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The synthesis, characterization and molecular structures of two mixed metal octahedral carbido clusters, $Ru_5RhC(CO)_{14}(\eta^5\text{-}C_5Me_5)$ and $Ru_5RhC(CO)_9(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)_2$

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Abstract

Ionic coupling between the dianionic ruthenium cluster $[Ru_5C(CO_{14}]^{2-}$ and the dicationic rhodium species $[Rh(C_5Me_5)(MeCN)_3]^{2+}$ in refluxing CH_2Cl_2 yields the hexanuclear mixed metal carbido cluster $Ru_5RhC(CO)_{14}(\eta^5\text{-}C_5Me_5)$ (**1**). Activation of **1** towards reaction with C_5H_6 or C_6H_8 by trimethylamine-*N*-oxide (Me_3NO) results in the formation of $Ru_5RhC(CO)_9(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)_2$ (**2**) and $Ru_5RhC(CO)_{11}(\eta^5\text{-}C_5Me_5)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$ (**3**) respectively. Complexes **1** and **2** have been structurally characterized by X-ray diffraction.

1. Introduction

We previously described the synthesis and molecular structure of a series of bis-arene hexaruthenium-carbido clusters, $Ru_6C(CO)_{11}(arene)_2$ [1–3]. Three different structural forms were observed. The bis-benzene species $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$ is unique in that one benzene coordinates terminally in an η^6-mode while the second adopts a position symmetrically straddling a ruthenium face in the μ_3-$\eta^2:\eta^2:\eta^2$-coordination mode. The bis-mesitylene complex $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_3Me_3)_2$ contains two terminal η^6-ligands which are attached to metal atoms that lie *trans* to one another. The third structural type was found for the mixed mesitylene/benzene cluster $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_3Me_3)(\eta^6\text{-}C_6H_6)$, in which the two arenes are both bound terminally but on ruthenium atoms that are adjacent to one another.

In all three of these bis-arene substituted clusters, the integrity of the hexaruthenium core remains intact and the octahedral geometry is maintained, with the interstitial carbon atom lying near to the centre of the octahedron. Although slight distortions are observed in the metal core, the stability of the cluster core is a desirable feature of this system. This feature, coupled with interest in the factors which govern the coordination type and location of the aromatic rings on the cluster surface, prompted this investigation.

2. Results and discussion

The synthetic method first used for the preparation of bis-arene hexaruthenium clusters was extended to the mixed metal system. The first step involves the introduction of the aromatic ring into the cluster system by ionic coupling; in the present case, the pentamethylcyclopentadienyl ligand (Cp*) was introduced into the hexanuclear cluster by reaction of the monorhodium fragment $[Rh(C_5Me_5)(MeCN)_3]^{2+}$ with $[Ru_5C(CO)_{14}]^{2-}$, yielding the mixed metal cluster $Ru_5RhC(CO)_{14}(\eta^5\text{-}C_5Me_5)$ (**1**). This cluster was initially characterized by spectroscopic methods, details of which are displayed in Table 1, along with spectroscopic data for products **2** and **3**. The mass spectrum exhibited a

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TABLE 1. Spectroscopic data for compounds 1–3

	IR (CH_2Cl_2)	^1H ($CDCl_3$)	MS
$Ru_5RhC(CO)_{14}(\eta^5\text{-}C_5Me_5)$ (1)	2074m 2024vs 1979w 1811w, br	2.16 (s)	1149 (calc. 1147)
$Ru_5RhC(CO)_9(\eta^5\text{-}C_5Me_5)$ $(\eta^5\text{-}C_5H_5)_2$ (2)	2031s 1990vs 1982vs 1930m	5.14 (s, 10H) 1.87 (d, 15H)	1139 (calc. 1137)
$Ru_5RhC(CO)_{11}(\eta^5\text{-}C_5Me_5)$ $(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$ (3)	2034m 1998vs 1940w 1889m, br	4.13 (s, 6H) 2.07 (s, 15H)	1143 (calc. 1141)

strong parent peak at $m/z = 1149$ (calculated, 1147) together with the sequential loss of fourteen carbonyl groups. The ^1H NMR spectrum of 1 contains a singlet at 2.16 ppm corresponding to the methyl protons on the Cp* ligand.

