Reactions of the Hexanuclear Mixed-metal Cluster $[Ru_5RhC(CO)_{14}(\eta^5\text{-}C_5Me_5)]$ and the Synthesis, Characterisation and Structural Analysis of the Pentanuclear Derivative $[Ru_4RhC(CO)_{12}(\eta^5\text{-}C_5Me_5)]$†

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

Treatment of the hexanuclear cluster $[Ru_5RhC(CO)_{14}(\eta^5\text{-}C_5Me_5)]$ **1** with 80 atmospheres of CO under 80 °C resulted in a series of decapping reactions yielding the complexes, $[Ru_3(CO)_{12}]$, $[Ru_5C(CO)_{15}]$ and a new green compound $[Ru_4RhC(CO)_{12}(\eta^5\text{-}C_5Me_5)]$ **2**. Cluster **2** crystallises in the monoclinic space group $P2_1/n$ with $a = 19.180(3)$, $b = 13.940(3)$ and $c = 10.728(2)$ Å, $\beta = 97.157(2)°$. The five metal atoms adopt a square-based pyramidal metal framework [Ru–Ru 2.776(1)–2.873(1), Ru–Rh 2.798(1)–2.881(1) Å]. The octahedral cluster $[Ru_5RhC(CO)_{14}(\eta^5\text{-}C_5Me_5)]$ **1** reacted at room temperature with a methanolic base to yield the methoxide adduct $[Ru_5RhC(CO)_{13}(CO_2Me)(\eta^5\text{-}C_5Me_5)]^-$ **3** which on acidification immediately regenerated the parent compound. On prolonged stirring, cluster **1** reacted irreversibly with the methanolic base to form the salt $[N(PPh_3)_2]_2[Ru_5RhC(CO)_{13}(\eta^5\text{-}C_5Me_5)]$ **4**.

In recent years, the chemistry of homonuclear carbido clusters of the iron triad has been well documented,[1–4] however, reports of the chemistry of their mixed-metal analogues still remains relatively rare. Several strategies have now been employed by various workers to synthesise these novel compounds and extend the investigations of their reactions in solution.[5–7] A synthetic route which has generated success in cluster build-up of such heteronuclear compounds involves 'redox-condensation', a term first applied by Chini and co-workers[8] to reactions between metal carbonyls and carbonylate ions. Reactions of this sort often involve condensation of a metal in a formally negative oxidation state with one in oxidation state zero, but may also include reactions between metal halides or cations and carbonylate anions. For example, the octahedral hexanuclear cluster $[Ru_5RhC(CO)_{14}(\eta^5\text{-}C_5Me_5)]$ has recently been synthesised by the reaction of the salt $[N(PPh_3)_2]_2[Ru_5C(CO)_{14}]$ with an equivalent amount of the complex $[Rh(C_5Me_5)(NCMe)_3][BF_4]_2$.[6] The pentamethylcyclopentadienylrhodium unit, $Rh(C_5Me_5)$, is extremely robust and has been widely used as a metal half-sandwich in mono- and bi-nuclear complex chemistry,[9] where it can remain intact through multiple transformations involving acidic, basic, oxidising and reducing conditions. The fifteen equivalent protons of the η^5-C_5Me_5 ligand provide a convenient nuclear magnetic resonance marker, assisting in the characterisation of products. For these reasons the cluster $[Ru_5RhC(CO)_{14}(\eta^5\text{-}C_5Me_5)]$ which incorporates the $Rh(C_5Me_5)$ unit offers considerable scope for examination of the cluster reactivity.

