3** (^{11}B δ +164.3 and +150.0, integrals 1:1). We have been unable fully to characterise the green material due to it being formed in insufficient quantity: 400 MHz ^{1}H NMR ($CDCl_3$, 298 K) δ 7.7–7.4 [m, $N(PPh_3)_2{}^+$]; IR (CH_2Cl_2, cm^{-1}) ν_{CO} 2058vs, 2044m, 2014w, 1800(br) and 1685(br); FAB mass spectrum m/z 1804 (P^-) with 13 CO losses.

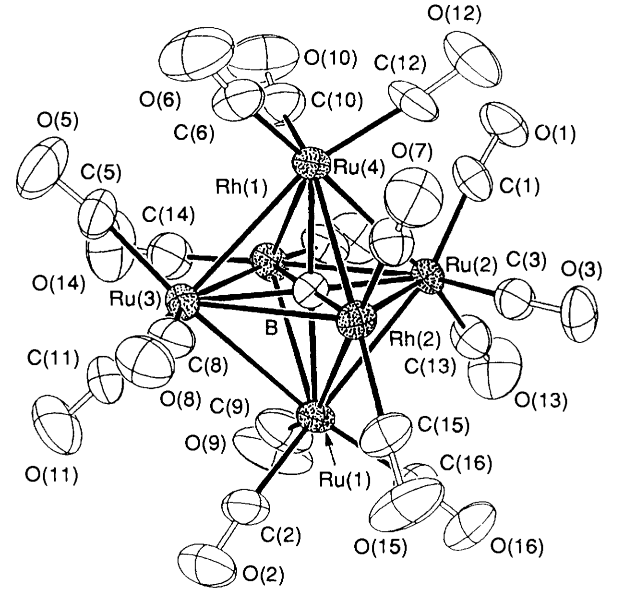

Fig. 1 Molecular structure of the anion of compound **1**

The triplet nature of each of the two resonances at δ +191.4 and +193.4 suggested the presence of two Rh–B interactions (J_{RhB} = 26 Hz in each case). This fact, in addition to the chemical shift data, led us to propose that **2** and **1** were the clusters $[Rh_2Ru_4H(CO)_{16}B]$ and $[N(PPh_3)_2][Rh_2Ru_4(CO)_{16}B]$ respectively. Mass spectral data and the appearance of a sharp resonance at δ −17.81 in the ^{1}H NMR spectrum of **2**, but not **1**, are consistent with this proposal. The presence of *two* rhodium atoms is supported by an analysis of the isotopic pattern of the parent ion in the mass spectrum of each of **1** and **2**. The ^{103}Rh–^{11}B spin–spin coupling constant of 26 Hz in each of the ^{11}B NMR spectra of clusters **1** and **2** is similar to the values observed by Fehlner and co-workers[10,12] for *cis*- (23.3 Hz) and *trans*-$[Fe_4Rh_2(CO)_{16}B]^-$ (25.8 Hz). In the case of *trans*-$[Fe_4Rh_2(CO)_{16}B]^-$, protonation leads not to $[Fe_4Rh_2H(CO)_{16}B]$ but to $[Fe_3Rh_3H(CO)_{16}B]$.[12] It is therefore interesting that both the anion of **1** and its conjugate acid **2** are produced in the same reaction pot.

A crystal of compound **1** of X-ray-diffraction quality was grown from a solution of CH_2Cl_2 layered with hexane, and the crystal structure has been determined. Atomic coordinates are collected in Table 2, and selected bond distances and angles in Table 3. The molecular structure of the anion is shown in Fig. 1; Fig. 2 shows the disordered core (see Experimental section). The hexametal core is octahedral and the boron atom resides at the centre of the cavity. Four of the metal atoms have three CO ligands and are identified as ruthenium atoms, and two, with two CO ligands each, as rhodium atoms. It is expected that the connectivity of a rhodium atom will be lower than that of a ruthenium atom. The presence of two rhodium atoms was confirmed by spectroscopic and mass spectrometric methods (see above). A satisfactory valence-electron count of 86 is obtained for **1** given a formula of $[Ru_4Rh_2(CO)_{16}B]^-$. The Ru–B and Rh–B distances are all similar, lying in the range 2.04(1)–2.09(1) Å.

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* The ^{11}B NMR spectra shifts are sensitive to solvent. We have previously reported the chemical shifts for these isomers in CD_2Cl_2: δ +2.8 and +21.0.[17]

Table 1 Crystallographic data for $[N(PPh_3)_2][Rh_2Ru_4(CO)_{16}B]$ **1** and $[N(PPh_3)_2][Rh_3Ru_6(CO)_{23}B_2]$ **3**[a]

Complex	**1**	**3**
(*a*) Crystal parameters		
Formula	$C_{52}H_{30}BNO_{16}P_2Rh_2Ru_4$	$C_{59}H_{30}B_2NO_{23}P_2Rh_3Ru_6$
M	1607.6	2119.6
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a/Å	16.370(5)	10.666(2)
b/Å	10.330(3)	17.540(4)
c/Å	33.532(9)	18.658(3)
α/°	—	91.06(2)
β/°	96.33(2)	104.15(2)
γ/°	—	92.54(2)
U/Å^3	5635.8(29)	3379.8(12)
Z	4	2
Crystal dimensions/mm	0.30 × 0.32 × 0.38	0.22 × 0.31 × 0.41
Colour	Dark red	Dark red
D_c/g cm^{-3}	1.895	2.083
μ(Mo-Kα)/cm^{-1}	17.41	21.40
T/K	296	298
Transmission (minimum, maximum)	0.622, 0.700	0.559, 0.681
(*b*) Data collection		
2θ Scan range/°	4–50	4–55
Data collected (h, k, l)	±19, ±12, +39	±13, ±21, +23
Reflections collected	10 872	7890
Independent reflections	9908	7851
Independent observed reflections [$F_o \geqslant n\sigma(F_o)$]	5082 (n = 4)	5317 (n = 5)
(*c*) Refinement		
R[b]	0.0520	0.0387
R'[c]	0.0618	0.0602
Δ/σ(maximum)	0.001	0.047
$\Delta\rho$/e Å^{-3}	0.62	1.06
N_o/N_v	7.0	6.1
Goodness of fit[d]	0.97	1.43

[a] Details in common: Siemens P4 diffractometer; graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å); three standard reflections every 197. [b] $\Sigma|F_o - F_c|/\Sigma F_o$. [c] $\Sigma(|F_o - F_c|w^{\frac{1}{2}})/\Sigma(F_o w^{\frac{1}{2}})$. [d] $[\Sigma w|F_o - F_c|^2/(N_o - N_v)]^{\frac{1}{2}}$ where N_o is the number of observations and N_v the number of variables.