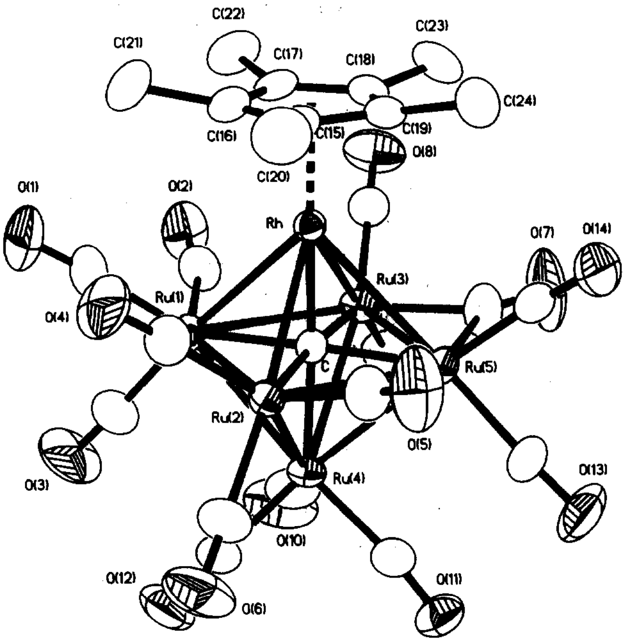

Fig. 1. Molecular structure of $Ru_5RhC(CO)_{24}(\eta^5\text{-}C_5Me_5)$ (1). Relevant bond lengths (Å) include: Rh–Ru(1) 2.849(4), Rh–Ru(2) 2.8304(4), Rh–Ru(3) 2.903(5), Rh–Ru(5) 2.897(4), Ru(1)–Ru(2) 2.950(4), Ru(1)–Ru(3) 2.933(5), Ru(1)–Ru(4) 2.826(5), Ru(2)–Ru(4) 2.869(5), Ru(2)–Ru(5) 2.946(4), Ru(3)–Ru(4) 2.921(5), Ru(3)–Ru(5) 2.815(5), Ru(4)–Ru(5) 2.957(5), Rh–C 1.93(3), Ru(1)–C 2.05(3), Ru(2)–C 2.05(3), Ru(3)–C 2.07(3), Ru(4)–C 2.09(3), Ru(5)–C 2.07(3), mean Rh–C(Cp*) 2.229(4), mean C–C 1.42(6), mean C–C(Me) 1.50(6), mean Ru–C(CO) 1.89(5), Ru(3)–C(7) 2.06(5), Ru(5)–C(7) 2.07(5), mean C–O 1.14(7), C(7)–O(7) 1.17(7).

TABLE 2. Crystallographic data and details of measurements for $Ru_5Rh(CO)_{14}(\eta^5\text{-}C_5Me_5)$ (1) and $Ru_5RhC(CO)_9(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)$ (2)

(a) *Crystal data*		
Formula	$C_{25}H_{15}O_{14}RhRu_5$	$C_{30}H_{25}O_9RhRu_5$
Mol. wt.	1147.6	1137.7
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$
a (Å)	9.3405(14)	20.429(16)
b (Å)	10.9553(24)	23.018(19)
c (Å)	17.058(3)	16.779(15)
α (°)	92.464(8)	90(–)
β (°)	100.598(12)	126.59(3)
γ (°)	114.835(9)	90(–)
V (Å^3)	1542.9	6335.1
Temperature (K)	298	150
Z	2	8
μ (mm^{-1})	2.923	2.836
ρ (g cm^{-3}) (calc)	2.470	2.385
Crystal size (mm^3)	0.78×0.39×0.19	0.86×0.66×0.19
Crystal colour	Black	Dark red
Crystal shape	Lath	Tablet
(b) *Data collection*		
Diffractometer	Stoë Stadi-4	Stoë Stadi-4
Radiation	Mo	Mo
λ (Å)	0.71073	0.71073
Monochromator	Graphite	Graphite
2θ scan range (°)	5–45	5–45
Scan mode	$\omega-2\theta$	$\omega-2\theta$
Std reflections	3	3
Reflections collected	5690	4217
Unique reflections with $F > 4\sigma(F)$	3739	3933
(c) *Structure refinement*		
Final R	0.0190	0.0254
R_w	0.0278	0.0388
S	1.071	1.255
$\Delta\rho_{max}$ (e Å^{-3})	0.47	0.77
$\Delta\rho_{min}$ (e Å^{-3})	−0.32	−0.53

