Synthesis of the Mixed-metal Clusters $[Ru_5RhC(CO)_{14}(cod)Y]$ [Y = H, $Au(PEt_3)$ or $Au(PPh_3)$; cod = cycloocta-1,5-diene]; Reactions of $[Ru_5RhC(CO)_{14}(cod)\{Au(PR_3)\}]$ (R = Ph or Et) and Crystal Structure of $[Ru_5RhC(CO)_{14}(cod)\{\mu_3\text{-}Au(PPh_3)\}]$†

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Treatment of the pentaruthenium salt $[N(PPh_3)_2]_2[Ru_5C(CO)_{14}]$ with an excess of $[Rh(cod)_2][SbF_6]$ (cod = cycloocta-1,5-diene) yielded the monoanion $[Ru_5RhC(CO)_{14}(cod)]^-$ which has been isolated as its $[N(PPh_3)_2]^+$ salt **1**. Reaction of the monoanion with $HBF_4{\cdot}Et_2O$ gave the hydrido derivative $[Ru_5RhH(C)(CO)_{14}(cod)]$ **2**. Compound **1** reacted with the gold salts $[Au(PPh_3)]Cl$ and $[Au(PEt_3)]Cl$, respectively, to yield the cluster compounds $[Ru_5RhC(CO)_{14}(cod)\{Au(PPh_3)\}]$ **3** and $[Ru_5RhC(CO)_{14}(cod)\{Au(PEt_3)\}]$ **4**. Compound **3** crystallises in the triclinic space group $P\bar{1}$ (no. 2) with $a = 15.993(3)$, $b = 9.728(2)$, $c = 13.900(3)$ Å, $\alpha = 90.29(2)$, $\beta = 99.97(2)$, $\gamma = 88.36(2)$°. The metal core geometry consists of a central Ru_5Rh octahedron with one Ru_3 face capped by a μ_3-$Au(PPh_3)$ fragment [Ru–Ru 2.787(1)–3.093(1); Ru–Rh 2.892(1)–2.952(1); Ru–Au 2.735(1)–3.082(1) Å]. The reactions of **3** and **4** with norbornadiene, PPh_3 and $P(OMe)_3$ are reported.

In recent years mixed-metal compounds have gained much interest owing to the induced asymmetry in electronic and steric properties arising from the presence of more than one type of metal atom.[1] In particular, there has been considerable interest in possible synergistic effects between the metals in these cluster complexes in terms of specific reactivity or enhancement of catalytic activity.[2,3]

In the course of our investigations into the chemistry of ruthenium–rhodium mixed-metal compounds, in which both elements could act as potential sites for organometallic activity, we recently reported the synthesis, reactions and crystal structure of the cluster compounds $[Ru_5RhC(CO)_{14}(\eta^5\text{-}C_5Me_5)]$, $[Ru_4RhC(CO)_{12}(\eta^5\text{-}C_5Me_5)]$ and $[Ru_4RhH(C)(CO)_{11}(\eta^5\text{-}C_5Me_5)I]$.[4–6] We observed that the presence of the substitution labile rhodium organic fragment $Rh(\eta^5\text{-}C_5Me_5)$ in these cluster species does not promote reactivity at the rhodium atom and subsequent work has been directed to synthesis of related cluster compounds containing a more labile rhodium–organic linkage. The (cycloocta-1,5-diene)rhodium fragment, Rh(cod), was selected as a suitable candidate on account of its ready availability and widespread use in mono- and polynuclear chemistry.[7] The use of the neutral compound $[\{Rh(cod)Cl\}_2]$ was shown by Tachikawa *et al.*[8] to lead to the mixed-metal iron–rhodium cluster $[Fe_5RhC(CO)_{14}(cod)]^-$ by the carbonylate anion–metal halide condensation route; in the present work a cation, $[Rh(cod)_2]^+$, was used with the purpose of enhancing rapid and facile reaction with the pentaruthenium dianion $[Ru_5C(CO)_{14}]^{2-}$

Results and Discussion

The pentaruthenium salt $[N(PPh_3)_2]_2[Ru_5C(CO)_{14}]$ reacts immediately on mixing with $[Rh(cod)_2][SbF_6]$ in dichloromethane at room temperature. The red product, which was not successfully purified, is tentatively formulated as the monoanion $[Ru_5RhC(CO)_{14}(cod)]^-$ **1** on the basis of its IR data and of its reactions with tetrafluoroboric acid–diethyl ether to give $[Ru_5RhH(C)(CO)_{14}(cod)]$ **2** and with the gold salts $[Au(PR_3)]Cl$ (R = Ph or Et) to give $[Ru_5RhC(CO)_{14}(cod)\{Au(PR_3)\}]$ (R = Ph **3** or Et **4**) respectively. These three red compounds have been formulated on the basis of their IR, ^1H NMR and mass spectroscopic data (Table 1). The solution IR spectra for **2**–**4** were found to be very similar and the compounds were accordingly assumed, at first, to have similar structures with the gold atom occupying similar sites on the metal polyhedron, as expected from the isolobal principle.[9]

