Reactions of the Pentanuclear Mixed-metal Cluster Compound $[Ru_4RhC(CO)_{12}(\eta^5\text{-}C_5Me_5)]$. Synthesis, Characterisation and Crystal Structure of the Pentanuclear Derivative $[Ru_4RhC(CO)_{11}H(\eta^5\text{-}C_5Me_5)I]$†

Trushar Adatia,[*,a] **Hilary Curtis,**[b] **Brian F. G. Johnson,**[b] **Jack Lewis,**[*,b] **Mary McPartlin**[a] **and Jill Morris**[a]
[a] *School of Chemistry, University of North London, London N7 8DB, UK*
[b] *University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK*

Treatment of the pentanuclear cluster $[Ru_4RhC(CO)_{12}(\eta^5\text{-}C_5Me_5)]$ **1** with an excess of $[NEt_4][BH_4]$ yielded the monoanion $[Ru_4RhC(CO)_{11}H(\eta^5\text{-}C_5Me_5)]^-$ which has been isolated as its $[NEt_4]^+$ salt **2**. Reaction of the monoanion with iodine solution gave the novel derivative $[Ru_4RhC(CO)_{11}H(\eta^5\text{-}C_5Me_5)I]$ **3**. Compound **3** crystallises in the monoclinic space group $P2_1/n$ with $a = 15.243(3)$, $b = 18.683(3)$, $c = 10.425(2)$ Å, $\beta = 90.0(2)°$. The five metal atoms adopt a wingtip-bridged butterfly arrangement with the rhodium forming one of the 'hinge' atoms [Ru–Ru 2.816(1)–2.899(1), Ru–Rh 2.816(1)–2.826(1) Å]. The parent cluster $[Ru_4RhC(CO)_{12}(\eta^5\text{-}C_5Me_5)]$ **1** reacted at room temperature with the neutral ligands $P(OMe)_3$ and PPh_3 to yield compounds $[Ru_4RhC(CO)_{10}\{P(OMe)_3\}_2(\eta^5\text{-}C_5Me_5)]$ **4** (three isomers) and $[Ru_4RhC(CO)_{10}(PPh_3)_2(\eta^5\text{-}C_5Me_5)]$ **5**. Compound **1** reacts with $[N(PPh_3)_2]Cl$ to yield the adduct $[Ru_4RhC(CO)_{12}(\eta^5\text{-}C_5Me_5)Cl]^-$ which on protonation produces $[Ru_4RhC(CO)_{12}H(\eta^5\text{-}C_5Me_5)Cl]$ **6**.

In recent years a great deal of research has been focused on developing synthetic routes to study mixed-metal clusters of ruthenium. In particular, it is the observed changes in reactivity, relative to the homonuclear analogues, that has stimulated interest in this class of compounds.

In the course of our investigations into the chemistry of ruthenium–rhodium mixed-metal compounds, we have recently reported the synthesis and reactions of the novel octahedral cluster $[Ru_5RhC(CO)_{14}(\eta^5\text{-}C_5Me_5)]$.[1–3] Interesting similarities and differences in reactivity of this compound have been established in comparison to the analogous homonuclear cluster $[Ru_6C(CO)_{17}]$.[1,2] As with the hexanuclear carbido cluster $[Ru_6C(CO)_{17}]$, one of the key reactions of the mixed-metal cluster $[Ru_5RhC(CO)_{14}(\eta^5\text{-}C_5Me_5)]$ involves a series of decapping processes to yield the complexes $[Ru_3(CO)_{12}]$ and $[Ru_5C(CO)_{15}]$. In addition, the ruthenium–rhodium heteronuclear species also yields a new green square-pyramidal compound $[Ru_4RhC(CO)_{12}(\eta^5\text{-}C_5Me_5)]$ **1**.[2] The current investigation of the reactivity of **1** has been undertaken, in order to compare its behaviour with that of the widely studied homonuclear analogue $[Ru_5C(CO)_{15}]$. An important feature of the chemistry of $[Ru_5C(CO)_{15}]$ is its facile reactions with neutral ligands and nucleophiles, to form wingtip-bridged butterfly adducts, some of which can then lose CO, returning to the square-based pyramidal metal core.[4–7] For example, with phosphines and phosphites, the pentaruthenium carbido cluster reacts to form mono-, di- or tri-substituted derivatives,[6] whereas with CO and halides, the compounds $[Ru_5C(CO)_{16}]$ and $[Ru_5C(CO)_{15}X]^-$ are formed.[7] As with many carbonyl clusters, the carbido cluster $[Ru_5C(CO)_{15}]$ also reacts with bases to generate the dianion $[Ru_5C(CO)_{14}]^{2-}$,[5] which exhibits extensive reactions with electrophiles.[8,9] The stability of the pentamethylcyclopentadienylrhodium unit, $Rh(\eta^5\text{-}C_5Me_5)$, has been widely studied in mono- and bi-nuclear metal complexes.[10] It was anticipated that incorporation of this group in the structure of the high-nuclearity mixed-metal compound $[Ru_4RhC(CO)_{12}(\eta^5\text{-}C_5Me_5)]$ **1** would result in interesting changes in reactivity relative to the homonuclear analogue $[Ru_5C(CO)_{15}]$.