The molecular structure of 1 was elucidated by a single crystal X-ray diffraction study and is shown in Fig. 1, along with the atomic labelling scheme. Relevant crystal data are listed in Table 2. The five ruthenium atoms and single rhodium atom form an octahedral arrangement. The Cp* ligand is bound in a terminal fashion to the rhodium atom. The carbonyl distribution is reminiscent of that observed in $Ru_6C(CO)_{14}$-$(\eta^6\text{-arene})$ (arene = $C_6H_3Me_3$ and C_6H_5Me) [4,5] in which there is one bridging, two semibridging, and eleven essentially terminal carbonyl groups.

Substitution of subsequent five- and six-membered aromatic rings onto the cluster involves oxidative decarbonylation by addition of 3 equiv. of Me_3NO to a CH_2Cl_2 solution of $Ru_5RhC(CO)_{14}(\eta^5\text{-}C_5Me_5)$ (1) containing an excess of cyclohexa-1,3-diene or cyclopentadiene. The complex obtained from the former diene was characterized by spectroscopy as Ru_5-$RhC(CO)_{11}(\eta^5\text{-}C_5Me_5)(\mu^3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$ (3). The mass spectrum shows a molecular ion at $m/z = 1143$ (calculated 1141) and successive loss of eleven carbonyl groups. The ^1H NMR spectrum displays two singlets at 4.13 and 2.07 ppm with the integration ratio of 6:15, consistent with the coordination of both benzene and Cp*. The chemical shift for the protons of the Cp* ligand is very close to the corresponding value for **1**. The chemical shift for the protons of the benzene moiety is at a substantially higher field compared with that for benzene coordinated in an η^6-mode. For example, in $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$, singlets at 5.54 and 4.14 ppm may be assigned to the proton resonances of the terminal and face-capping benzene, respectively [1,6]. In this cluster (**3**), the benzene prefers to adopt a face-capping coordination mode as in the bis-benzene complex, in contrast to the mesitylene/benzene complex in which the two arenes both bind in an η^6-fashion *cis* to one another. $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_3Me_3)(\eta^6\text{-}C_6H_6)$ is in fact formed from the $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_3Me_3)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$ isomer after storage at low temperature for a prolonged period [3]. However, no such isomerization has been observed for **3**.

Treatment of **1** with 3 equiv. of Me_3NO in CH_2Cl_2 containing an excess of C_5H_6 resulted in the isolation of several products in low yield, and $Ru_5RhC(CO)_9(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)_2$ (**2**) in moderate yield. The mass spectrum of **2** shows a strong molecular ion at m/z 1139 (calculated, 1137) followed by the sequential loss of nine carbonyl ligands. The ^1H NMR spectrum contains a singlet at 5.14 and a doublet at 1.87 ppm with relative intensities 2:3, consistent with two η^5-Cp moieties and one η^5-Cp* ligand, respectively. Either of two isomers would be consistent with this spectrum, and in order to elucidate the structure of **2**, a single crystal X-ray structure determination was carried out. The molecular structure of **2** is shown in Fig. 2, along with the atomic labelling scheme, and relevant crystal data are listed in Table 2.