Reactions of the two gold derivatives **3** and **4** with norbornadiene (bicyclo[2.2.1]hepta-2,5-diene), PPh_3 and $P(OMe)_3$ have shown that the cod ligand is less substitution labile than anticipated. In each case there was no indication of substitution products being formed and slow reduction occurred to form materials which appear to be anionic. Reactions of **3** and **4** with carbon monoxide proved to be more successful leading to clusters without the cod ligand. At 80 °C under 80 atm pressure of CO they give the new hexa- and hepta-nuclear cluster species $[Ru_4RhC(CO)_{14}\{Au(PR_3)\}]$ (R = Ph **5** or Et **6**) and $[Ru_5RhC(CO)_{16}\{Au(PR_3)\}]$ (R = Ph **7** or Et **8**) together with $[Ru_3(CO)_{12}]$. These compounds were formulated on the basis of their spectroscopic data (Table 1). The infrared spectra for the ethyl and phenyl derivatives were found to be very similar, and the compounds were therefore assumed to be isostructural. The retention of the carbido-centred metal octahedral core in the formulation of **3** and **4** contrasts with the reactions of $[Ru_6C(CO)_{17}]$[10] and $[Ru_5RhC(CO)_{14}(\eta^5\text{-}C_5Me_5)]$,[4,5] which both lose a ruthenium atom under these conditions. This indicates that the bridging $Au(PR_3)$ unit in **3** and **4** helps to maintain the integrity of the metal core. Interestingly, even under these severe conditions about 10% of the starting material

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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: atm = 101 325 Pa.

Table 1 Spectroscopic data for compounds **1**–**8**

Compound	$\tilde{\nu}_{max}(CO)^a/cm^{-1}$	^1H NMR [b]	Mass spectrum (*m*/*z*)
1	2062m 2022s 2006m 1860w (br)		
2	2081m 2039s 2030(sh) 1990m 1885vw (br) 1834w (br)	−18.6 [d, *J*(Rh–H) = 1.5, hydride] 1.9–2.4 (m, br, CH_2) 5.22 (s, br, CH)	1122 and loss of 14 CO groups
3	2063m 2023s 2018(sh) 1975m 1865w (br) 1832w (br)	1.7–2.4 (m, br, CH_2) 4.9 (s, br, CH) 7.5–7.7 (m, Ph)	1578 and loss of six CO groups
4	2062m 2022s 2015(sh) 1976m 1862w (br) 1832w (br)	0.9–1.6 (m, complex, CH_3) 1.8–2.5 (m, complex, Et and cod CH_2) 4.9 (s, br, CH)	1435 and loss of six CO groups
5	2058s 2044s 2040m 2010w	7.46–7.60 (m, Ph)	
6	2054s 2042s (br) 2008w	0.8–1.5 (m, CH_3) 1.7–2.2 (m, CH_2)	1227 and loss of four CO groups
7	2083w 2042vs 2022(sh) 1870w (br)	7.40–7.72 (m, Ph)	
8	2082w 2041vs 2020(sh) 1862w (br)	0.8–1.5 (m, CH_3) 1.8–2.3 (m, CH_2)	1384 and loss of seven CO groups

[a] Measured in CH_2Cl_2. [b] Chemical shifts (δ) in ppm and coupling constants in Hz; measured in CD_2Cl_2.

remains unchanged after 4 h of reaction, possibly a further indication of the difficulty associated with displacing the cod ligand. Although cod has been effectively used as a labile centre in reactions of compounds of the iron subgroup,[11,12] reports of this role in complexes of the cobalt triad remain relatively rare.

The structure of the mixed-metal heptanuclear cluster $[Ru_5RhC(CO)_{14}(cod)\{\mu_3\text{-}Au(PPh_3)\}]$ **3** has been determined by a single-crystal X-ray diffraction study and is displayed in Fig. 1, with selected bond lengths and angles in Table 2. The metal core contains an Ru_5Rh octahedron with the carbido atom encapsulated in the central cavity. The $Au(PPh_3)$ fragment strongly bridges the Ru(2)–Ru(4) edge [mean Ru–Au 2.749(1) Å] and leans across the Ru(1)–Ru(2)–Ru(4) face, resulting in a considerably longer bond to Ru(1) [Ru(1)–Au 3.082(1) Å] (Table 2). As expected the bond Ru(2)–Ru(4) [3.093(1) Å] bridged by the $Au(PPh_3)$ ligand is markedly longer than any of the remaining Ru–Ru distances in the structure [2.787(1)–2.901(1) Å].