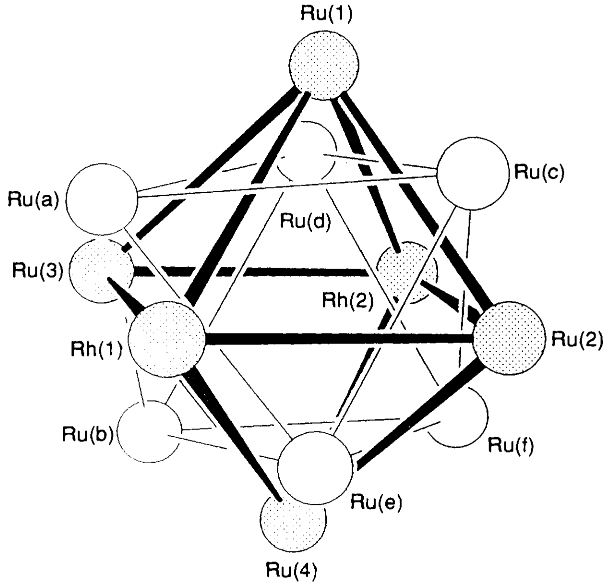

Fig. 2 The disordered M_6 core of the anion of compound **1**. Atoms 1–6 belong to the major core, a–f define the minor core

Spectroscopic data indicate that the neutral compound **2** differs from the anion of **1** only in the presence of a single cluster-bound hydrogen atom and it seems reasonable to propose that **2** also has a *trans* arrangement of rhodium atoms. That the ^1H NMR spectral signature of **2** is a sharp singlet implies that the hydrogen atom bridges a Ru–Ru rather than a Rh–Ru edge.

The identity of the third product to be isolated in moderate yield (15%) from the reaction of $[(N(PPh_3)_2][Ru_3(CO)_9BH_4]$ with $[\{Rh(CO)_2Cl\}_2]$ was not readily elucidated without the aid of a crystal structure determination. A suitable crystal of compound **3** was grown from a CH_2Cl_2 solution layered with hexane. The molecular structure of the anion is shown in Fig. 3. Atomic coordinates are listed in Table 4, and selected bond distances and angles in Table 5. The central octametal core of the anion consists of two trigonal prisms which share one square face; one external square face of the double prism is capped by the ninth metal atom. As in the case of **1**, it is not possible unambiguously to distinguish between the rhodium and ruthenium atoms in the cage. Unlike the ^{11}B NMR spectrum of **1**, that of **3** exhibits broader signals and the ^{103}Rh–^{11}B spin–spin coupling could not be resolved. In order for the cluster to bear a single negative charge (*i.e.* and be an even-valence-electron cluster species), the possible ratios of Ru : Rh atoms are 8 : 1, 6 : 3, 4 : 5, 2 : 7 or 0 : 9 corresponding to formulae $[RhRu_8(CO)_{23}B_2]^-$, $[Rh_3Ru_6(CO)_{23}B_2]^-$, $[Rh_5Ru_4(CO)_{23}B_2]^-$, $[Rh_7Ru_2(CO)_{23}B_2]^-$ or $[Rh_9(CO)_{23}B_2]^-$, respectively.* Simulation of the isotopic distribution of the parent ion in the mass spectrum of **3** allows the last three formulae to be ruled out, and indeed points in favour of $[Rh_3Ru_6(CO)_{23}B_2]^-$ over $[RhRu_8(CO)_{23}B_2]^-$. The disposition of the carbonyl ligands [Figs. 3 and 4(*a*)] in the structure of **3** is instructive.

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* An attempt to confirm the ratio of Ru : Rh by elemental analysis gave 3.34 : 2.04 ≈ 1.6 : 1.