Results and Discussion

Under ambient conditions, the hexanuclear carbido cluster $[Ru_5RhC(CO)_{14}(\eta^5\text{-}C_5Me_5)]$ **1** forms immediately on reaction of $[N(PPh_3)_2]_2[Ru_5C(CO)_{14}]$ with $[Rh(C_5Me_5)(NCMe)_3][SbF_6]_2$. The very dark brown product is stable indefinitely in air in the solid state, and is virtually unaffected by heating in *n*-octane even up to a temperature of 125 °C for a period of twenty hours under nitrogen. This stability reflects the strength of the rhodium–pentamethylcyclopentadienyl bond together with the compact octahedral structure[10] of the cluster, which presents no easy pathway for attack. The cluster $[Ru_5RhC(CO)_{14}(\eta^5\text{-}C_5Me_5)]$ **1** reacts with methanolic sodium carbonate or potassium hydroxide to yield the anion tentatively formulated as $[Ru_5RhC(CO)_{13}(CO_2Me)(\eta^5\text{-}C_5Me_5)]^-$ **3**. On prolonged stirring with KOH–MeOH a dianion **4** is formed, formulated as $[Ru_5RhC(CO)_{13}(\eta^5\text{-}C_5Me_5)]^{2-}$ on the basis of fast atom bombardment (FAB) mass spectroscopy results (Scheme 1). This behaviour directly parallels that observed for the cluster $[Ru_6C(CO)_{17}]$, which is rapidly attacked by the methoxide ion to form the adduct $[Ru_6C(CO)_{16}(CO_2Me)]^-$, and on prolonged stirring with methanolic base, or rapidly with aqueous base, reacts irreversibly to form the dianion $[Ru_6C(CO)_{16}]^{2-}$.[11] At 80 °C and under eighty atmospheres of carbon monoxide cluster **1** again behaves similarly to its homonuclear analogue, undergoing a series of decapping reactions to form pentanuclear carbides. As with $[Ru_6C(CO)_{17}]$, the major product is $[Ru_5C(CO)_{15}]$, but a new green compound $[Ru_4RhC(CO)_{12}(\eta^5\text{-}C_5Me_5)]$ **2** is also formed as established by X-ray analysis. The decapping process is believed to involve nucleophilic attack of carbon monoxide on the cluster, (Scheme 2), followed by displacement of either a ruthenium or a rhodium atom. Initial characterisation of the pentanuclear cluster $[Ru_4RhC(CO)_{12}(\eta^5\text{-}C_5Me_5)]$ **2** was carried out by infrared, ^1H and ^{13}C NMR spectroscopic techniques (Tables 1 and 2). The carbonyl stretch frequencies in cluster **2** are consistent with the presence of only terminal CO groups. Variable-temperature ^{13}C NMR spectra of **2** suggest carbonyl fluxionality. At +20 °C the carbonyl signals are collapsed but at −80 °C these signals differentiate as six peaks in approximate ratio 2:2:2:3:1:2, all in the terminal region. At this temperature the carbide resonance is also detected at δ 409.1. The coupling constant, J(Rh–C) 51 Hz, is significantly higher than previously reported values for rhodium mixed-metal carbide clusters[12] (Table 3). In contrast with the carbide, no splitting of the cyclopentadienyl carbon signal was observed

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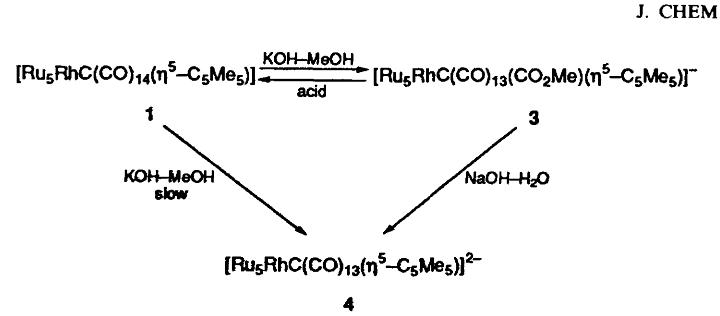
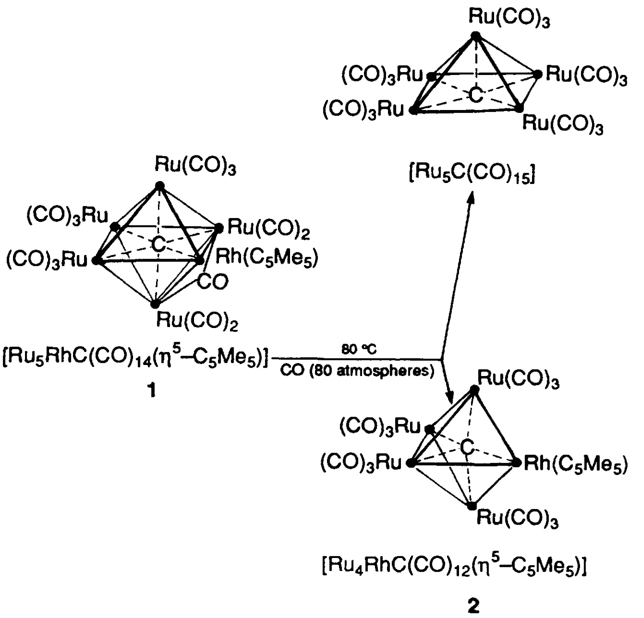
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.
Non-SI unit employed: atmosphere = 101 325 Pa.