The metal core is similar to that in **1**, with the six metal atoms constituting an octahedron. Again, the Cp* ligand is bound solely to the rhodium atom. The two Cp ligands coordinate *cis* to both the Cp* moiety and each other. The ruthenium atoms to which the Cp ligands coordinate also share a bridging carbonyl ligand. There is one other bridging carbonyl group and seven terminal carbonyl ligands.

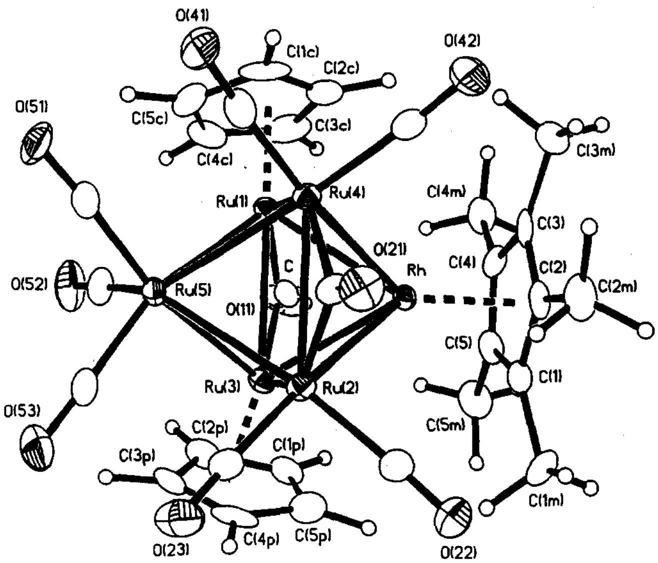

Fig. 2. Molecular structure of $Ru_5RhC(CO)_9(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)_2$ (**2**). Relevant bond lengths (Å) include: Rh–Ru(1) 2.819(6), Rh–Ru(2) 2.898(6), Rh–Ru(3) 2.818(6), Rh–Ru(4) 2.902(6), Ru(1)–Ru(3) 2.774(6), Ru(1)–Ru(4) 2.985(6), Ru(1)–Ru(5) 2.799(6), Ru(2)–Ru(3) 3.011(6), Ru(2)–Ru(4) 2.794(6), Ru(2)–Ru(5) 2.950(6), Ru(3)–Ru(5) 2.778(6), Ru(4)–Ru(5) 2.975(6), Rh–C 1.93(5), Ru(1)–C 2.02(5), Ru(2)–C 2.07(5), Ru(3)–C 2.03(5), Ru(4)–C 2.07(5), Ru(5)–C 2.09(5), mean Rh–C(Cp*) 2.23(5), mean C–C(Cp*) 1.43(8), mean C–C(Me, Cp*) 1.49(8), mean Ru(1)–C(Cp) 2.21(7), mean C–C(Cp) 1.41(9), mean Ru(3)–C(Cp) 2.21(6), mean C–C(Cp) 1.42(9), Ru(1)–C(11) 2.04(6), Ru(3)–C(11) 2.03(6), C(11)–O(11) 1.16(9), Ru(2)–C(21) 2.05(6), Ru(4)–C(21) 2.05(6), mean Ru–C(CO) 1.88(6), mean C–O 1.15(8).

The ease with which two Cp ligands are introduced on to the cluster framework compared with the C_6H_6 moiety may be rationalized in terms of electron counting on the Ru_5 unit. Considering this subunit of the cluster, a total of 28 electrons are required from ligands attached to it in order to be complete. In **1**, fourteen carbonyls contribute these 28 electrons. In **3**, six electrons are donated by the benzene ring and the remaining 22 from 11 carbonyl groups. However, in **2**, if the Cp ligand is considered neutral, it will formally donate five electrons to the cluster. Thus an odd number of electrons means that an ideal situation of 28 electrons cannot be reached when only one Cp is used in conjunction with carbonyl ligands. Clearly when two Cp ligands are introduced into the system, donating a total of ten electrons, a total electronic contribution of 28 can be reached with the seven terminal and two bridging carbonyl ligands on the Ru_5 unit.