Table 2 Atomic coordinates (× 10^4) for compound **1**

Atom	*x*	*y*	*z*
Rh(1)	1317.2(6)	1521.7(12)	1510.9(3)
Rh(2)	3108.8(6)	2242.0(11)	763.9(3)
Ru(1)	1946.3(7)	3853.9(10)	1087.7(3)
Ru(2)	2989.7(6)	2246.3(10)	1654.7(3)
Ru(3)	1328.5(6)	1510.3(11)	661.3(3)
Ru(4)	2584.6(7)	−20.8(10)	1148.0(3)
B	2203(8)	1894(13)	1144(4)
P(1)	7189(2)	3074(3)	1887(1)
P(2)	7196(2)	4520(3)	1112(1)
N	7134(5)	4187(8)	1566(2)
O(1)	3617(6)	307(11)	2297(3)
O(2)	1268(7)	5320(11)	342(3)
O(3)	4692(5)	3081(10)	1494(3)
O(4)	1336(7)	1761(12)	2402(3)
O(5)	457(9)	−978(13)	415(4)
O(6)	2459(10)	−2075(12)	509(4)
O(7)	4366(6)	526(11)	465(3)
O(8)	1952(7)	1843(10)	−152(3)
O(9)	626(8)	4729(14)	1586(4)
O(10)	1666(9)	−1724(13)	1677(4)
O(11)	−243(7)	2975(13)	408(4)
O(12)	4274(7)	−981(12)	1453(3)
O(13)	2826(8)	4305(13)	2278(3)
O(14)	−421(7)	705(16)	1335(4)
O(15)	3624(9)	4691(11)	377(3)
O(16)	3078(7)	6062(10)	1373(4)
C(1)	3352(7)	997(15)	2052(4)
C(2)	1515(9)	4731(13)	604(4)
C(3)	4038(8)	2729(14)	1511(4)
C(4)	1356(8)	1633(15)	2068(5)
C(5)	822(10)	−103(16)	511(5)
C(6)	2481(10)	−1264(15)	735(5)
C(7)	3891(8)	1128(14)	591(4)
C(8)	1813(8)	1757(13)	176(5)
C(9)	1090(10)	4264(18)	1403(5)
C(10)	1949(11)	−956(17)	1492(5)
C(11)	341(9)	2447(16)	520(5)
C(12)	3647(9)	−573(14)	1349(4)
C(13)	2891(9)	3556(15)	2040(4)
C(14)	245(10)	1076(17)	1385(5)
C(15)	3403(9)	3801(13)	527(4)
C(16)	2686(9)	5217(13)	1280(4)
C(111)	8855(7)	3488(12)	2055(4)
C(112)	9587(8)	3545(13)	2298(4)
C(113)	9601(9)	3300(13)	2698(5)
C(114)	8917(9)	2985(12)	2853(4)
C(115)	8173(7)	2950(12)	2624(3)
C(116)	8137(6)	3193(10)	2220(3)
C(121)	7822(7)	640(10)	1744(3)
C(122)	7783(8)	−543(11)	1548(4)
C(123)	7119(9)	−912(11)	1309(4)
C(124)	6437(8)	−132(12)	1255(4)
C(125)	6451(7)	1063(12)	1442(3)
C(126)	7148(7)	1463(10)	1681(3)
C(131)	6004(7)	2137(11)	2356(3)
C(132)	5371(8)	2296(15)	2582(4)
C(133)	5057(8)	3511(17)	2650(4)
C(134)	5387(8)	4546(15)	2482(4)
C(135)	6032(7)	4427(12)	2250(3)
C(136)	6358(6)	3209(11)	2184(3)
C(141)	7792(7)	2296(11)	793(3)
C(142)	7735(9)	1189(12)	558(4)
C(143)	6997(9)	912(13)	323(4)
C(144)	6365(9)	1732(13)	319(4)
C(145)	6411(8)	2824(13)	540(3)
C(146)	7125(6)	3147(10)	781(3)
C(151)	8509(7)	6138(10)	1356(4)
C(152)	9212(8)	6828(13)	1302(5)
C(153)	9544(8)	6721(13)	944(5)
C(154)	9195(9)	5974(14)	645(5)
C(155)	8488(8)	5277(12)	693(4)
C(156)	8143(6)	5344(11)	1049(3)
C(161)	6401(8)	6353(13)	612(4)
C(162)	5743(9)	7147(13)	481(4)
C(163)	5067(9)	7167(13)	685(4)
C(164)	5037(8)	6435(13)	1015(4)
C(165)	5686(7)	5645(12)	1143(4)
C(166)	6371(7)	5579(10)	942(3)

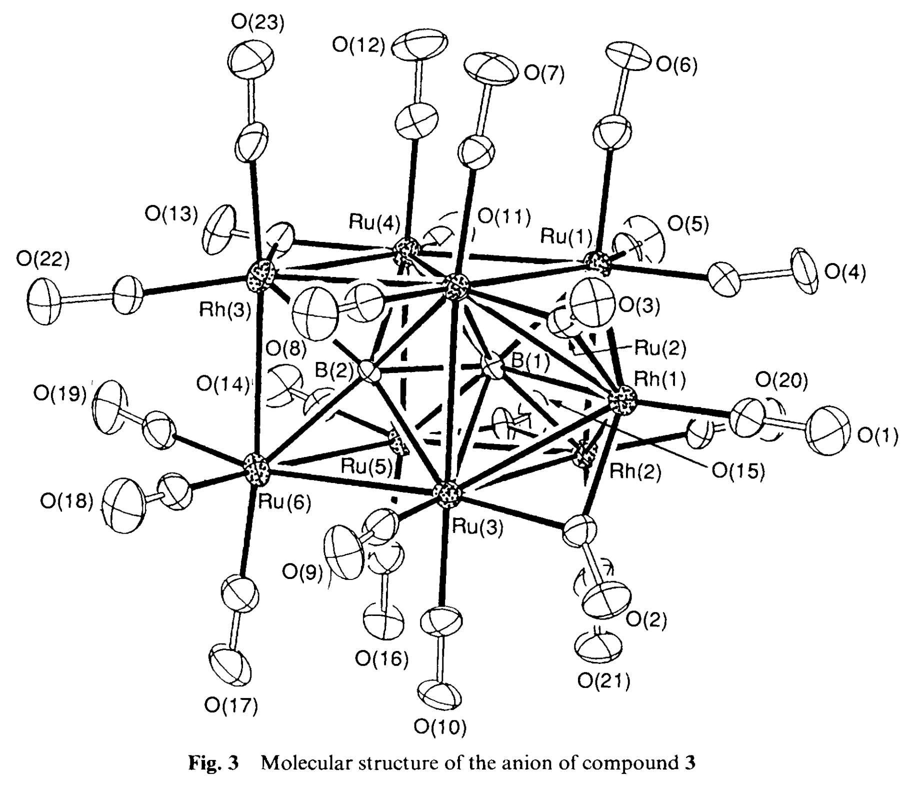

Fig. 3 Molecular structure of the anion of compound **3**

Table 3 Selected bond distances (Å) and angles (°) for the anion in compound **1** (majority structure only)