Scheme 1



Scheme 2

Table 1 Analytical and physical data for compounds 1–4

		Analysis^a (%)		
Compound	ν_{max}(CO)^b/cm^{-1}	C	H	N
1	2075s, 2025vs, (br), 2005(sh), 1980m (br), 1815w (br)	26.4 (26.2)	1.3 (1.3)	
2	2075m, 2070(sh), 2047s, 2032m, 2010s, 1992w, 1975(sh)	28.1 (27.9)	1.5 (1.5)	
3	2041m, 1997s	43.6 (43.4)	2.9 (2.8)	0.8 (0.8)
4	2022w (br), 1999m, 1954s, 1941s, 1889w (br)	52.6 (52.5)	3.4 (3.4)	1.3 (1.3)

^{a} Calculated values in parentheses. ^{b} Measured in dichloromethane solution.

at a data-point separation of 4 Hz, suggesting a coupling constant *J*(Rh–C) of this order or less. This is consistent with other Rh(C_5Me_5) compounds, which show *J*(Rh–C) up to about 8 Hz, and with the idea that the carbon–metal bond essentially involves only the carbon 2p-π orbitals of the cyclopentadienyl ligand.[6,13]

The molecular structure of the pentanuclear mixed-metal cluster [$Ru_4RhC(CO)_{12}(\eta^5-C_5Me_5)$] **2** has been established by single-crystal X-ray diffraction analysis and is displayed in Fig. 1. Selected interatomic distances and angles are summarised in Table 4. In the solid state the pentanuclear cluster **2** adopts a square-based pyramidal or *nido*-octahedral metal-core geometry. The square base of the metal framework is defined by the metal atoms Ru(2), Ru(3), Ru(4) and Rh, with Ru(1) forming the apex of the pyramid, and the carbido atom co-ordinates to all five metal atoms.

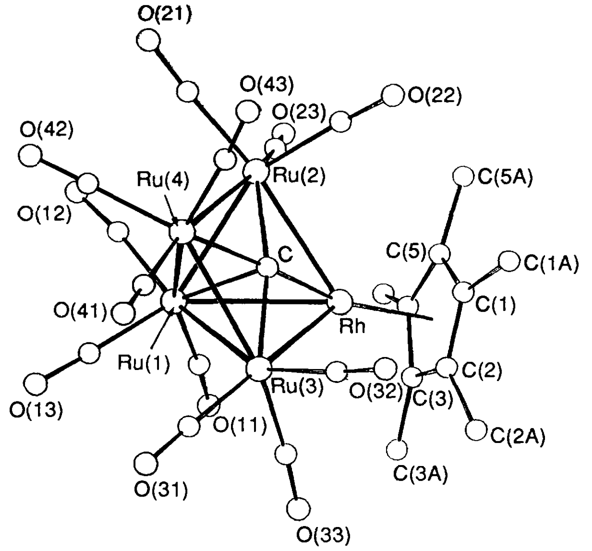


Fig. 1 The molecular structure of the pentanuclear cluster [$Ru_4RhC(CO)_{12}(\eta^5-C_5Me_5)$] **2** showing the crystallographic numbering scheme. The carbon atom of each carbonyl group has the same numbering as the oxygen atom