Results and Discussion

The pentanuclear cluster $[Ru_4RhC(CO)_{12}(\eta^5\text{-}C_5Me_5)]$ **1** is rapidly reduced in the presence of $[NEt_4][BH_4]$ to form the salt $[NEt_4][Ru_4RhC(CO)_{11}H(\eta^5\text{-}C_5Me_5)]$ **2** which was not successfully purified but has been tentatively formulated on the basis of its spectroscopic data and its reaction with molecular iodine which produces the derivative $[Ru_4RhC(CO)_{11}H(\eta^5\text{-}C_5Me_5)I]$ **3**. Compound **3** has been characterised by IR and ^1H NMR studies (Table 1) and in the solid state by X-ray diffraction. At ambient temperature, two hydride resonances in the approximate ratio of 1:3 are observed in the ^1H NMR spectrum of **3** (δ −25.96 and −27.07), with the first exhibiting coupling to the rhodium atom ($J_{Rh-H} = 24$ Hz), indicating that in solution, complex **3** exists as two isomeric forms **3a** and **3b** respectively. Correspondingly there are two separate methyl resonances for the $\eta^5\text{-}C_5Me_5$ unit at δ 2.09 and 2.06. In the current study, single-crystal X-ray analysis of one isomer of cluster **3** shows a structure in which the hydrido ligand bridges the hinge Ru–Rh bond of the metal core (Fig. 1) resulting from attack of the I^+ electrophile on the central Ru–Ru apical-basal bond in the proposed square-pyramidal structure of the hydrido derivative **2**. This identifies the isomer as **3a** with the Rh–H coupled signal in its NMR data. Three possible structural arrangements of the proposed wingtip-bridged butterfly metal core are possible for **3b**; two arising from attack of the electrophile, I^+, on a Ru–Ru apical-basal bond with the $Rh(\eta^5\text{-}C_5Me_5)$ unit occupying a wingtip site and the third structure in which the cleavage of a Ru–Ru apical-basal bond by the I^+ ligand results in the $Rh(\eta^5\text{-}C_5Me_5)$ adopting a position in which it bridges the Ru_4 butterfly. In terms of steric requirements, the latter structure would be most probable as the

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

Table 1 Spectroscopic data for compounds **2**–**6**

Compound	$\nu_{max}(CO)^a$ /cm^{-1}	^{1}H NMR^b	Mass spectrum (m/z)
2	2031m	2.006 (s, C_5Me_5)	
	1993 (sh)	3.250 (q, CH_2, J = 7)	
	1976s (br)	1.800 (t, CH_2CH_3)	
	1941 (sh)		
3	2084m	−25.96 (d, H, J_{Rh-H} = 24)	1092 (M^+), 1064 (M − CO^+)
	2043s	2.094 (s, C_5Me_5)	
	2012m	−27.07 (s, H)	
	1996m	2.057 (s, C_5Me_5)	
	1990 (sh)		
	1970 (sh)		
	1950 (sh)		
4^c Isomer 1	2036m	2.045 (s, C_5Me_5)	1182 (each isomer)
	2026s	3.554	
	1990s (br)	3.577 } P(OMe)$_3$	
	1971m	3.602	
Isomer 2		2.058 (s, C_5Me_5)	
		3.494 3.660 } [d, P(OMe)$_3$, J = 12]	
Isomer 3		2.084 (s, C_5Me_5)	
		3.431 3.489 } [d, P(OMe)$_3$, J = 12]	
5	2075s	2.247 (s, C_5Me_5)	1197
	2057s	7.259	
	2022m	7.482 } (m, Ph)	
	3005s		
6	2095m	−21.0 (d, H, J_{Rh-H} = 25.4)	990
	2071s	2.055 (s, C_5Me_5)	
	2052s		
	2014m		

^{a} Measured in CH_2Cl_2. ^{b} Chemical shifts (δ) in ppm (measured in $CDCl_3$); coupling constants in Hz. ^{c} Ratio of isomers at equilibrium, by NMR integrated intensities, 1.7:1.3:1. Equilibrium was reached from any single isomer within 12 h in CH_2Cl_2 solution at room temperature.