Rh(1)–Ru(1)	3.033(2)	Rh(1)–Ru(2)	2.828(2)
Rh(1)–Ru(3)	2.851(2)	Rh(1)–Ru(4)	2.980(2)
Rh(2)–Ru(1)	2.833(2)	Rh(2)–Ru(2)	3.015(2)
Rh(2)–Ru(3)	2.994(2)	Rh(2)–Ru(4)	2.847(2)
Ru(1)–Ru(2)	2.928(2)	Ru(1)–Ru(3)	2.934(2)
Ru(2)–Ru(4)	2.926(2)	Ru(3)–Ru(4)	2.942(2)
Rh(1)–B	2.04(1)	Rh(2)–B	2.09(1)
Ru(1)–B	2.07(1)	Ru(2)–B	2.06(1)
Ru(3)–B	2.08(1)	Ru(4)–B	2.07(1)
Ru(1)–Rh(1)–Ru(2)	59.8(1)	Ru(1)–Rh(1)–Ru(3)	59.7(1)
Ru(2)–Rh(1)–Ru(3)	93.4(1)	Ru(1)–Rh(1)–Ru(4)	86.9(1)
Ru(2)–Rh(1)–Ru(4)	60.4(1)	Ru(3)–Rh(1)–Ru(4)	60.5(1)
Ru(1)–Rh(2)–Ru(2)	60.0(1)	Ru(1)–Rh(2)–Ru(3)	60.4(1)
Ru(2)–Rh(2)–Ru(3)	86.9(1)	Ru(1)–Rh(2)–Ru(4)	93.5(1)
Ru(2)–Rh(2)–Ru(4)	59.8(1)	Ru(3)–Rh(2)–Ru(4)	60.4(1)
Rh(1)–Ru(1)–Rh(2)	89.4(1)	Rh(1)–Ru(1)–Ru(2)	56.6(1)
Rh(2)–Ru(1)–Ru(2)	63.1(1)	Rh(1)–Ru(1)–Ru(3)	57.1(1)
Rh(2)–Ru(1)–Ru(3)	62.5(1)	Ru(2)–Ru(1)–Ru(3)	89.6(1)
Rh(1)–Ru(2)–Rh(2)	89.9(1)	Rh(1)–Ru(2)–Ru(1)	63.6(1)
Rh(2)–Ru(2)–Ru(1)	56.9(1)	Rh(2)–Ru(2)–Ru(4)	57.2(1)
Ru(1)–Ru(2)–Ru(4)	89.9(1)	Rh(1)–Ru(2)–Ru(4)	62.4(1)
Rh(1)–Ru(3)–Rh(2)	89.9(1)	Rh(1)–Ru(3)–Ru(1)	63.2(1)
Rh(2)–Ru(3)–Ru(1)	57.1(1)	Rh(2)–Ru(3)–Ru(4)	57.3(1)
Rh(1)–Ru(3)–Ru(4)	61.9(1)	Ru(1)–Ru(3)–Ru(4)	89.5(1)
Rh(1)–Ru(4)–Rh(2)	90.2(1)	Rh(1)–Ru(4)–Ru(2)	57.2(1)
Rh(2)–Ru(4)–Ru(2)	62.9(1)	Rh(1)–Ru(4)–Ru(3)	57.6(1)
Rh(2)–Ru(4)–Ru(3)	62.3(1)	Ru(2)–Ru(4)–Ru(3)	89.5(1)
Ru(1)–B–Ru(4)	172.0(7)	Ru(2)–B–Ru(3)	175.0(7)
Rh(1)–B–Rh(2)	179.0(6)		

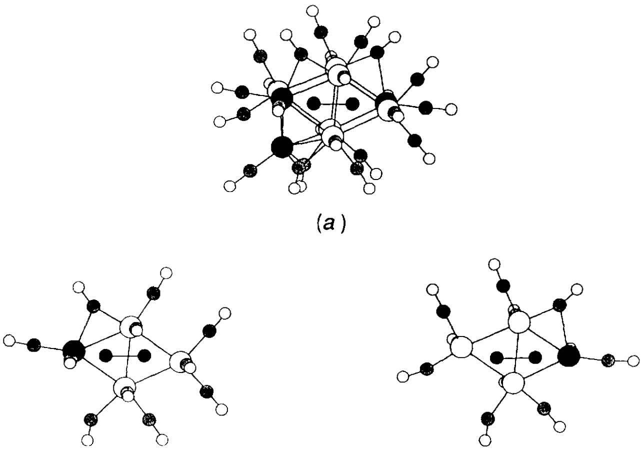

Fig. 4 (*a*) View of the structure of compound **3** from above; the proposed sites of the rhodium atoms are shown as large filled circles and the ruthenium atoms are represented by large open circles. (*b*) The top face of **3**, with the two boron atoms present but the capping metal atom removed. (*c*) The bottom face of **3**, with the two boron atoms present but the capping metal atom removed. The same orientation of the cluster is used in each scheme

First, note that the capping atom possesses only one terminal carbonyl ligand; in addition, two bridging ligands are associated with the cap. We assign this metal cap as a rhodium atom. To aid the next part of the discussion, Fig. 4(*b*) and 4(*c*) show the top and bottom faces, respectively, of the cluster with the capping {Rh(CO)} group removed. One metal atom on each rhomboidal M_4 face possesses two terminal carbonyl ligands plus one involved in a bridging interaction to the capping atom Rh(1). We then note that two metal atoms on each rhomboidal M_4 face bear three terminal carbonyl ligands each and this we take as typical of ruthenium rather than rhodium sites. The fourth metal atom per M_4 face possesses only two terminal carbonyl ligands and is additionally involved in the weaker half of a semibridging carbonyl ligand interaction. We propose therefore that the latter metal atom [*i.e.* the shaded atom in each of Fig. 4(*b*) and 4(*c*)] is assigned as a rhodium atom. Fig. 3 is labelled accordingly.