The range of metal–metal distances in cluster **2** [Ru–Ru 2.776(1)–2.873(1), Ru–Rh 2.798(1)–2.881(1) Å] is lower than that reported for the parent hexanuclear compound [$Ru_5RhC(CO)_{14}(\eta^5-C_5Me_5)$] **1** [Ru–Ru 2.813(1)–2.959(1), Ru–Rh 2.825(1)–2.895(1) Å].[10] The mean Ru–Ru bond in **2** [2.810(1) Å] is notably shorter than that observed in **1** [2.890(1) Å], the homonuclear analogue [$Ru_5C(CO)_{15}$] [2.840(2) Å][14] and the organopentaruthenium cluster, [$Ru_5C(CO)_{13}(\eta^6-C_6H_8)$] [2.831(2) Å].[7] However, the mean Ru–Ru bond in **2** closely resembles the mean distance calculated for the arene derivative, [$Ru_5C(CO)_{13}(\eta^6-C_6H_6)$] [2.813(2) Å].[7] The range of Ru–Rh distances in the pentanuclear cluster **2** are significantly longer than that in the tetranuclear clusters [$Ru_3RhH_3(CO)_{12}$] [2.757(3)–2.762(3) Å] and [$Ru_2Rh_2H_2(CO)_{12}$] [2.756(3)–2.768(3) Å].[15] This could be a result of the increased nuclearity in **2** coupled with the expansion of the metal framework due to the presence of a carbido atom. The four metal–metal bonds associated with the square base in the structure of **2** show a marked variation with one metal–metal bond [Ru(3)–Ru(4) 2.873(1) Å] being significantly longer than the other three [Ru(2)–Ru(4) 2.830(1), Ru(2)–Rh 2.798(1) and Ru(3)–Rh 2.810(1) Å]. The apical bonds from Ru(1) also vary, with the Ru(1)–Rh bond markedly longer than the other three apical Ru–Ru bonds (Table 4). This may be attributed to the presence of a different coinage metal atom in the Ru_4Rh framework which does not carry any carbonyl groups, and to the steric influence enforced by the bulky C_5Me_5 group co-ordinating to the rhodium atom. This steric influence could also account for the observation that the isomer with the Rh(C_5Me_5) unit at the basal site appears to form in preference

Table 2 Proton and ^{13}C NMR data[a] for compounds **1–4**

Compound	T/°C	$^1H^b(\delta)$	$^{13}C^c(\delta)$
1	Ambient	2.05 (s, C_5Me_5)	12.2 (s, C_5*Me_5*) 104.3 (s, *C_5*Me_5) 201.0 (s, CO)
	−60		12.1 (s, C_5*Me_5*) 104.1 (s, *C_5*Me_5) 202.0 (br s, CO) 422.4 [d, *J*(Rh–C) (carbide)] 44
2	Ambient	2.18 (s, C_5Me_5)	11.1 (s, C_5*Me_5*) 102.7 (s, *C_5*Me_5)
	−80		11.1 (s, C_5*Me_5*) 102.7 (s, *C_5*Me_5) 189.7 (s, 2CO) 192.6 (s, 1CO) 197.0 (s, 3CO) 198.1 (s, 2CO) 198.6 (s, 2CO) 200.5 (s, 2CO) 409.1 [d, *J* (Rh–C) (carbide)] 51
3	Ambient	2.08 (s, C_5Me_5) 4.44 (s, CO_2Me) 7.5–8.1 (m, $[N(PPh_3)_2]^+$)	
4	Ambient	2.08 (s, C_5Me_5) 7.3–7.9 (m, $[N(PPh_3)_2]^+$)	

[a] Chemical shifts (δ) in ppm, coupling constants (*J*) in Hz. [b] Measured in CD_2Cl_2. [c] Measured in $CDCl_3$.

Table 3 Carbon-13 NMR data for cluster carbides coupled to rhodium

Compound	δ (carbide)	*J*(Rh–C)/Hz	Reference
$[Rh_6C(CO)_{15}]^{2-}$	264.7	13.7	12(*a*)
$[Rh_6HC(CO)_{15}]^-$	291.2	10, 15	12(*b*)
$[\{Cu(NCMe)\}\{Rh_6C(CO)_{15}\}]^-$	281.8	13.2	12(*c*)
$[\{Cu(NCMe)\}_2\{Rh_6C(CO)_{15}\}]$	300.3	12.7	12(*c*)
$[\{Au(PEt_3)\}\{Rh_6C(CO)_{15}\}]^-$	285.3	10.7, 12.7	12(*c*)
$[Ag_2Rh_6C(CO)_{15}]$	300.3	12.7	12(*c*)
$[RhFe_3C(CO)_{12}]^-$	461.1	19.5	12(*d*)
$[Ru_5RhC(CO)_{14}(\eta^5\text{-}C_5Me_5)]$ **1**	422.4	44	
$[Ru_4RhC(CO)_{12}(\eta^5\text{-}C_5Me_5)]$ **2**	409.1	51	