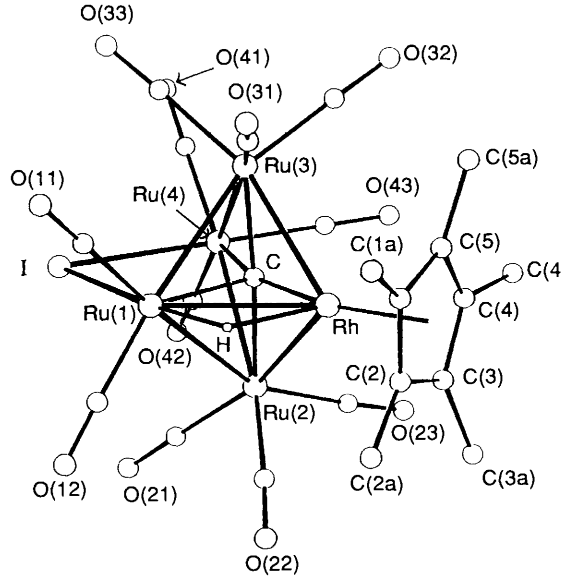

Fig. 1 The molecular structure of the pentanuclear cluster [$Ru_4RhC(CO)_{11}H(\eta^5$-$C_5Me_5)I$] **3** showing the crystallographic numbering scheme. The carbon atom of each carbonyl group has the same numbering as the oxygen atom

Rh atom co-ordinated to the bulky C_5Me_5 group would adopt the least sterically demanding position within the metal framework. Alternatively, the differences in the ^{1}H NMR spectra of **3** may arise from a second isomer differing only in the site of the μ-H ligand. No crystals of a second isomer **3b** have been obtained so far, and so its solid-state structure cannot be confirmed.

Interestingly, the pentanuclear mixed-metal cluster [$Ru_4RhC(CO)_{12}(\eta^5$-$C_5Me_5)$] **1** shows no reaction with methanolic sodium carbonate which is in marked contrast to the behaviour exhibited by the homonuclear analogue, [$Ru_5C(CO)_{15}$], which becomes rapidly reduced to [$Ru_5C(CO)_{14}]^{2-}$ under similar conditions;[5] this may be interpreted as evidence of reduced electrophilicity in the heteronuclear cluster **1**. The pentanuclear carbido cluster **1** reacts with trimethyl phosphite at room temperature to yield three isomers formulated as [$Ru_4RhC(CO)_{10}\{P(OMe)_3\}_2(\eta^5$-$C_5Me_5)$] **4** on the basis of mass spectrometry data (Table 1). The three isomers are separable by thin layer chromatography, but all interconvert in dichloromethane solution over a few hours. Their ^{1}H NMR spectra are interesting in that the first eluted isomer exhibits a methyl virtual coupling pattern indicating that the two phosphite ligands are bound to the same metal atom, whereas the spectra of the other isomers show normal first-order behaviour, with inequivalent phosphites in each case (Table 1). Compound **1** also reacts with triphenylphosphine to produce a dark green complex formulated as [$Ru_4RhC(CO)_{10}(PPh_3)_2(\eta^5$-$C_5Me_5)$] **5** on the basis of its ^{1}H NMR and FAB mass spectral data (Table 1). No evidence of isomerism is detected in this case and the reaction is much slower than that for [$Ru_5C(CO)_{15}$].[11] Both **4** and **5** are 74e clusters and may be assumed to adopt square-pyramidal metal core arrangements similar to that already established for precursor **1**.[2] A possible reason for observing no isomers in solution of **5**, compared to three for its analogue **4**, may be the change in the nature of the phosphine ligand; the presence of two bulky PPh_3 ligands in **5** may sterically dictate a structure in which these groups only form bonds to two *trans*-basal Ru atoms. The pentanuclear cluster [$Ru_4RhC(CO)_{12}(\eta^5$-$C_5Me_5)$] **1** is only sparingly soluble in acetonitrile. Infrared studies show no evidence for adduct formation, whereas [$Ru_5C(CO)_{15}(NCMe)$] is formed from [$Ru_5C(CO)_{15}$] directly on dissolution in acetonitrile.[11] Nucleophilic reactivity of **1** appears to be enhanced with the chloride salt, [N(PPh$_3$)$_2$]Cl, which reacts instantaneously, presumably, to form the anionic adduct [Ru$_4$RhC(CO)$_{12}$(η^5-C$_5$Me$_5$)Cl]$^-$ which on protonation with HBF$_4$·Et$_2$O produces the compound [Ru$_4$RhC(CO)$_{12}$H(η^5-C$_5$Me$_5$)Cl] **6** which has been characterised on the basis of its spectroscopic data (Table 1). On bubbling nitrogen through the solution or exposure to silica thin layer chromatography plates the newly formed complex reverts to form the parent compound **1**. This type of behaviour closely parallels that of [Ru$_5$C(CO)$_{15}$], which readily forms the derivatives [Ru$_5$C(CO)$_{15}$H(X)] (X = Cl or Br). These adducts in turn eject CO to give [Ru$_5$C(CO)$_{14}$H(X)], on bubbling nitrogen through a refluxing hexane solution for X = Br and on heating at 90 °C in the presence of HCl for X = Cl.[5]