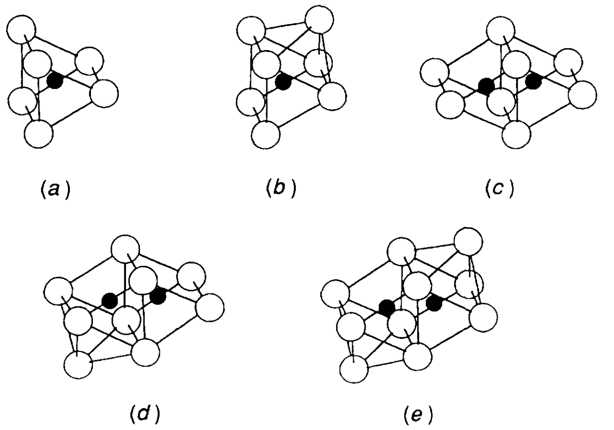

Fig. 5 Schematic representations of the M_xE_y cores of a series of trigonal and double trigonal-prismatic clusters with interstitial atoms: (*a*) $[Ru_6H_2(CO)_{18}B]^-$, (*b*) $[Ni_4Os_3(CO)_{15}C]^{2-}$ and $[Ni_7(CO)_{12}C]^{2-}$, (*c*) $[Co_6Ni_2(CO)_{16}C_2]^{2-}$, (*d*) $[Rh_3Ru_6(CO)_{23}B_2]^-$, anion of **3**, and (*e*) $[Ni_{10}(CO)_{16}C_2]^{2-}$

Each trigonal-prismatic cavity of the central {Rh_2Ru_6} core of compound **3** contains an interstitial boron atom. The metal-to-boron distances within this double trigonal-prismatic unit are longer than in the octahedral core of the anion of **1**. This general trend follows from the differing sizes of the two types of cavity and is an observation previously noted when we compared the structures of the trigonal-prismatic anion $[Ru_6H_2(CO)_{18}B]^-$[14] with that of $[Ru_6H(CO)_{17}B]$.[8,9] The presence of the rhodium capping atom in **3** causes a displacement of atom B(1) away from the centre of its interstitial cavity; the distance Rh(1) ··· B(1) is 2.53(1) Å. This causes the diboron unit to be skewed as indicated in the view shown in Fig. 4 and from an inspection of the metal–boron bond distances in Table 5. The two boron atoms are displaced towards one another such that the B(1)–B(2) separation is 1.80(2) Å. This value lies within the range generally observed for boron–boron distances in borane clusters[27] and is shorter than some such distances; for example, it is much shorter than the very long distances of 1.973(4) Å for the two unbridged edges in the open face of $B_{10}H_{14}$.[28] It is however too long to be considered a localised two-centre two-electron bond; the covalent radius of a boron atom is 0.82 Å. Interestingly, in the dicarbido cluster $[Co_6Ni_2(CO)_{16}C_2]^{2-}$ [Fig. 5(*c*)], which also possesses a double trigonal-prismatic framework, the C–C separation is relatively short, *viz.* 1.494(11) Å, compared to a typical single C–C bond distance of 1.54 Å.[29]

The diboron-centred, capped double trigonal-prismatic structure of the anion of compound **3** [Fig. 5(*d*)] appears to be the first cluster of its type, not only with respect to the environment of the boron atoms but with respect to the metal framework. There are however several carbido clusters to which **3** is related, and Fig. 5 compares the core structures of a series of boride and carbide clusters which contain trigonal-prismatic or double trigonal-prismatic metal cores. The anion $[Co_6Ni_2(CO)_{16}C_2]^{2-}$ was mentioned above.[29] Shriver and co-workers[30] have prepared and structurally characterised the dianion $[Ni_4Os_3(CO)_{15}C]^{2-}$ [Fig. 5(*b*)] which exhibits a carbon-centred capped trigonal-prismatic core, and related to this is $[Ni_7(CO)_{12}C]^{2-}$.[31] The dianionic cluster $[Ni_{10}(CO)_{16}C_2]^{2-}$ [Fig. 5(*e*)] exhibits a double trigonal-prismatic core as in **3** but in this case two opposing square faces are capped.[32] The framework is further extended in the nickel cluster anions $[Ni_{11}(CO)_{15}C_2]^{2-}$ and $[Ni_{12}(CO)_{16}C_2]^{2}$.[31] In