The IR spectra of the gold-containing clusters **3** and **4** were found to be similar to that of the hydrido analogue $[Ru_5RhH(C)(CO)_{14}(cod)]$ **2** indicating that the bonding mode of the hydride in **2** was probably similar to that for the isolobal $Au(PPh_3)$ unit in cluster **3**. Similar correspondence in the IR spectra was previously observed for the nitrosyl gold cluster $[Ru_6C(CO)_{15}(NO)\{Au(PPh_3)\}]$ **9**[13] and its hydrido analogue $[Ru_6H(C)(CO)_{15}(NO)]$ **10**.[14] Crystal structure analysis showed that the $Au(PPh_3)$ group in **9** was in an asymmetrically face-capping position, strongly bridging one edge and forming a weak bond with the third Ru atom, and the hydride ligand in **10** was in a very similar site bridging the same edge and leaning towards the third Ru atom. Although crystals of $[Ru_5RhH(C)(CO)_{14}(cod)]$ **2** suitable for X-ray analysis could not be obtained, it may be concluded that the hydride in it bridges the edge corresponding to Ru(2)–Ru(4) in **3** and leans towards Ru(1), the third atom of that face.

The IR spectrum of $[Ru_5RhC(CO)_{14}(cod)\{\mu_3\text{-}Au(PPh_3)\}]$ **3** indicates the presence of both terminal and bridging carbonyl groups. This is consistent with the crystal structure in which eleven of the carbonyl ligands are terminal, one bridges the vector Ru(3)–Ru(5) [Ru(3)–C(35) 2.004(11), Ru(5)–C(35) 2.141(12) Å], and two form markedly asymmetric bridges across the edges Ru(2)–Ru(5) [Ru(2)–C(22) 1.919(12), Ru(5)–C(22) 2.299(13) Å] and Ru(3)–Ru(4) [Ru(3)–C(34) 2.420(12), Ru(4)–C(34) 1.886(12) Å]. The carbon atoms C(1), C(2), C(5) and C(6) of the cod ligand co-ordinate to the rhodium atom with the C(1)–C(2) and C(5)–C(6) lengths [mean 1.372(11) Å] being significantly shorter than the remaining C–C bonds [range 1.483(11)–1.529(15) Å].

The Ru–Ru distances in compound **3** [2.787(1)–3.093(1) Å] are similar in range to those observed in the Ru_6Au nitrosyl cluster $[Ru_6C(CO)_{15}(NO)\{\mu_3\text{-}Au(PPh_3)\}]$ **9** [2.803(2)–3.099(2) Å][13] but are in a wider range than those in the analogous cyclopentadienyl hexanuclear compound $[Ru_5RhC(CO)_{14}(\eta^5\text{-}C_5Me_5)]$ **11** [Ru–Ru 2.813(1)–2.959(1) Å].[5] Interestingly, despite the marked lengthening of the bond

Table 2 Selected bond lengths (Å) and angles (°) for [$Ru_5RhC(CO)_{14}(cod)\{\mu_3\text{-}Au(PPh_3)\}$] **3** with estimated standard deviations (e.s.d.s) in parentheses

Au–Ru(1)	3.082(1)	Au–Ru(2)	2.763(1)	Ru(5)–Rh	2.952(1)	Ru(1)–C	2.135(10)
Au–Ru(4)	2.735(1)	Ru(1)–Ru(2)	2.833(1)	Ru(2)–C	2.063(10)	Ru(3)–C	2.035(10)
Ru(1)–Ru(3)	2.901(1)	Ru(1)–Ru(4)	2.840(1)	Ru(4)–C	2.011(9)	Ru(5)–C	2.048(10)
Ru(1)–Ru(5)	2.854(1)	Ru(2)–Ru(4)	3.093(1)	Rh–C	1.968(10)	Au–P	2.280(3)
Ru(2)–Ru(5)	2.815(1)	Ru(3)–Ru(4)	2.805(1)	Rh–C(1)	2.178(11)	Rh–C(2)	2.178(11)
Ru(2)–Rh	2.928(1)	Ru(3)–Ru(5)	2.787(1)	Rh–C(5)	2.186(9)	Rh–C(6)	2.185(10)
Ru(3)–Rh	2.926(1)	Ru(4)–Rh	2.892(1)				

Ru–CO (terminal) 1.815(12)–1.880(12), [bridging, CO(35)] 2.004(11) and 2.141(12), [semibridging, CO(22) and CO(34)] 1.886(12)–2.420(12)