Table 4 Selected bond lengths (Å) and angles (°) for $[Ru_4RhC(CO)_{12}(\eta^5\text{-}C_5Me_5)]$ **2**, with estimated standard deviations (e.s.d.s) in parentheses

Ru(1)–Ru(2)	2.792(1)	Ru(1)–Ru(3)	2.776(1)
Ru(1)–Ru(4)	2.795(1)	Ru(1)–Rh	2.881(1)
Ru(2)–Ru(4)	2.830(1)	Ru(2)–Rh	2.798(1)
Ru(3)–Ru(4)	2.873(1)	Ru(3)–Rh	2.810(1)
Ru(1)–C	2.146(7)	Ru(2)–C	2.037(7)
Ru(3)–C	2.011(7)	Ru(4)–C	2.033(8)
Rh–C	1.943(8)		
Ru–CO(terminal)	1.855(11)–1.892(11)		
Rh–C (C_5Me_5 ring)	2.179(8)–2.260(8)		
Ru(3)–Ru(1)–Ru(2)	92.5(1)	Ru(4)–Ru(1)–Ru(2)	60.9(1)
Ru(4)–Ru(1)–Ru(3)	62.1(1)	Rh–Ru(1)–Ru(2)	59.1(1)
Rh–Ru(1)–Ru(3)	59.5(1)	Rh–Ru(1)–Ru(4)	88.7(1)
Ru(4)–Ru(2)–Ru(1)	59.6(1)	Rh–Ru(2)–Ru(1)	62.1(1)
Rh–Ru(2)–Ru(4)	89.7(1)	Ru(4)–Ru(3)–Ru(1)	59.3(1)
Rh–Ru(3)–Ru(1)	62.1(1)	Rh–Ru(3)–Ru(4)	88.6(1)
Ru(2)–Ru(4)–Ru(1)	59.5(1)	Ru(3)–Ru(4)–Ru(1)	58.6(1)
Ru(3)–Ru(4)–Ru(2)	89.7(1)	Ru(2)–Rh–Ru(1)	58.9(1)
Ru(3)–Rh–Ru(1)	58.4(1)	Ru(3)–Rh–Ru(2)	91.7(1)
Ru–C–O(terminal)	173(8)–179(9)		

to the alternative isomer in which this fragment would have to adopt a more sterically hindered apical position. The basal isomer may also be kinetically and thermodynamically more favoured due to the probability of basal co-ordination being four times as likely as the apical one.

In the pentanuclear cluster **2** the metal–carbide bond lengths show a marked variation with the Rh–C distance of 1.943(8) Å being significantly shorter than the Ru–C lengths [2.011(7)–2.146(7) Å, Table 4]. Interestingly, this feature is consistent with what has been observed in numerous penta- and hexaruthenium carbidoarene clusters where shortening of the Ru–C bonds occurs systematically when a tricarbonyl unit is replaced by a poorer π-acceptor arene ligand as for example in the clusters $[Ru_6C(CO)_{14}(\eta^6\text{-arene})]$ [arene = $C_6H_3Me_3$-1,3,5, $C_6H_4Me_2$-1,3 or C_6H_5Me][16] and $[Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)]$.[7] In cluster **2** the carbido atom is found to lie 0.17(2) Å below the square plane, and results in the apical Ru(1)–C bond being 0.119(7) Å longer than the mean of the other three basal Ru–C distances. The cyclopentadienyl ligand in **2** is found to bond in a terminal fashion to the rhodium atom with the range of Rh–C (C_5Me_5 ring) distances [2.179(8)–2.260(8) Å] being similar to that observed in the related hexanuclear cluster, $[Ru_5RhC(CO)_{14}(\eta^5\text{-}C_5Me_5)]$ [2.217(9)–2.254(9) Å],[10] and to those reported for numerous mononuclear rhodium(I) complexes.[17,18]

Experimental

Spectroscopic and analytical data for compounds **1–4** are summarised in Tables 1 and 2.