Table 4 Atomic coordinates (× 10^4) for compound **3**

Atom	*x*	*y*	*z*
Rh(1)	7 060(1)	2 208(1)	3 064(1)
Rh(2)	4 895(1)	2 604(1)	1 924(1)
Rh(3)	9 517(1)	2 742(1)	899(1)
Ru(1)	6 196(1)	1 213(1)	1 795(1)
Ru(2)	8 737(1)	2 090(1)	2 130(1)
Ru(3)	7 366(1)	3 530(1)	2 265(1)
Ru(4)	7 137(1)	1 873(1)	613(1)
Ru(5)	5 783(1)	3 265(1)	762(1)
Ru(6)	8 201(1)	4 123(1)	1 032(1)
P(1)	7 894(2)	7 659(2)	3 392(2)
P(2)	5 223(2)	7 881(2)	3 487(2)
N	6 379(8)	7 771(6)	3 100(6)
O(1)	6 752(10)	1 717(7)	4 541(6)
O(2)	7 316(10)	3 660(6)	3 913(6)
O(3)	9 728(7)	1 846(6)	3 780(5)
O(4)	5 491(9)	494(6)	3 131(6)
O(5)	3 688(9)	587(7)	763(7)
O(6)	7 396(9)	−320(5)	1 710(7)
O(7)	10 107(8)	600(6)	2 203(7)
O(8)	11 366(7)	2 919(6)	2 684(6)
O(9)	9 888(7)	4 333(6)	3 093(6)
O(10)	6 025(9)	4 986(5)	2 436(6)
O(11)	4 675(7)	1 347(7)	−488(5)
O(12)	8 319(9)	366(6)	382(7)
O(13)	7 917(8)	2 456(7)	−757(6)
O(14)	5 396(10)	3 343(8)	−892(6)
O(15)	3 108(7)	2 404(7)	373(6)
O(16)	4 400(8)	4 729(6)	768(7)
O(17)	6 995(11)	5 661(7)	1 077(9)
O(18)	10 864(7)	4 859(7)	1 736(6)
O(19)	8 293(11)	4 278(9)	−560(7)
O(20)	2 978(8)	1 507(7)	2 363(7)
O(21)	3 476(9)	3 978(6)	2 254(7)
O(22)	11 370(9)	3 795(7)	348(8)
O(23)	11 027(9)	1 367(7)	709(8)
C(1)	6 846(10)	1 894(8)	3 965(8)
C(2)	7 222(10)	3 284(7)	3 377(8)
C(3)	8 909(9)	1 986(7)	3 241(7)
C(4)	5 832(10)	857(7)	2 706(8)
C(5)	4 613(10)	831(8)	1 154(8)
C(6)	7 004(11)	260(8)	1 729(9)
C(7)	9 570(10)	1 159(8)	2 152(8)
C(8)	10 379(9)	2 626(8)	2 423(8)
C(9)	8 959(10)	4 029(8)	2 747(7)
C(10)	6 506(10)	4 446(8)	2 357(8)
C(11)	5 543(10)	1 546(8)	−73(8)
C(12)	7 894(10)	913(8)	489(8)
C(13)	7 845(10)	2 314(9)	−191(8)
C(14)	5 572(10)	3 324(9)	−271(8)
C(15)	4 092(9)	2 673(8)	673(7)
C(16)	4 922(10)	4 223(8)	742(8)
C(17)	7 412(12)	5 089(9)	1 044(10)
C(18)	9 885(11)	4 586(8)	1 471(8)
C(19)	8 253(11)	4 238(9)	1(10)
C(20)	3 715(9)	1 920(8)	2 196(8)
C(21)	3 982(11)	3 483(10)	2 133(9)
C(22)	10 662(10)	3 417(9)	578(10)
C(23)	10 477(10)	1 899(9)	772(9)
B(1)	6 725(9)	2 390(7)	1 690(8)
B(2)	7 805(9)	2 953(7)	1 280(7)
C(101)	8 845(14)	7 087(10)	4 790(10)
C(102)	9 129(17)	6 518(12)	5 247(12)
C(103)	8 897(18)	5 803(13)	5 002(14)
C(104)	8 371(21)	5 612(11)	4 297(13)
C(105)	8 034(18)	6 181(10)	3 806(11)
C(106)	8 325(10)	6 943(8)	4 037(8)
C(111)	7 867(14)	7 676(16)	1 917(9)
C(112)	8 464(20)	7 558(22)	1 342(11)
C(113)	9 588(15)	7 201(16)	1 442(11)
C(114)	10 183(16)	6 936(16)	2 092(12)
C(115)	9 669(14)	7 056(14)	2 706(11)
C(116)	8 480(10)	7 429(8)	2 597(8)
C(121)	8 174(11)	9 218(8)	3 577(9)
C(122)	8 854(12)	9 909(9)	3 762(9)
C(123)	10 137(12)	9 933(9)	4 140(10)
C(124)	10 727(12)	9 270(10)	4 305(11)
C(125)	10 057(11)	8 557(9)	4 138(10)
C(126)	8 771(9)	8 548(7)	3 742(8)
C(131)	6 089(12)	7 819(11)	4 973(9)
C(132)	6 621(16)	8 163(15)	5 692(12)
C(133)	6 703(15)	8 870(12)	5 834(10)
C(134)	6 209(17)	9 349(10)	5 273(10)
C(135)	5 727(11)	9 070(8)	4 553(8)
C(136)	5 682(10)	8 255(8)	4 430(8)
C(141)	4 263(11)	6 447(10)	2 939(12)
C(142)	3 476(17)	5 791(11)	2 883(15)
C(143)	2 566(16)	5 740(12)	3 334(12)
C(144)	2 584(14)	6 329(12)	3 833(13)
C(145)	3 467(13)	6 933(10)	3 954(10)
C(146)	4 273(10)	7 003(7)	3 498(8)
C(151)	3 086(12)	8 757(10)	3 153(10)
C(152)	2 236(16)	9 166(16)	2 723(14)
C(153)	2 412(16)	9 410(12)	2 000(11)
C(154)	3 423(14)	9 149(8)	1 767(9)
C(155)	4 331(11)	8 704(9)	2 240(8)
C(156)	4 160(10)	8 512(9)	2 931(8)

$[Ni_{10}(CO)_{16}C_2]^{2-}$, $[Ni_{11}(CO)_{15}C_2]^{2-}$ and $[Ni_{12}(CO)_{16}C_2]^{2-}$ the $C_{carbide} \cdots C_{carbide}$ distances are 1.40, 1.46 and 1.43(2) Å, respectively. The metal skeleton of **3** clearly fits into this series of condensed polyhedra.

We are not able to speculate about the mechanism of the formation of the anion of compound **3**, although it is apparent that Ru_3B units, present in the starting cluster $[Ru_3(CO)_9BH_4]^-$, are recognisable motifs in the framework of **3**. The isolation of **1** from the 1 h reaction of $[N(PPh_3)_2][Ru_3(CO)_9BH_4]$ with $[\{Rh(CO)_2Cl\}_2]$ may suggest degradation and reassembly of fragments. This type of process is certainly well represented throughout cluster chemistry. However, we cannot rule out the very likely possibility that the direct precursor to **1** is not $[Ru_3(CO)_9BH_4]^-$ at all but $[Ru_4H(CO)_{12}(BH)]^-$. We have previously reported that, after standing in solution over a period of time, both the neutral cluster $[Ru_3(CO)_9BH_5]$ and its conjugate base $[Ru_3(CO)_9BH_4]^-$ undergo a spontaneous self assembly to form $[Ru_4H(CO)_{12}(BH_2)]$ and $[Ru_6H(CO)_{17}B]$, or $[Ru_4H(CO)_{12}(BH)]^-$ and $[Ru_6(CO)_{17}B]^-$, respectively.[9,24] We have also observed that the reaction of $[Rh_4H(CO)_{12}(BH)]^-$ with $[\{Rh(CO)_2Cl\}_2]$ yields the anion of **1** in good yield.[21]