Ru(2)–Au–Ru(1)	57.7(1)	Ru(4)–Au–Ru(1)	58.1(1)	Ru(3)–Ru(4)–Ru(1)	61.8(1)	Ru(3)–Ru(4)–Ru(2)	87.5(1)
Ru(4)–Au–Ru(2)	68.5(1)	P–Au–Ru(1)	140.8(1)	Rh–Ru(4)–Au	112.3(1)	Rh–Ru(4)–Ru(1)	91.4(1)
P–Au–Ru(2)	134.7(1)	P–Au–Ru(4)	153.2(1)	Rh–Ru(4)–Ru(2)	58.5(1)	Rh–Ru(4)–Ru(3)	61.8(1)
Ru(2)–Ru(1)–Au	55.5(1)	Ru(3)–Ru(1)–Au	112.7(1)	Ru(2)–Ru(5)–Ru(1)	60.0(1)	Ru(3)–Ru(5)–Ru(1)	61.9(1)
Ru(3)–Ru(1)–Ru(2)	90.8(1)	Ru(4)–Ru(1)–Au	54.8(1)	Ru(3)–Ru(5)–Ru(2)	93.6(1)	Rh–Ru(5)–Ru(1)	89.9(1)
Ru(4)–Ru(1)–Ru(2)	66.1(1)	Ru(4)–Ru(1)–Ru(3)	58.5(1)	Rh–Ru(5)–Ru(2)	61.0(1)	Rh–Ru(5)–Ru(3)	61.2(1)
Ru(5)–Ru(1)–Au	114.0(1)	Ru(5)–Ru(1)–Ru(2)	59.3(1)	Ru(3)–Rh–Ru(2)	88.4(1)	Ru(4)–Rh–Ru(2)	64.2(1)
Ru(5)–Ru(1)–Ru(3)	57.9(1)	Ru(5)–Ru(1)–Ru(4)	90.6(1)	Ru(4)–Rh–Ru(3)	57.6(1)	Ru(5)–Rh–Ru(2)	57.2(1)
Ru(1)–Ru(2)–Au	66.8(1)	Ru(4)–Ru(2)–Au	55.3(1)	Ru(5)–Rh–Ru(3)	56.6(1)	Ru(5)–Rh–Ru(4)	87.6(1)
Ru(4)–Ru(2)–Ru(1)	57.1(1)	Ru(5)–Ru(2)–Au	126.4(1)	Ru(2)–C–Ru(1)	84.9(4)	Ru(3)–C–Ru(1)	88.1(4)
Ru(5)–Ru(2)–Ru(1)	60.7(1)	Ru(5)–Ru(2)–Ru(4)	86.3(1)	Ru(3)–C–Ru(2)	170.1(6)	Ru(4)–C–Ru(1)	86.4(3)
Rh–Ru(2)–Au	110.4(1)	Rh–Ru(2)–Ru(1)	90.8(1)	Ru(4)–C–Ru(2)	98.8(4)	Ru(4)–C–Ru(3)	87.8(4)
Rh–Ru(2)–Ru(4)	57.3(1)	Rh–Ru(2)–Ru(5)	61.8(1)	Ru(5)–C–Ru(1)	86.0(4)	Ru(5)–C–Ru(2)	86.4(4)
Ru(4)–Ru(3)–Ru(1)	59.7(1)	Ru(5)–Ru(3)–Ru(1)	60.2(1)	Ru(5)–C–Ru(3)	86.1(4)	Ru(5)–C–Ru(4)	170.4(6)
Ru(5)–Ru(3)–Ru(4)	92.7(1)	Rh–Ru(3)–Ru(1)	89.5(1)	Rh–C–Ru(1)	177.9(6)	Rh–C–Ru(2)	93.1(4)
Rh–Ru(3)–Ru(4)	60.6(1)	Rh–Ru(3)–Ru(5)	62.2(1)	Rh–C–Ru(3)	93.9(4)	Rh–C–Ru(4)	93.2(4)
Ru(1)–Ru(4)–Au	67.1(1)	Ru(2)–Ru(4)–Au	56.2(1)	Rh–C–Ru(5)	94.6(4)		
Ru(2)–Ru(4)–Ru(1)	56.9(1)	Ru(3)–Ru(4)–Au	128.1(1)				

Ru–C–O (terminal) 172(1)–179(1), [bridging, CO(35)] 142(1) and 137(1), [semibridging, CO(22) and CO(34)] 127(1)–156(1)

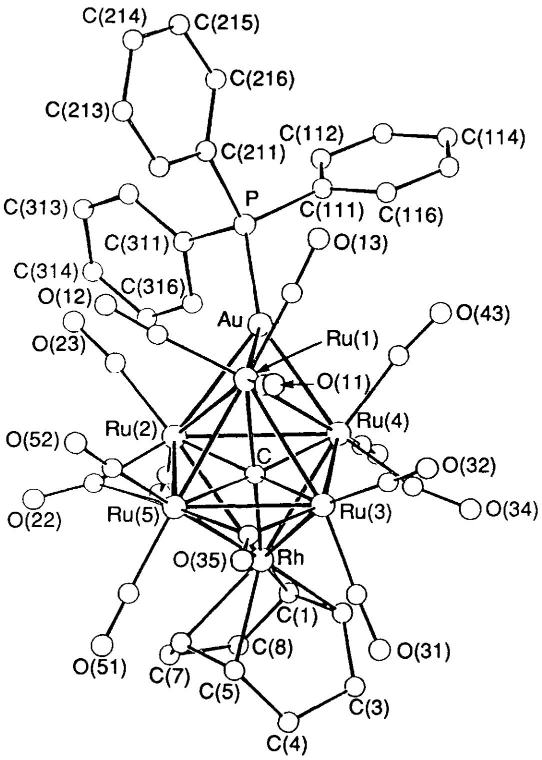

Fig. 1 Molecular structure of the heptanuclear cluster [$Ru_5RhC(CO)_{14}(cod)\{\mu_3\text{-}Au(PPh_3)\}$] **3** showing the crystallographic numbering scheme. The carbon atom of each carbonyl group has the same numbering as that of the oxygen atom