Infrared spectra were recorded on a Perkin Elmer 983 spectrophotometer. Proton NMR spectra were recorded on a Bruker WP 80 SY instrument. Carbon-13 NMR spectra were recorded on a Bruker WM 250 instrument. Mass spectra were recorded on an MS-12 instrument and the fast atom bombardment mass spectra on an AEMS 50 machine.

Synthesis of $[Rh(C_5Me_5)(NCMe)_3][SbF_6]_2$.—Crude $[Rh_2(C_5Me_5)_2Cl_4]$ was prepared from a purchased sample of $RhCl_3{\cdot}xH_2O$ (1 g) and was stirred in freshly distilled acetonitrile (50 cm^3). Excess of silver hexafluoroantimonate was added, which resulted in an immediate precipitation of silver chloride and a change in the colour of the solution from red to yellow. The solution was carefully filtered through a bed of Celite (approximately 2 cm thick), then reduced in volume to 10 cm^3. Diethyl ether was added to precipitate the yellow-orange product, which was collected, washed with diethyl ether and used without further purification. IR (Nujol mull): 2320 and 2293 cm^{-1}. ^{1}H NMR(CD$_3$CN): δ 1.68 (s, C$_5$Me$_5$) and 1.8–2.2 (various peaks, co-ordinated and free NCMe).

Table 5 X-Ray crystal structure determination data for [Ru$_4$RhC(CO)$_{12}$(η^5-C$_5$Me$_5$)] **2**

(*a*) Crystal data	
Molecular formula	C$_{23}$H$_{15}$O$_{12}$RhRu$_4$
M	990.67
Crystal dimensions/mm	0.23 × 0.21 × 0.13
Cell determined from 25 reflections in 2θ range/°	15 < 2θ < 25
Crystal system	Monoclinic
Space group	*P*2$_1$/*n*
a/Å	19.180(3)
b/Å	13.940(3)
c/Å	10.728(2)
β/°	97.157(2)
U/Å^3	2845.99
D$_c$/g cm^{-3}	2.312
Z	4
F(000)	1880
μ(Mo-Kα)/mm^{-1}	0.79
T/K	298
(*b*) Data collection	
Diffractometer	Philips PW1100
2θ Range/°	6.0–50.0
No. of reflections measured	4317
hkl Range	−27 to 27, 0–18, 0–15
Scan mode	ω–2θ
No. steps in scan	30
Step width/°	0.05
Minimum counts for reflection to be measured (counts s^{-1})	10
n, where *F* > *n*σ(*F*)	6
Total no. of reflections [*I* > 3σ(*I*)]	3946
No. of standard reflections	3
Variation in intensity (%)	< 5
Maximum, minimum transmission factors	1.045, 0.923
(*c*) Structure refinement	
No. of reflections used in refinement	3750
No. of refined parameters	191
R	0.0397
R′ = Σ*w*$^{\frac{1}{2}}$/Σ*w*$^{\frac{1}{2}}$|*F*$_o$|	0.0441
Maximum, minimum electron-density peak/e Å^{-3}	0.33, −0.51

Synthesis of [Ru$_5$RhC(CO)$_{14}$(η^5-C$_5$Me$_5$)] **1**.—The salt [N(PPh$_3$)$_2$]$_2$[Ru$_5$C(CO)$_{14}$] (0.212 g, 0.107 mmol) was dissolved in dichloromethane (20 cm^3) and mixed with a suspension of [Rh(C$_5$Me$_5$)(NCMe)$_3$][SbF$_6$]$_2$ (0.2 g, 0.24 mmol, excess) in dichloromethane (10 cm^3). The solution immediately became dark brown. After stirring for 10 min, the solution was eluted through a short column of Kieselgel 60 with dichloromethane–hexane (1 : 1). The dark brown product (0.114 g, 0.10 mmol, 70%) was crystallised by repeated addition of hexane and partial evaporation of the eluted solution. [*m*/*z* 1150 (*M*$^+$) and a sequence of peaks due to the loss of CO from *M*$^+$].