3. Experimental details

3.1. General

All reactions were carried out with freshly distilled solvents under dinitrogen. Subsequent work up of products was carried out without precautions to exclude air and standard laboratory grade solvents were used. Infrared spectra were recorded on a Perkin-Elmer 1600 Fourier-Transform instrument. Mass spectra were obtained by positive fast atom bombardment on a

TABLE 3. Atomic coordinates for **1** with e.s.d.s

	x	y	z	U_{iso}
Rh	0.16374(3)	0.86534(3)	0.747240(20)	0.02625(21)
Ru(1)	0.30944(3)	0.72161(3)	0.841200(20)	0.03395(23)
Ru(2)	0.22764(3)	0.67162(3)	0.663720(20)	0.03135(22)
Ru(3)	−0.02855(4)	0.66363(3)	0.837050(20)	0.03609(23)
Ru(4)	0.06075(4)	0.47174(3)	0.758940(20)	0.03434(23)
Ru(5)	−0.10832(3)	0.61453(3)	0.667760(20)	0.03306(23)
C	0.1073(4)	0.6746(3)	0.75212(19)	0.0279(23)
C(1)	0.5199(5)	0.8667(5)	0.8571(3)	0.055(3)
O(1)	0.6489(4)	0.9473(4)	0.8692(3)	0.090(3)
C(2)	0.2656(5)	0.7719(4)	0.9399(3)	0.055(3)
O(2)	0.2816(4)	0.8146(4)	1.00402(19)	0.079(3)
C(3)	0.4055(6)	0.6123(5)	0.8879(3)	0.069(4)
O(3)	0.4674(6)	0.5514(5)	0.9178(3)	0.120(4)
C(4)	0.4316(5)	0.8122(4)	0.6620(3)	0.053(3)
O(4)	0.5557(4)	0.8938(4)	0.65912(25)	0.082(3)
C(5)	0.1040(5)	0.6822(5)	0.5640(3)	0.058(3)
O(5)	0.0610(4)	0.6999(4)	0.50086(20)	0.087(3)
C(6)	0.2876(5)	0.5437(5)	0.6163(3)	0.058(3)
O(6)	0.3261(5)	0.4738(4)	0.58584(23)	0.100(3)
C(7)	−0.2353(5)	0.6261(5)	0.7527(3)	0.057(3)
O(7)	−0.3637(4)	0.6197(5)	0.75232(24)	0.113(4)
C(8)	−0.0497(5)	0.7890(4)	0.9060(3)	0.048(3)
O(8)	−0.0655(5)	0.8598(3)	0.95135(21)	0.084(3)
C(9)	−0.1502(6)	0.5349(4)	0.8963(3)	0.060(3)
O(9)	−0.2287(5)	0.4581(4)	0.93182(25)	0.102(3)
C(10)	0.0227(6)	0.3886(5)	0.8532(3)	0.065(4)
O(10)	0.0076(6)	0.3326(4)	0.90802(23)	0.111(4)
C(11)	−0.1103(5)	0.3198(4)	0.6910(3)	0.046(3)
O(11)	−0.2060(4)	0.2201(3)	0.65299(21)	0.0640(24)
C(12)	0.2121(5)	0.4021(4)	0.7471(3)	0.052(3)
O(12)	0.2959(4)	0.3525(3)	0.7443(3)	0.087(3)
C(13)	−0.2739(5)	0.4548(4)	0.6062(3)	0.054(3)
O(13)	−0.3778(5)	0.3618(4)	0.5676(3)	0.093(3)
C(14)	−0.2085(5)	0.6980(4)	0.5989(3)	0.049(3)
O(14)	−0.2811(5)	0.7380(4)	0.55604(24)	0.089(3)
C(15)	0.2649(4)	1.0475(4)	0.68357(23)	0.039(3)
C(16)	0.3557(4)	1.0798(4)	0.76404(24)	0.039(3)
C(17)	0.248(15)	1.0684(3)	0.81612(23)	0.038(3)
C(18)	0.092(14)	1.0303(4)	0.76663(25)	0.041(3)
C(19)	0.1024(4)	1.0199(3)	0.68482(23)	0.038(3)
C(20)	0.3293(6)	1.0654(5)	0.6083(3)	0.061(3)
C(21)	0.5362(5)	1.1469(4)	0.7882(3)	0.055(3)
C(22)	0.2991(6)	1.1114(4)	0.90526(24)	0.057(3)
C(23)	−0.0542(5)	1.0274(4)	0.7943(3)	0.063(3)
C(24)	−0.0197(5)	1.0159(5)	0.6134(3)	0.059(3)