The molecular structure of the pentanuclear mixed-metal cluster [Ru$_4$RhC(CO)$_{11}$H(η^5-C$_5$Me$_5$)I] **3** is displayed in Fig. 1 with selected interatomic distances and angles summarised in Table 2. In the solid state, the five metal atoms in cluster **3** define a wingtip-bridged butterfly or *arachno* pentagonal-bipyramidal metal core geometry. The metal atoms, Ru(1), Ru(2), Ru(3) and Rh, bond to form the butterfly arrangement with Ru(4) bridging the wingtip atoms Ru(2) and Ru(3). The dihedral angle between the 'wings' of the butterfly [Ru(1)–Ru(2)–Rh and Ru(1)–Ru(3)–Rh] is 108.2°. The carbido atom resides in the *arachno* pentagonal-bipyramidal cavity co-ordinating to all five metal atoms. The Rh(η^5-C$_5$Me$_5$) unit is at one end of the hinge of the butterfly opposite to the iodide group which bridges the atoms Ru(1) and Ru(4) and the hydrido ligand bridges the hinge of the butterfly defined by the atoms Ru(1) and Rh (Fig. 1). The eleven carbonyl groups in **3** are all essentially terminal [176.5(7)–179(8)°]. The overall molecular structure of **3** is similar to that proposed for the derivatives [Ru$_5$C(CO)$_{15}$H(X)] (X = Cl, Br or I),[4,5] and that characterised for the pentaruthenium clusters [Ru$_5$C(CO)$_{14}${μ-Au(PPh$_3$)}(μ-X)] (X = Br[5] or I[12]).

The metal core arrangement described by **3** may be regarded as being derived from the square-pyramidal framework of [Ru$_4$RhC(CO)$_{12}$(η^5-C$_5$Me$_5$)] **1**,[2] by breaking the base to apex bond between Ru(1) and Ru(4) with these atoms subsequently being bridged by the three-electron donor μ-I ligand. Distances from the 'hinge' metal atoms, Ru(1) and Rh, to the bridging atom Ru(4), [Ru(1)···Ru(4) 3.447(1) Å; Rh···Ru(4) 4.050(1) Å] reflect the asymmetry of the bridging arrangement. Similar variations have also been observed in the related structures [Ru$_5$C(CO)$_{14}${μ-Au(PPh$_3$)}(μ-X)] (X = Br[5] or I[12]) where the shorter of the two non-bonding distances associated with a Ru atom bridging the 'butterfly' metal core arises between two Ru atoms bridged by the halogen atom.

The M–M distances in [Ru$_4$RhC(CO)$_{11}$H(η^5-C$_5$Me$_5$)I] **3** are in a higher range than that established for the parent pentanuclear compound [Ru$_4$RhC(CO)$_{12}$(η^5-C$_5$Me$_5$)] **1**[2] [Ru–Ru 2.816(1)–2.899(1), Ru–Rh 2.816(1)–2.826(1) Å for **3**; Ru–Ru 2.776(1)–2.873(1), Ru–Rh 2.798(1)–2.881(1) Å for **1**]. The overall increase in M–M bond lengths is a result of the metal core rearrangement that occurs when the square-based pyramidal metal core in **1** 'opens' to the wingtip-bridged butterfly arrangement in **3**. The Ru–Ru and Ru–Rh distances within the 'butterfly' in **3** are very similar, with the 'hinge' Ru(1)–Rh bond being slightly longer than the remaining four M–M bonds in this unit (Table 2). However, the Ru–Ru bonds associated with the bridging atom, Ru(4), are longer than the remaining M–M distances within the structure. The mean Ru–Ru bond in **3** [2.856(1) Å] is notably longer than that observed in the parent cluster **1**[2] [2.810(1) Å] and in the homonuclear analogue [Ru$_5$C(CO)$_{15}$][11] [2.840(2) Å]. The mean Ru–Ru bond in **3** is however shorter than that found in the pentaruthenium derivative [Ru$_5$C(CO)$_{14}${Au(PPh$_3$)}(μ-I)] [2.874(1) Å][5] and is significantly shorter relative to that in the analogue [Ru$_5$C(CO)$_{14}${Au(PPh$_3$)}(μ-Br)] [2.937(3) Å].[12]