bridged by the $Au(PPh_3)$ ligand in **3** [Ru(2)–Ru(4) 3.093(1) Å], the mean Ru–Ru distance of 2.866(1) Å is considerably shorter than that of 2.899(1) Å in the cyclopentadienyl derivative **11**, where there is no gold atom. In contrast the mean Ru–Rh distance of 2.925(1) Å in **3** is markedly longer than the corresponding value of 2.865(1) Å in **11**. As a consequence of these two effects, the overall means of the M–M distances defining the octahedral core in **3** and **11** are very similar [2.886(1) and 2.888(1) Å]. In **3** the metal–carbide distances within the Ru_5Rh octahedral framework show marked variation with the Rh–C distance of 1.968(10) Å being markedly shorter than the Ru–C lengths [2.011(9)–2.135(10) Å; Table 2]. This is unexpected in view of the general lengthening of the Ru–Rh bonds relative to the Ru–Ru distances and corresponds to the carbido atom being 0.13 Å above the equatorial plane towards the Rh atom. The mean Ru–C bond length of 2.058(10) Å in **3** closely resembles the mean of 2.061(8) Å in the cyclopentadienyl analogue **11**. In contrast the Rh–C distance of 1.968(1) Å in **3** is longer than that of 1.944(7) Å in **11** despite the carbido atom in the latter being only 0.05 Å above the equatorial plane towards the Rh atom. This difference may be attributed to the change in the nature of the π system co-ordinating to the rhodium which imposes different electronic requirements.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 983 spectrophotometer, proton NMR at 80 MHz on a Bruker WP 80 SY instrument, mass spectra on MS12 or MS 30 instruments and fast atom bombardment (FAB) mass spectra on an AMES 50 instrument.

Preparation of [$Rh(cod)_2$][SbF_6].—The salt was prepared from $RhCl_3{\cdot}xH_2O$ by a method analogous to that used to prepare the corresponding hexafluorophosphate salt.[15] The salt $RhCl_3{\cdot}xH_2O$ (1.50 g) was refluxed for 28 h with cycloocta-1,5-diene (2 cm^3) in ethanol–water (5 : 1, 40 cm^3). The product was collected, washed with hexane and methanol–water (5 : 1) to give [$\{Rh(cod)Cl\}_2$] (1.1 g, 3.91 mmol). This product (0.136 g, 0.480 mmol) was dissolved in dichloromethane (6 cm^3) containing cod (5 cm^3). The silver salt $AgSbF_6$ [0.270 g, 0.470 mmol (excess)] was added and the mixture stirred for 1 h. The product mixture was reduced in volume to *ca.* 10 cm^3 and diethyl ether was added to precipitate orange [Rh(cod)$_2$][SbF_6] (0.266 g, 0.480 mmol, 87% based on [{Rh(cod)Cl}$_2$]). The product was used without further purification.

Reaction of [N(PPh$_3$)$_2$]$_2$[Ru$_5$C(CO)$_{14}$] *with* [Rh(cod)$_2$][SbF$_6$].—The salt [Rh(cod)$_2$][SbF$_6$] (0.033 g, 0.060 mmol, excess) was added to a solution of [N(PPh$_3$)$_2$]$_2$[Ru$_5$C(CO)$_{14}$] (0.032 g, 0.016 mmol) in dichloromethane (15 cm^3), causing immediate darkening of the red solution. The solution was filtered through a bed of Celite and evaporated to give an unstable dark red powder, tentatively formulated as [N(PPh$_3$)$_2$][Ru$_5$RhC(CO)$_{14}$(cod)] **1** (0.017 g, 0.010 mmol, 64%) [Found (Calc. for $C_{59}H_{42}NO_{14}PRhRu_5$): C, 43.1(42.7); H, 2.6 (2.5); N, 1.0 (0.85)%].