Kratos MS50TC. ^1H NMR spectra were recorded with a Bruker WM200 spectrometer. $[Ru_5C(CO)_{14}][PPN]_2$, $[Ru(C_6H_6)(MeCN)_3][BF_4]_2$ and $[Rh(C_5Me_5)(MeCN)_3][BF_4]_2$ were prepared by published methods [1,7–9]. Hexamethyldewarbenzene, trimethylamine-*N*-oxide (Me_3NO), cyclohexa-1,3-diene and dicyclopentadiene were purchased from Aldrich chemicals. Me_3NO was dried then sublimed prior to use. Dicyclopentadiene was converted into the monomer directly before use, otherwise no further purification procedures were utilized.

3.2. Preparation of $Ru_5RhC(CO)_{14}(\eta^5\text{-}C_5Me_5)$ (1)

$[Ru_5C(CO)_{14}][PPN]_2$ (100 mg) in CH_2Cl_2 (25 ml) was added dropwise during 10 min to a refluxing solution of $[Rh(C_5Me_5)(MeCN)_3][BF_4]_2$ (27 mg) in CH_2Cl_2 (25 ml). The mixture was heated under reflux for an additional 20 min by which time a dark brown solution had been formed. IR spectroscopy indicated complete consumption of the starting material. One brown product was extracted by column chromatography with CH_2Cl_2 (50%)/hexane (50%) as eluant. The

TABLE 4. Fractional coordinates for **2** with standard deviations

	x	y	z
Rh	0.18024(2)	0.15560(1)	0.17644(3)
Ru(1)	0.27983(2)	0.07022(2)	0.17778(3)
Ru(2)	0.255506(2)	0.13586(2)	0.38487(3)
Ru(3)	0.35153(2)	0.16370(2)	0.30710(3)
Ru(4)	0.18355(2)	0.04199(2)	0.25381(3)
Ru(5)	0.36417(2)	0.05333(2)	0.38211(3)
C	0.2654(3)	0.10498(18)	0.2772(3)
C(1)	0.1157(3)	0.24095(19)	0.1444(3)
C(2)	0.0586(3)	0.19316(21)	0.1088(3)
C(3)	0.0555(3)	0.16336(20)	0.0309(3)
C(4)	0.1139(3)	0.19004(20)	0.0234(3)
C(5)	0.1499(3)	0.23719(20)	0.0903(3)
C(1M)	0.1257(4)	0.28971(21)	0.2072(4)
C(2M)	0.0048(3)	0.18151(24)	0.1402(4)
C(3M)	−0.0056(3)	0.11885(23)	−0.0378(4)
C(4M)	0.1245(4)	0.17765(25)	−0.0558(4)
C(5M)	0.2063(3)	0.28192(22)	0.0949(4)
C(1C)	0.2174(4)	−0.01288(23)	0.1004(4)
C(2C)	0.1931(4)	0.03098(24)	0.0299(4)
C(3C)	0.2623(4)	0.05026(24)	0.0385(4)
C(4C)	0.3305(3)	0.01974(25)	0.1152(4)
C(5C)	0.3036(4)	−0.01919(22)	0.1549(4)
C(1P)	0.4016(3)	0.24803(21)	0.3029(4)
C(2P)	0.4673(3)	0.20646(22)	0.3557(4)
C(3P)	0.4734(3)	0.189069(22)	0.4411(4)
C(4P)	0.4132(4)	0.21912(23)	0.4411(4)
C(5P)	0.3678(3)	0.25500(21)	0.3546(4)
C(11)	0.3356(3)	0.14412(22)	0.1785(4)
O(11)	0.3542(3)	0.16431(17)	0.1311(3)
C(21)	0.1665(3)	0.07718(19)	0.3525(3)
O(21)	0.12485(23)	0.06928(16)	0.3769(3)
C(22)	0.1990(3)	0.19739(21)	0.3906(3)
O(22)	0.16493(23)	0.23293(16)	0.4014(3)
C(23)	0.3127(3)	0.13139(19)	0.5231(4)
O(23)	0.3456(3)	0.13143(15)	0.6064(3)
C(41)	0.1814(3)	−0.03634(23)	0.2851(4)
O(41)	0.17734(24)	−0.08402(16)	0.3003(3)
C(42)	0.0716(3)	0.03291(20)	0.1552(4)
O(42)	0.00311(24)	0.02469(16)	0.0978(3)
C(51)	0.3600(3)	−0.02801(23)	0.4004(4)
O(51)	0.36467(24)	−0.07690(16)	0.4143(3)
C(52)	0.4470(3)	0.05126(21)	0.3637(4)
O(52)	0.499900(25)	0.05089(18)	0.3550(3)
C(53)	0.4341(3)	0.07038(21)	0.5201(4)
O(53)	0.48253(25)	0.08026(18)	0.6022(3)
O(1W)	0.00000(0)	0.0419(13)	0.75000(0)