The range of Ru–Rh distances in the structure of [Ru$_4$RhC(CO)$_{11}$H(η^5-C$_5$Me$_5$)I] **3** [2.816(1)–2.826(1) Å] are notably longer than that in the tetranuclear clusters [Ru$_3$RhH$_3$(CO)$_{12}$] [2.757(3)–2.762(3) Å] and [Ru$_2$Rh$_2$H$_2$(CO)$_{12}$] [2.756(3)–2.768(3) Å].[13] In **3** the hinge bond, Ru(1)–Rh [2.826(1) Å], is slightly longer than the other two Ru–Rh distances [Ru(2)–Rh 2.822(1), Ru(3)–Rh 2.816(1) Å] consistent with the observations that hydrido ligands often lengthen the M–M bonds they bridge.[14] Marked lengthening of Ru–Ru 'hinge' bonds has also been observed in the related structures [Ru$_5$C(CO)$_{14}${Au(PPh$_3$)}(μ-X)] (X = Br[5] or I[12]), where the unit μ-AuPPh$_3$, isolobal to μ-H, bridges the 'hinge' vector. The Ru–I distances in **3** show an interesting variation, with the bond to Ru(1) [2.771(1) Å] being significantly shorter than to Ru(4) [2.810(1) Å]. Similar variation in Ru–I bond lengths is also a feature in the cluster [Ru$_5$C(CO)$_{14}${Au(PPh$_3$)}(μ-I)], where the Ru–I bond associated with the 'hinge' atom is notably shorter than the Ru–I bond involved with the bridging Ru atom.[12] In the pentanuclear cluster [Ru$_4$RhC(CO)$_{11}$H(η^5-C$_5$Me$_5$)I] **3** the carbide bonds to the 'hinge' atoms, Ru(1) and Rh, are considerably longer than the corresponding bonds associated with the 'wingtip' atoms, Ru(2) and Ru(3) (Table 2). However, the carbide bond to the bridging metal atom, Ru(4), is the longest M–C distance in the structure. The mean Ru–C length of 2.034(6) Å in **3** is shorter than the corresponding mean of 2.057(7) Å found in the parent cluster [Ru$_4$RhC(CO)$_{12}$(η^5-C$_5$Me$_5$)] **1**[2] which could again be attributed to the change in metal core geometry established between **1** and **3**. The cyclopentadienyl ligand in **3** is found to bond in a terminal fashion to the rhodium atom with the range of Rh–C(η^5-C$_5$Me$_5$) distances [2.179(7)–2.228(7) Å] being slightly lower than that found in the related pentanuclear cluster **1** [2.179(8)–2.260(8) Å].[2]

Table 2 Selected bond lengths (Å) and angles (°) for [Ru$_4$RhC(CO)$_{11}$H(η^5-C$_5$Me$_5$)I] **3**, with estimated standard deviations in parentheses