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References

1 C. E. Housecroft, in *Inorganometallic Chemistry* (*Modern Inorganic Chemistry*), ed. T. P. Fehlner, Plenum, New York, 1992, ch. 3, p. 73.
2 C. E. Housecroft, *Adv. Organomet. Chem.*, 1991, **33**, 1.
3 J. S. Bradley, *Adv. Organomet. Chem.*, 1983, **22**, 1.
4 E. L. Muetterties, *Prog. Inorg. Chem.*, 1981, **28**, 203.
5 M. D. Vargas and J. N. Nicholls, *Adv. Inorg. Chem. Radiochem.*, 1986, **30**, 123.
6 W. L. Gladfelter, *Adv. Organomet. Chem.*, 1985, **24**, 41.
7 T. P. Fehlner, *Adv. Inorg. Chem.*, 1990, **35**, 199.
8 F.-E. Hong, T. J. Coffy, D. A. McCarthy and S. G. Shore, *Inorg. Chem.*, 1989, **28**, 3284.

Table 5 Selected bond distances (Å) and angles (°) for the anion in compound **3**

Rh(1)–Rh(2)	2.853(1)	Rh(1)–Ru(1)	2.854(1)	Ru(4)–Ru(5)	2.934(2)	Ru(5)–Ru(6)	2.856(1)
Rh(1)–Ru(2)	2.797(1)	Rh(1)–Ru(3)	2.828(2)	Rh(2)–B(1)	2.15(1)	Ru(1)–B(1)	2.14(1)
Rh(2)–Ru(1)	2.894(1)	Rh(2)–Ru(3)	2.958(1)	Ru(2)–B(1)	2.19(1)	Ru(3)–B(1)	2.25(1)
Rh(2)–Ru(5)	2.818(2)	Rh(3)–Ru(2)	2.868(2)	Ru(4)–B(1)	2.34(1)	Ru(5)–B(1)	2.40(1)
Rh(3)–Ru(4)	2.831(1)	Rh(3)–Ru(6)	2.889(2)	Rh(3)–B(2)	2.16(1)	Ru(2)–B(2)	2.29(1)
Ru(1)–Ru(2)	2.979(1)	Ru(1)–Ru(4)	2.879(2)	Ru(3)–B(2)	2.24(1)	Ru(4)–B(2)	2.24(1)
Ru(2)–Ru(3)	3.011(1)	Ru(2)–Ru(4)	2.935(1)	Ru(5)–B(2)	2.23(1)	Ru(6)–B(2)	2.16(1)
Ru(3)–Ru(5)	2.916(1)	Ru(3)–Ru(6)	2.861(2)	B(1)–B(2)	1.80(2)		
Rh(2)–Rh(1)–Ru(1)	60.9(1)	Rh(2)–Rh(1)–Ru(2)	94.9(1)	Rh(1)–Ru(3)–Ru(5)	107.3(1)	Rh(2)–Ru(3)–Ru(5)	57.3(1)
Ru(1)–Rh(1)–Ru(2)	63.6(1)	Rh(2)–Rh(1)–Ru(3)	62.8(1)	Ru(2)–Ru(3)–Ru(5)	88.9(1)	Rh(1)–Ru(3)–Ru(6)	145.4(1)
Ru(1)–Rh(1)–Ru(3)	95.6(1)	Ru(2)–Rh(1)–Ru(3)	64.7(1)	Rh(2)–Ru(3)–Ru(6)	116.6(1)	Ru(2)–Ru(3)–Ru(6)	89.6(1)
Rh(1)–Rh(2)–Ru(1)	59.6(1)	Rh(1)–Rh(2)–Ru(3)	58.2(1)	Ru(5)–Ru(3)–Ru(6)	59.3(1)	Rh(3)–Ru(4)–Ru(1)	121.2(1)
Ru(1)–Rh(2)–Ru(3)	92.0(1)	Rh(1)–Rh(2)–Ru(5)	109.3(1)	Rh(3)–Ru(4)–Ru(2)	59.6(1)	Ru(1)–Ru(4)–Ru(2)	61.6(1)
Ru(1)–Rh(2)–Ru(5)	91.9(1)	Ru(3)–Rh(2)–Ru(5)	60.6(1)	Rh(3)–Ru(4)–Ru(5)	89.9(1)	Ru(1)–Ru(4)–Ru(5)	89.8(1)
Ru(2)–Rh(3)–Ru(4)	62.0(1)	Ru(2)–Rh(3)–Ru(6)	91.9(1)	Ru(2)–Ru(4)–Ru(5)	91.0(1)	Rh(2)–Ru(5)–Ru(3)	62.1(1)
Ru(4)–Rh(3)–Ru(6)	90.6(1)	Rh(1)–Ru(1)–Rh(2)	59.5(1)	Rh(2)–Ru(5)–Ru(4)	89.3(1)	Ru(3)–Ru(5)–Ru(4)	90.5(1)
Rh(1)–Ru(1)–Ru(2)	57.3(1)	Rh(2)–Ru(1)–Ru(2)	90.3(1)	Rh(2)–Ru(5)–Ru(6)	121.5(1)	Ru(3)–Ru(5)–Ru(6)	59.4(1)
Rh(1)–Ru(1)–Ru(4)	107.5(1)	Rh(2)–Ru(1)–Ru(4)	88.9(1)	Ru(4)–Ru(5)–Ru(6)	89.2(1)	Rh(3)–Ru(6)–Ru(3)	90.5(1)
Ru(2)–Ru(1)–Ru(4)	60.1(1)	Rh(1)–Ru(2)–Rh(3)	144.9(1)	Rh(3)–Ru(6)–Ru(5)	90.3(1)	Ru(3)–Ru(6)–Ru(5)	61.3(1)
Rh(1)–Ru(2)–Ru(1)	59.1(1)	Rh(3)–Ru(2)–Ru(1)	116.6(1)	Rh(3)–B(2)–Ru(3)	136.4(5)	Ru(2)–B(2)–Ru(6)	136.9(5)
Rh(1)–Ru(2)–Ru(3)	58.1(1)	Rh(3)–Ru(2)–Ru(3)	88.0(1)	Ru(4)–B(2)–Ru(6)	135.3(6)	Rh(3)–B(2)–Ru(5)	136.1(6)
Ru(1)–Ru(2)–Ru(3)	89.3(1)	Rh(1)–Ru(2)–Ru(4)	107.5(1)	Ru(3)–B(2)–Ru(4)	136.1(6)	Ru(2)–B(2)–Ru(5)	135.5(6)
Rh(3)–Ru(2)–Ru(4)	58.4(1)	Ru(1)–Ru(2)–Ru(4)	58.3(1)	Rh(2)–B(1)–Ru(2)	146.9(7)	Rh(2)–B(1)–Ru(4)	128.8(5)
Ru(3)–Ru(2)–Ru(4)	88.6(1)	Rh(1)–Ru(3)–Rh(2)	59.0(1)	Ru(1)–B(1)–Ru(3)	147.1(7)	Ru(1)–B(1)–Ru(5)	129.4(5)
Rh(1)–Ru(3)–Ru(2)	57.1(1)	Rh(2)–Ru(3)–Ru(2)	88.4(1)	Ru(2)–B(1)–Ru(5)	131.5(6)	Ru(3)–B(1)–Ru(4)	129.9(6)