Reactions of [Ru$_5$RhC(CO)$_{14}$(η^5-C$_5$Me$_5$)] **1**.—1 *Thermal stability*. Compound **1** (0.005 g, 0.004 mmol) was heated at 125 °C in *n*-octane (10 cm^3) for 24 h. The solvent was evaporated and the residue redissolved in dichloromethane. Spot thin-layer chromatography and solution infrared spectroscopy showed it to be at least 90% [Ru$_5$RhC(CO)$_{14}$(η^5-C$_5$Me$_5$)], with a small amount of baseline material immobile in non-polar solvents.

2 *Base reactions*. (*a*) Compound **1** (0.02 g, 0.017 mmol) was stirred overnight at −37 °C in a methanol solution (15 cm^3) containing potassium hydroxide (0.1 g, 0.18 mmol) and [N(PPh$_3$)$_2$]Cl (0.1 g, 0.17 mmol). The solution was filtered through a prechilled Schlenk sinter, which left a brown residue which was extracted with dichloromethane. From microanalysis, IR and NMR data the compound was tentatively formulated as the salt [N(PPh$_3$)$_2$][Ru$_5$RhC(CO)$_{13}$(CO$_2$Me)-(η^5-C$_5$Me$_5$)] **3**.

(*b*) Compound **1** (0.02 g, 0.017 mmol) was stirred at room temperature in methanol (10 cm^3) with sodium carbonate (0.1 g, 0.943 mmol). When all the dark brown material had dissolved (after half an hour) the solution was filtered to remove Na$_2$CO$_3$. The infrared spectrum of the methanol solution showed absorbances at 2035m and 1998s cm^{-1} indicating the same product as in (*a*). One drop of HBF$_4$ in Et$_2$O was added, giving a brown precipitate immediately. This was redissolved in dichloromethane and identified by its infrared spectrum to be the starting material.

(*c*) Compound **1** (0.03 g, 0.026 mmol) was stirred for 5 h at room temperature in a methanol solution (15 cm^3) containing potassium hydroxide (0.1 g, 1.80 mmol). Excess of [N(PPh$_3$)]$_2$Cl in methanol was added to precipitate the brown

Table 6 Fractional atomic coordinates for [Ru$_4$RhC(CO)$_{12}$(η^5-C$_5$Me$_5$)] **2** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru(1)	0.168 79(3)	0.161 89(4)	0.000 86(6)	C(32)	−0.029 0(5)	0.343 6(7)	−0.037 4(9)
Ru(2)	0.228 39(3)	0.331 78(4)	0.102 49(6)	O(32)	−0.065 2(4)	0.409 7(6)	−0.031 3(8)
Ru(3)	0.035 54(3)	0.242 43(5)	−0.041 04(6)	C(33)	−0.011 1(5)	0.148 2(7)	0.038 4(10)
Ru(4)	0.152 17(3)	0.330 37(5)	−0.141 04(6)	O(33)	−0.039 5(4)	0.086 1(6)	0.083 1(8)
Rh	0.110 32(3)	0.259 92(4)	0.200 33(6)	C(41)	0.088 8(5)	0.322 8(7)	−0.288 9(9)
C	0.127 0(4)	0.301 2(5)	0.033 6(7)	O(41)	0.050 0(4)	0.327 3(5)	−0.380 1(7)
C(11)	0.150 8(5)	0.064 3(7)	0.114 5(9)	C(42)	0.230 9(5)	0.298 2(7)	−0.221 0(9)
O(11)	0.140 1(3)	−0.000 4(5)	0.175 6(7)	O(42)	0.278 5(4)	0.277 1(6)	−0.270 1(7)
C(12)	0.266 4(5)	0.145 0(6)	0.011 2(9)	C(43)	0.160 2(5)	0.464 7(7)	−0.152 3(9)
O(12)	0.326 0(4)	0.127 1(6)	0.008 4(7)	O(43)	0.170 1(4)	0.546 4(6)	−0.161 5(8)
C(13)	0.144 4(5)	0.093 2(7)	−0.148 0(10)	C(1)	0.067 3(4)	0.352 9(6)	0.335 1(8)
O(13)	0.131 4(5)	0.050 8(6)	−0.241 2(9)	C(2)	0.022 8(4)	0.271 9(6)	0.315 4(8)
C(21)	0.307 0(4)	0.363 8(6)	0.022 4(8)	C(3)	0.062 0(4)	0.188 0(6)	0.357 8(8)
O(21)	0.355 8(4)	0.387 4(5)	−0.023 5(7)	C(4)	0.131 3(4)	0.219 1(6)	0.403 1(8)
C(22)	0.214 4(4)	0.457 2(6)	0.158 6(8)	C(5)	0.135 7(4)	0.319 6(6)	0.391 6(8)
O(22)	0.201 8(3)	0.532 6(5)	0.192 0(6)	C(1A)	0.043 6(5)	0.456 7(7)	0.317 2(10)
C(23)	0.286 0(4)	0.285 9(6)	0.247 4(9)	C(2A)	−0.056 7(5)	0.275 9(7)	0.281 3(10)
O(23)	0.322 6(3)	0.256 6(5)	0.331 5(7)	C(3A)	0.032 5(5)	0.090 1(7)	0.372 0(9)
C(31)	−0.006 0(5)	0.192 4(8)	−0.196 7(11)	C(4A)	0.187 1(4)	0.154 0(7)	0.470 1(9)
O(31)	−0.032 5(4)	0.159 0(6)	−0.289 9(9)	C(5A)	0.192 8(4)	0.386 1(7)	0.453 1(9)