Ru(1)–Ru(2)	2.816(1)	Ru(1)–Ru(3)	2.818(1)
Ru(1)···Ru(4)	3.447(1)	Ru(1)–Rh	2.826(1)
Ru(2)–Ru(4)	2.899(1)	Ru(2)–Rh	2.822(1)
Ru(3)–Ru(4)	2.891(1)	Ru(3)–Rh	2.816(1)
Ru(1)–C	2.078(6)	Ru(2)–C	1.976(6)
Ru(3)–C	1.976(6)	Ru(4)–C	2.104(6)
Rh–C	1.999(6)	Ru(1)–I	2.771(1)
Ru(4)–I	2.810(1)		
Ru–CO(terminal)	1.863(9)–1.921(9)		
Rh–C(η^5-C$_5$Me$_5$)	2.179(7)–2.228(7)		
Ru(3)–Ru(1)–Ru(2)	89.0(1)	Ru(4)–Ru(1)–Ru(2)	54.0(1)
Ru(3)–Ru(4)–Ru(2)	86.0(1)	Ru(4)–Ru(1)–Ru(3)	53.8(1)
Ru(4)–Ru(2)–Ru(1)	74.2(1)	Ru(4)–Ru(3)–Ru(1)	74.3(1)
Ru(2)–Ru(4)–Ru(1)	51.8(1)	Ru(3)–Ru(4)–Ru(1)	51.9(1)
Ru(2)–Rh–Ru(1)	59.8(1)	Ru(3)–Rh–Ru(1)	59.9(1)
Ru(3)–Rh–Ru(2)	88.9(1)	Rh–Ru(1)–Ru(2)	60.0(1)
Rh–Ru(1)–Ru(3)	59.9(1)	Rh–Ru(1)–Ru(4)	79.7(1)
Rh–Ru(2)–Ru(1)	60.2(1)	Rh–Ru(2)–Ru(4)	90.1(1)
Rh–Ru(3)–Ru(1)	60.2(1)	Rh–Ru(3)–Ru(4)	90.4(1)
Ru–C–O(terminal)	176.5(7)–179(8)		

Experimental

Infrared and NMR spectroscopic data for compounds **2**–**6** are summarised in Table 1. Analytical data for these compounds will be presented in this section.

Infrared spectra were recorded on a Perkin Elmer 983 spectrophotometer. The proton NMR spectra of the clusters were recorded at 80 MHz on a Bruker WP 80 SY instrument. Carbon-13 NMR spectra were recorded on a Bruker WM 250 instrument. Mass spectra were recorded on MS 12 or MS 30 instruments. Fast atom bombardment spectra (FAB) were obtained from an AMES 50 instrument.

Reactions of [$Ru_4RhC(CO)_{12}(\eta^5\text{-}C_5Me_5)$] **1**.—(*a*) *With sodium carbonate.* The compound [$Ru_4RhC(CO)_{12}(\eta^5\text{-}C_5Me_5)$] (0.002 g, 0.002 mmol) was stirred with sodium carbonate (0.050 g, 0.472 mmol) in methanol (5 cm^3) for 1 h. Spot thin layer chromatography and IR spectroscopy on the filtered solution showed the presence of only the starting material.

Table 3 X-Ray crystal structure determination data for [$Ru_4RhC(CO)_{11}H(\eta^5\text{-}C_5Me_5)I$] **3**

(*a*) Crystal data	
Molecular formula	$C_{22}H_{16}IO_{11}RhRu_4$
M	1090.45
Crystal dimensions/mm	0.18 × 0.22 × 0.23
No. reflections used to measure unit cell	25
2θ range/° for unit-cell reflections	15–25
Crystal symmetry	Monoclinic
Space group	$P2_1/n$
a/Å	15.243(3)
b/Å	18.683(3)
c/Å	10.425(2)
β/°	90.0(2)
U/Å^3	2968.88
D_c/g cm^{-3}	2.440
Z	4
F(000)	2040
μ(Mo-Kα)/mm^{-1}	1.73
T/K	298
(*b*) Data collection	
Diffractometer	Philips PW1100
2θ Range/°	6.0–50.0
No. of reflections measured	4517
Range *hkl*	−22 to 22, 0–25, 0–14
Scan mode	ω–2θ
No. steps in scan	30
Step width/°	0.05
Minimum counts for reflection to be measured/counts s^{-1}	10
Total no. of reflections [$I > 3\sigma(I)$]	4106
Number of standard reflections	3
Variation in intensity	< 0.05
Method of absorption correction	Empirical[16]
Transmission factors T_{max}, T_{min}	1.119, 0.985
(*c*) Structure refinement	
Number of reflections used in refinement [$F > 6\sigma(F)$]	4099
Number of refined parameters	196
Weighting scheme	$[\sigma^2(F)]^{-1}$
Converged residuals	
R	0.0340
$R' = \Sigma w^{\frac{1}{2}}(\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert)/\Sigma w^{\frac{1}{2}}\lvert F_o\rvert$	0.0343
$\rho_{max,min}$/e Å^{-3}	0.35, −0.50

(*b*) *With* [NEt_4][BH_4]. The compound [$Ru_4RhC(CO)_{12}(\eta^5\text{-}C_5Me_5)$] (0.014 g, 0.014 mmol) was stirred with [NEt_4][BH_4] (0.030 g, 0.207 mmol) in freshly distilled tetrahydrofuran (20 cm^3) for 10 min. The filtered sample was evaporated and redissolved in CH_2Cl_2 with *n*-hexane added to precipitate a brown powder, which was tentatively identified as [NEt_4][$Ru_4RhC(CO)_{11}H(\eta^5\text{-}C_5Me_5)$] **2**, but not successfully purified (Found: C, 33.7; H, 3.9; N, 1.30. $C_{30}H_{36}NO_{11}RhRu_4$ requires C, 32.9; H, 3.3; N, 1.30%).