Preparation of [Ru$_5$RhC(CO)$_{14}$(cod)Y].—(*a*) Y = H. One drop of HBF_4·Et_2O was added to a mixture of [N(PPh$_3$)$_2$]$_2$[Ru$_5$C(CO)$_{14}$] (0.030 g, 0.015 mmol) and [Rh(cod)$_2$][SbF$_6$] (0.014 g, 0.025 mmol, excess) in dichloromethane (10 cm^3). The mixture was stirred for 5 min, reduced in volume and separated by thin-layer chromatography eluting with 50% dichloromethane–50% hexane, to give one red band and some insoluble material. The red product was precipitated by alternately reducing the solvent volume and adding hexane, to give [Ru$_5$RhH(C)(CO)$_{14}$(cod)] **2** (0.012 g, 0.011 mmol, 72%) [Found (Calc. for $C_{23}H_{13}O_{14}RhRu_5$: C, 24.8 (24.6); H, 1.2 (1.2)%].

(*b*) Y = Au(PPh$_3$). The salt [Au(PPh$_3$)]Cl (0.010 g, 0.020 mmol) was added to a mixture of [N(PPh$_3$)$_2$]$_2$[Ru$_5$C(CO)$_{14}$] (0.030 g, 0.015 mmol) and [Rh(cod)$_2$][SbF$_6$] (0.028 g, 0.051 mmol, excess) in dichloromethane (10 cm^3). The solution was stirred for 10 min and then eluted through a short column of Kieselgel 60 with 50% dichloromethane–50% hexane. The red product was precipitated by alternately reducing the solution volume and adding hexane, to give [Ru$_5$RhC(CO)$_{14}$(cod){Au(PPh$_3$)}] **3** (0.0165 g, 0.010 mmol, 69%) [Found (Calc. for $C_{41}H_{27}AuO_{14}PRhRu_5$: C, 31.3 (31.2); H, 1.7 (1.7)%].

(*c*) Y = Au(PEt$_3$). The salt [Au(PEt$_3$)]Cl (0.011 g, 0.031 mmol) was added to a mixture of [N(PPh$_3$)$_2$]$_2$[Ru$_5$C(CO)$_{14}$] (0.031 g, 0.016 mmol) and [Rh(cod)$_2$][SbF$_6$] (0.025 g, 0.045 mmol, excess) in dichloromethane (15 cm^3). The solution was stirred for 10 min and then eluted through a short column of Kieselgel 60 with 50% dichloromethane–50% hexane. The red product was precipitated by alternately reducing the solution volume and adding hexane, to give [Ru$_5$RhC(CO)$_{14}$(cod){Au(PEt$_3$)}] **4** (0.014 g, 0.010 mmol, 63%) [Found (Calc. for $C_{29}H_{27}AuO_{14}PRhRu_5$: C, 24.4 (24.3); H, 1.9 (1.9)%].

Reactions of [Ru$_5$RhC(CO)$_{14}$(cod){Au(PR$_3$)}] (R = Ph **3** *or* Et **4**).—(*a*) *With norbornadiene*. Compound **3** (0.010 g, 0.006 mmol) or **4** (0.011 g, 0.008 mmol) was stirred for 1 h with norbornadiene (*ca.* 0.1 cm^3) in dichloromethane (20 cm^3) at room temperature. The red product, in each case, was not mobile on thin-layer chromatography plates eluted with dichloromethane and showed a broad infrared absorption at 1998 **3** or 1995 cm^{-1} **4**. The compounds were not accordingly assumed to be anionic and not further characterised.

(*b*) *With* P(OMe)$_3$. Compound **3** (0.010 g, 0.006 mmol) or **4** (0.010 g, 0.008 mmol) and P(OMe)$_3$ (*ca.* 0.1 cm^3) were allowed to react as in (*a*). Again, in each case, the product was immobile on chromatography with dichloromethane, and showed a broad IR band at 1999 (**3**) or 1996 cm^{-1} (**4**). It was accordingly assumed that the products were anionic and they were not further characterised.

(*c*) *With* PPh$_3$. Compound **3** (0.008 g, 0.005 mmol) and PPh$_3$ (0.013 g, 0.05 mmol) were allowed to react as in (*a*). Again the red product was immobile on chromatography with dichloromethane, and showed a broad band at 1994 cm^{-1} in its IR spectrum. It was accordingly assumed to be anionic and not further characterised.

Table 3 Details of crystal structure determination for compound **3**

(*a*) Crystal data	
Molecular formula	$C_{41}H_{27}AuO_{14}PRhRu_5$
M	1580.03
Crystal dimensions/mm	0.22 × 0.23 × 0.18
Cell determined from *n*	25
reflections in 2θ range/°	15–25
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	15.993(3)
b/Å	9.728(2)
c/Å	13.900(3)
α/°	90.29(2)
β/°	99.97(2)
γ/°	88.36(2)
U/Å^3	2129.03
D_c/g cm^{-3}	2.465
Z	2
F(000)	1488
μ(Mo-Kα)/mm^{-1}	3.93
T/K	298
(*b*) Data collection	
Diffractometer	Philips PW1100
2θ range/°	6.0–50.0
No. of reflections measured	5120
hkl range	−22 to 22, −14 to 14, 0–20
Scan mode	ω–2θ
No. steps in scan	30
Step width/°	0.05
Minimum counts s^{-1} for reflection to be measured	10
$F > n\sigma(F)$	6
Total no. of reflections [$I > 3\sigma(I)$]	4980
Number of standard reflections	3
Variation in intensity (%)	< 5
Method of absorption correction	Empirical[18]
Maximum, minimum transmission factors	1.043, 0.835
(*c*) Structure refinement	
Number of reflections used in refinement	4956
Number of refined parameters	265
Converged residual	
R	0.0501
$R' = \Sigma w^{\frac{1}{2}}(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma w^{\frac{1}{2}}\lvert F_o\rvert$	0.0506
Maximum, minimum ρ/e Å^{-3}	0.30, −0.48