9 S. M. Draper, C. E. Housecroft, A. K. Keep, D. M. Matthews, X. Song and A. L. Rheingold, *J. Organomet. Chem.*, 1992, **423**, 241.

10 R. Khattar, J. Puga, T. P. Fehlner and A. L. Rheingold, *J. Am. Chem. Soc.*, 1989, **111**, 1877.

11 A. K. Bandyopadhyay, R. Khattar and T. P. Fehlner, *Inorg. Chem.*, 1989, **28**, 4434.

12 A. K. Bandyopadhyay, R. Khattar, J. Puga, T. P. Fehlner and A. L. Rheingold, *Inorg. Chem.*, 1992, **31**, 465.

13 C. E. Housecroft, D. M. Matthews, A. L. Rheingold and X. Song, *J. Chem. Soc., Chem. Commun.*, 1992, 842.

14 C. E. Housecroft, D. M. Matthews, A. Waller, A. J. Edwards and A. L. Rheingold, *J. Chem. Soc., Dalton Trans.*, 1993, 3059.

15 S. B. Colbran, C. M. Hay, B. F. G. Johnson, F. J. Lahoz, J. Lewis and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1986, 1766.

16 S. B. Colbran, F. J. Lahoz, P. R. Raithby, J. Lewis, B. F. G. Johnson and C. J. Cardin, *J. Chem. Soc., Dalton Trans.*, 1988, 173.

17 A. K. Chipperfield and C. E. Housecroft, *J. Organomet. Chem.*, 1988, **349**, C17.

18 C. E. Housecroft, D. M. Matthews, A. L. Rheingold and X. Song, *J. Chem. Soc., Dalton Trans.*, 1992, 2855.

19 F.-E. Hong, D. A. McCarthy, J. P. White, C. E. Cottrell and S. G. Shore, *Inorg. Chem.*, 1990, **29**, 2874.

20 A. K. Chipperfield, C. E. Housecroft and A. L. Rheingold, *Organometallics*, 1990, **9**, 681.

21 J. R. Galsworthy, A. D. Hattersley, C. E. Housecroft, A. L. Rheingold and A. Waller, unpublished work; A. D. Hattersley, Ph.D. Thesis, University of Cambridge, 1993.

22 SHELXTL-PC, G. Sheldrick, Siemens XRD, Madison, WI, 1991.

23 J. R. Galsworthy, C. E. Housecroft, R. Ostrander and A. L. Rheingold, *J. Chem. Soc., Dalton Trans.*, 1994, 69.

24 J. R. Galsworthy, C. E. Housecroft and A. L. Rheingold, *Organometallics*, 1993, **12**, 4167.

25 N. P. Rath and T. P. Fehlner, *J. Am. Chem. Soc.*, 1988, **110**, 5345.

26 T. P. Fehlner, P. T. Czech and R. F. Fenske, *Inorg. Chem.*, 1990, **29**, 3103.

27 R. A. Beaudet, in *Advances in Boron and the Boranes*, eds. J. F. Liebman, A. Greenberg and R. E. Williams, VCH, New York, 1988, pp. 417–490.

28 A. Tippe and W. C. Hamilton, *Inorg. Chem.*, 1969, **8**, 464 and refs. therein.

29 A. Arrigoni, A. Ceriotto, R. D. Pergola, G. Longoni, M. Manassero, N. Masciocchi and M. Sansoni, *Angew. Chem., Int. Ed., Engl.*, 1984, **23**, 322.

30 G. B. Karet, R. L. Espe, C. L. Stern and D. F. Shriver, *Inorg. Chem.*, 1992, **31**, 2658.

31 A. Ceriotto, G. Piro, G. Longoni, M. Manassero, N. Masciocchi and M. Sansoni, *New J. Chem.*, 1988, **12**, 501.

32 A. Ceriotto, G. Longoni, M. Manassero, N. Masciocchi, L. Resconi and M. Sansoni, *J. Chem. Soc., Chem. Commun.*, 1985, 181.

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