(*c*) *With trimethyl phosphite.* The compound [$Ru_4RhC(CO)_{12}(\eta^5\text{-}C_5Me_5)$] (0.012 g, 0.012 mmol) was stirred with five drops of trimethyl phosphite for 1 h in freshly distilled dichloromethane (30 cm^3). The products were separated by thin layer chromatography on silica plates, eluting with dichloromethane–hexane (1:1), to give three isomers of [$Ru_4RhC(CO)_{10}\{P(OMe)_3\}_2(\eta^5\text{-}C_5Me_5)$] **4** (0.0120 g, 0.010 mmol, 76%) (Found: C, 27.5; H, 2.8. $C_{27}H_{33}O_{16}P_2RhRu_4$ requires C, 27.4; H, 2.8%).

(*d*) *With triphenylphosphine.* The compound [$Ru_4RhC(CO)_{12}(\eta^5\text{-}C_5Me_5)$] (0.015 g, 0.015 mmol) was stirred for 24 h with triphenylphosphine (0.050 g, 0.019 mmol) in dichloromethane (30 cm^3). The single dark green product was separated from excess PPh_3 by thin layer chromatography, eluting with dichloromethane–hexane (3:7), to give [$Ru_4RhC(CO)_{10}(PPh_3)_2(\eta^5\text{-}C_5Me_5)$] **5** (0.018 g, 0.025 mmol, 81%) (Found: C, 47.1; H, 3.1. $C_{57}H_{45}O_{10}P_2RhRu_4$ requires C, 46.9; H, 3.1%).

(*e*) *With chloride.* The salt [$N(PPh_3)_2$]Cl (0.004 g, 0.008 mmol), was added to [$Ru_4RhC(CO)_{12}(\eta^5\text{-}C_5Me_5)$] (0.003 g, 0.003 mmol) in dichloromethane (10 cm^3). The solution immediately changed from green to red resulting in the formation of the adduct [$Ru_4RhC(CO)_{12}(\eta^5\text{-}C_5Me_5)Cl$]$^-$. Protonation with $HBF_4\cdot Et_2O$ gave the product [$Ru_4RhC(CO)_{12}H(\eta^5\text{-}C_5Me_5)Cl$] **6** (0.004 g, 0.004 mmol, 43%) (Found: C, 27.0; H, 1.6. $C_{23}H_{14}ClO_{12}RhRu_4$ requires C, 26.8; H, 1.6%).

Synthesis of [$Ru_4RhC(CO)_{11}H(\eta^5\text{-}C_5Me_5)I$] **3**.—A solution of [$NEt_4$][$Ru_4RhC(CO)_{11}H(\eta^5\text{-}C_5Me_5)$] **2** in tetrahydrofuran was prepared as described in part (*b*). A solution of iodine (0.1%) was added dropwise to **2** and the reaction was followed by infrared spectroscopy. No further reaction was observed after the addition of 3 equivalents. The solution was evaporated and the residue extracted with *n*-hexane. The brown hexane solution was filtered through a bed of Celite, evaporated, and

Table 4 Fractional atomic coordinates for [$Ru_4RhC(CO)_{11}H(\eta^5\text{-}C_5Me_5)I$] **3**