(*d*) *With carbon monoxide*. Compound **3** (0.048 g, 0.030 mmol) was sealed in a glass liner in a Roth autoclave (100 cm^3) with heptane (*ca.* 40 cm^3). Carbon monoxide was admitted to 25 atm, and then released to 2 atm. This cycle was repeated to flush the air out. Carbon monoxide was then admitted to 80 atm and the autoclave was sealed and heated to 80 °C for 4 h with magnetic stirring. After cooling, the pressure was released and the solvent evaporated under a stream of nitrogen. The brownish residue was redissolved in dichloromethane and separated by thin-layer chromatography eluting with 70% hexane–30% dichloromethane to give the products [Ru$_3$(CO)$_{12}$] (0.0025 g, 0.004 mmol, 13%), yellow [Ru$_4$RhC(CO)$_{14}${Au(PPh$_3$)}] **5** (0.0112 g, 0.008 mmol, 27%), red [Ru$_5$RhC(CO)$_{16}${Au(PPh$_3$)}] **7** (0.015 g, 0.010 mmol, 32%) and starting material (0.005 g, 0.003 mmol) together with some brown baseline material [Found (Calc. for

Table 4 Fractional atomic coordinates for compound **3** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Au	−0.271 33(3)	0.343 74(5)	−0.104 16(3)	O(43)	−0.357 2(6)	0.660 3(9)	−0.022 4(6)
Ru(1)	−0.359 04(5)	0.240 73(9)	0.061 55(6)	C(51)	−0.186 5(8)	−0.037 6(12)	0.299 4(8)
Ru(2)	−0.198 09(5)	0.144 01(8)	0.026 97(6)	O(51)	−0.149 6(5)	−0.101 8(8)	0.358 8(6)
Ru(3)	−0.283 02(6)	0.344 70(9)	0.251 65(6)	C(52)	−0.335 0(8)	−0.060 3(12)	0.180 8(8)
Ru(4)	−0.234 37(5)	0.445 84(8)	0.081 58(6)	O(52)	−0.386 4(6)	−0.138 6(10)	0.167 0(7)
Ru(5)	−0.251 92(5)	0.072 34(8)	0.201 99(7)	C(1)	0.002 6(7)	0.359 3(11)	0.181 8(8)
Rh	−0.114 72(5)	0.270 61(8)	0.208 75(6)	C(2)	−0.028 2(7)	0.437 4(11)	0.252 4(8)
P	−0.293 6(2)	0.364 5(3)	−0.270 0(2)	C(3)	0.008 2(8)	0.433 6(12)	0.358 2(9)
C	−0.232 7(6)	0.257 1(10)	0.140 4(7)	C(4)	0.019 8(8)	0.288 0(12)	0.400 2(9)
C(11)	−0.440 3(8)	0.234 7(13)	0.139 5(9)	C(5)	−0.040 7(7)	0.187 0(10)	0.343 8(7)
O(11)	−0.495 1(6)	0.225 7(9)	0.183 5(6)	C(6)	−0.020 7(7)	0.111 7(11)	0.267 9(8)
C(12)	−0.391 6(8)	0.083 4(13)	−0.011 0(9)	C(7)	0.058 9(8)	0.120 5(12)	0.225 2(9)
O(12)	−0.415 4(6)	−0.008 8(10)	−0.057 1(7)	C(8)	0.078 9(8)	0.267 4(12)	0.205 8(9)
C(13)	−0.430 2(8)	0.349 7(12)	−0.030 7(9)	C(111)	−0.296 7(5)	0.536 8(7)	−0.316 2(5)
O(13)	−0.478 4(6)	0.411 9(10)	−0.085 2(7)	C(112)	−0.260 4(5)	0.568 8(7)	−0.397 2(5)
C(21)	−0.088 4(7)	0.157 4(11)	0.010 9(8)	C(113)	−0.261 2(5)	0.704 7(7)	−0.429 0(5)
O(21)	−0.019 6(6)	0.164 7(10)	−0.009 3(7)	C(114)	−0.298 5(5)	0.808 6(7)	−0.379 8(5)
C(22)	−0.184 0(8)	−0.033 8(13)	0.087 7(9)	C(115)	−0.334 9(5)	0.776 7(7)	−0.298 7(5)
O(22)	−0.160 0(6)	−0.148 8(10)	0.087 3(7)	C(116)	−0.334 0(5)	0.640 7(7)	−0.266 9(5)
C(23)	−0.227 4(7)	0.062 8(12)	−0.096 5(9)	C(211)	−0.388 2(5)	0.290 7(8)	−0.333 2(5)
O(23)	−0.241 3(6)	0.002 1(10)	−0.169 0(7)	C(212)	−0.418 9(5)	0.177 5(8)	−0.290 4(5)
C(31)	−0.207 2(8)	0.390 4(12)	0.362 7(8)	C(213)	−0.488 2(5)	0.107 8(8)	−0.340 5(5)
O(31)	−0.165 0(6)	0.422 5(9)	0.433 2(6)	C(214)	−0.526 9(5)	0.151 3(8)	−0.433 6(5)
C(32)	−0.370 1(9)	0.445 1(14)	0.290 0(10)	C(215)	−0.496 2(5)	0.264 4(8)	−0.476 4(5)
O(32)	−0.426 5(8)	0.504 3(13)	0.314 1(9)	C(216)	−0.426 8(5)	0.334 1(8)	−0.426 2(5)
C(34)	−0.232 4(8)	0.555 9(12)	0.194 0(8)	C(311)	−0.210 0(4)	0.276 6(7)	−0.316 9(5)
O(34)	−0.222 5(6)	0.656 8(9)	0.241 2(6)	C(312)	−0.225 3(4)	0.193 9(7)	−0.400 1(5)
C(35)	−0.309 5(7)	0.169 3(12)	0.313 7(8)	C(313)	−0.157 5(4)	0.130 1(7)	−0.435 5(5)
O(35)	−0.337 9(5)	0.127 2(8)	0.381 0(6)	C(314)	−0.074 4(4)	0.149 0(7)	−0.387 8(5)
C(41)	−0.145 7(8)	0.525 1(12)	0.038 6(9)	C(315)	−0.059 2(4)	0.231 7(7)	−0.304 7(5)
O(41)	−0.087 2(6)	0.577 1(10)	0.012 3(7)	C(316)	−0.126 9(4)	0.295 5(7)	−0.269 2(5)
C(43)	−0.310 9(8)	0.574 5(13)	0.010 9(9)				