salt $[N(PPh_3)_2]_2[Ru_5RhC(CO)_{13}(\eta^5\text{-}C_5Me_5)]$ **4** (0.043 g, 0.019 mmol, 75%). [m/z (FAB) 1121 (M^+ of anion) and 1065 (M^+ −2CO)].

Synthesis of $[Ru_4RhC(CO)_{12}(\eta^5\text{-}C_5Me_5)]$ **2**.—The compound $[Ru_5RhC(CO)_{14}(\eta^5\text{-}C_5Me_5)]$ **1** (0.39 g, 0.34 mmol) was sealed with *n*-heptane (30 cm^3) in a glass liner inside a 100 cm^3 Roth autoclave. The autoclave was filled with carbon monoxide at *ca.* 20 atmospheres and the pressure was then released. This cycle was repeated to flush out air. The autoclave was then pressurised to 80 atmospheres of carbon monoxide, and heated at 80 °C for 4 h with stirring. After cooling, the pressure was released, the *n*-heptane evaporated and the purple residue dissolved in dichloromethane. The products were separated by thin-layer chromatography on silica plates, eluting with dichloromethane (30%)–hexane (70%), to give yellow $[Ru_3(CO)_{12}]$, pink $[Ru_5C(CO)_{15}]$ (0.163 g, 0.17 mmol, 51%) and green $[Ru_4RhC(CO)_{12}(\eta^5\text{-}C_5Me_5)]$ (0.123 g, 0.12 mmol, 36%) together with some unrecovered brown baseline material.

Crystal Structure Determination of Cluster $[Ru_4RhC(CO)_{12}(\eta^5\text{-}C_5Me_5)]$ **2**.—Suitable crystals of cluster **2** were grown from the slow diffusion of *n*-pentane–dichloromethane at room temperature. Details of the crystal parameters, data collection parameters, and refinement data are summarised in Table 5. The method of data collection and processing have been described previously.[19] The positions of the metal atoms were deduced from a Patterson synthesis and the remaining non-hydrogen atoms were located from subsequent Fourier difference syntheses. Empirical absorption corrections were applied to the data after initial refinement of the isotropic parameters of all the non-hydrogen atoms.[20] During the final cycles of refinement, anisotropic thermal parameters were assigned to the metal atoms.[21] The hydrogens associated with each methyl substituent on the pentamethylcyclopentadienyl ligand were geometrically calculated to ride at 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 0.0397 and 0.0441 with weights of $w = 1/\sigma^2(F_o)$ assigned to individual reflections. The final atomic coordinates for cluster **2** are listed in Table 6.

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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