Atom	*x*	*y*	*z*
Ru(1)	0.125 87(3)	0.094 91(3)	0.320 07(5)
Ru(2)	0.209 27(4)	0.223 81(3)	0.251 36(6)
Ru(3)	0.282 75(4)	0.021 25(3)	0.264 99(6)
Ru(4)	0.334 25(4)	0.146 69(3)	0.408 87(6)
Rh	0.205 24(3)	0.108 67(3)	0.076 32(5)
I	0.189 74(4)	0.115 02(3)	0.566 33(5)
C	0.249 9(4)	0.123 4(3)	0.254 7(6)
C(11)	0.074 3(5)	0.005 2(4)	0.358 6(7)
O(11)	0.043 0(4)	−0.048 6(3)	0.384 5(6)
C(12)	0.021 7(5)	0.146 1(4)	0.339 4(8)
O(12)	−0.045 0(5)	0.176 6(4)	0.347 8(7)
C(21)	0.176 5(5)	0.281 2(4)	0.393 0(8)
O(21)	0.153 1(5)	0.315 0(4)	0.478 5(7)
C(22)	0.112 4(5)	0.258 5(4)	0.159 1(8)
O(22)	0.050 6(4)	0.280 6(4)	0.107 4(7)
C(23)	0.296 8(5)	0.283 6(4)	0.177 5(8)
O(23)	0.351 8(4)	0.316 9(4)	0.129 7(7)
C(31)	0.216 1(4)	−0.047 9(4)	0.173 8(7)
O(31)	0.175 1(4)	−0.090 6(3)	0.123 0(6)
C(32)	0.394 0(6)	−0.000 4(5)	0.195 1(8)
O(32)	0.462 5(5)	−0.013 3(4)	0.148 0(7)
C(33)	0.295 3(6)	−0.036 5(5)	0.414 0(9)
O(33)	0.299 7(5)	−0.071 4(4)	0.504 9(8)
C(41)	0.405 3(6)	0.088 2(5)	0.517 1(9)
O(41)	0.448 6(5)	0.054 1(4)	0.582 9(7)
C(42)	0.349 7(5)	0.233 3(5)	0.505 4(8)
O(42)	0.360 4(4)	0.284 0(4)	0.566 0(6)
C(43)	0.426 1(6)	0.163 6(5)	0.295 0(9)
O(43)	0.481 7(5)	0.173 4(4)	0.224 0(7)
C(1)	0.162 5(4)	0.056 8(4)	−0.105 3(7)
C(2)	0.135 6(5)	0.130 9(4)	−0.105 5(7)
C(3)	0.213 7(5)	0.173 6(4)	−0.102 0(7)
C(4)	0.287 8(5)	0.126 0(4)	−0.091 4(7)
C(5)	0.255 4(4)	0.054 3(4)	−0.099 2(7)
C(1a)	0.102 6(5)	−0.006 3(4)	−0.127 8(8)
C(2a)	0.043 3(5)	0.155 3(5)	−0.125 8(8)
C(3a)	0.216 7(5)	0.253 0(4)	−0.128 6(8)
C(4a)	0.381 5(5)	0.149 3(5)	−0.094 1(9)
C(5a)	0.309 9(5)	−0.011 1(4)	−0.120 1(8)

the product crystallised by slow diffusion of hexane into a dichloromethane solution at room temperature, to give $[Ru_4RhC(CO)_{11}H(\eta^5\text{-}C_5Me_5)I]$ **3** (0.005 g, 0.005 mmol, 35%) (Found: C, 24.4; H, 1.5. $C_{22}H_{16}IO_{11}RhRu_4$ requires C, 24.2; H, 1.5%).

Crystal Structure Determination for Cluster $[Ru_4RhC(CO)_{11}H(\eta^5\text{-}C_5Me_5)I]$ **3**.—Suitable crystals of complex **3** were grown from slow diffusion of *n*-pentane–dichloromethane at room temperature. Details of crystal parameters, data collection parameters, and refinement data are summarised in Table 3. The method of data collection and processing used for cluster **3** has been described previously.[15] For cluster **3** the positions of the metal atoms were deduced from a Patterson synthesis. The remaining non-hydrogen atoms were located from subsequent Fourier-difference syntheses. Absorption corrections were applied to the data after initial refinement of the isotropic parameters of all the non-hydrogen atoms.[16] During the final cycles of refinement anisotropic thermal parameters were assigned to the five metal atoms and the iodine atom.[17] Although the hydrido ligand was not located from the Fourier-difference syntheses, only one possible site [bridging the hinge Ru(1)–Rh bond] was obtained from potential energy minimisation calculations.[18] This atom was included in the calculation of structure factors, but its parameters were not refined. The hydrogens associated with each methyl substituent on the pentamethylcyclopentadienyl ligand were geometrically calculated to ride on the respective carbon atom at distances of 1.08 Å with fixed thermal parameters of 0.08 Å^2. Full-matrix refinement of the atomic positional and thermal parameters of all the non-hydrogen atoms converged at final R and R' values of 0.0340 and 0.0343 with weights of $w = 1/\sigma^2(F_o)$ assigned to individual reflections. The final atomic coordinates for complex **3** are listed in Table 4.

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

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