$C_{33}H_{15}AuO_{14}PRhRu_4$ **5**: C, 28.8 (28.9); H, 1.1 (1.1). Found (Calc. for $C_{35}H_{15}AuO_{16}PRhRu_5$ **7**: C, 27.6 (27.5); H, 1.1(1.0)%].

Reaction of [$Ru_5RhC(CO)_{14}$(cod){Au(PEt$_3$)}] **4** (0.021 g, 0.015 mmol) with carbon monoxide at 80 atm and 80 °C, as described above, yielded [$Ru_3(CO)_{12}$] (0.009 g, 0.014 mmol, 10%), yellow [$Ru_4RhC(CO)_{14}${Au(PEt$_3$)}] **6** (0.005 g, 0.004 mmol, 28%), red [$Ru_5RhC(CO)_{16}${Au(PEt$_3$)}] **8** (0.007 g, 0.005 mmol, 35%), starting material (0.0025 g, 0.002 mmol, 12%) and brown baseline material [Found (Calc. for $C_{21}H_{15}AuO_{14}PRhRu_4$ **6**: C, 20.6 (20.5); H, 1.2 (1.2). Found (Calc. for $C_{23}H_{15}AuO_{16}PRhRu_5$ **8**: C, 20.1(19.9); H, 1.1(1.1)%].

Crystal Structure Determination for the Cluster [$Ru_5RhC(CO)_{14}$(cod){Au(PPh$_3$)}] **3**.—Suitable crystals of complex **3** were grown by slow diffusion in pentane–dichloromethane at room temperature. Details of the crystal parameters, data collection parameters, and refinement data are summarised in Table 3. The method of data collection and processing used have been described previously.[16] 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.[17] During the final cycles of refinement, anisotropic thermal parameters were assigned to the seven metal atoms and the phosphorus atom.[18] The six carbon atoms of each phenyl ring of the Au(PPh$_3$) fragment were grouped as rigid hexagons (C–C 1.395 Å, C–C–C 120°) with the phenyl H atoms geometrically calculated to ride on the respective carbon atoms at C–H 1.08 Å, with fixed thermal parameters of 0.08 Å^2. The relevant hydrogen atoms of the cycloocta-1,5-diene ligand were also geometrically calculated to ride on the respective carbon atoms at the same distance and fixed thermal parameters. Full-matrix refinement of the atomic positional and thermal parameters of all the non-hydrogen atoms converged at final *R* and *R′* values of 0.0501 and 0.0506 with weights of $w = 1/\sigma^2(F_o)$ assigned to individual reflections. The final atomic coordinates 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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