product was characterised as $Ru_5RhC(CO)_{14}(\eta^5\text{-}C_5Me_5)$ (**1**) (48 mg).

3.3. *Preparation of* $Ru_5RhC(CO)_9(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)_2$ *(2)*

An excess of cyclopentadiene (1 ml) was added to a solution of **1** (30 mg) in CH_2Cl_2 (30 ml). The mixture was cooled to 0°C and a solution of Me_3NO (6 mg, 3.1 mol. equiv.) in CH_2Cl_2 (10 ml) was added dropwise. The mixture was then allowed to warm to room temperature and stirred for 25 min, after which IR spectroscopy indicated complete consumption of starting material. The resultant dark brown solution was filtered and the solvent removed from the filtrate *in vacuo*. The residue was dissolved in the minimum of CH_2Cl_2 and separated by thin layer chromatography with CH_2Cl_2 (30%)/hexane (70%) as eluant. The brown band was removed and characterized as $Ru_5RhC(CO)_9(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)_2$ (**2**) (6 mg).

3.4. *Preparation of* $Ru_5RhC(CO)_{11}(\eta^5\text{-}C_5Me_5)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$ *(3)*

An excess of cyclohexa-1,3-diene (0.5 ml) was added to a solution of **1** (33 mg) in CH_2Cl_2 (30 ml). The mixture was cooled to 0°C and a solution of Me_3NO (7 mg, 3.1 mol. equiv.) in CH_2Cl_2 (10 ml) was added dropwise. The mixture was allowed to warm to room temperature and stirred for 30 min after which IR spectroscopy indicated complete consumption of starting material. The resultant dark brown solution was filtered and the solvent removed *in vacuo*. The residue was dissolved in the minimum of CH_2Cl_2 and separated by thin layer chromatography with CH_2Cl_2 (30%)/hexane (70%) as eluant. A red band was removed and characterized as $Ru_5RhC(CO)_{11}(\eta^5\text{-}C_5Me_5)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$ (**3**) (4 mg).

3.5. *Crystal structure determination*

All X-ray measurements were made on a Stoë Stadi-4 four-circle diffractometer. Data were collected at room temperature for compound **1**, and at 150 K for compound **2**, utilizing an Oxford Cryosystems low-temperature device [10]. Details of crystal data, data collection and structure refinement are summarized in Table 2. The metal atoms were located by using automatic direct methods [11] and subsequent iterative cycles of least-squares refinement and difference Fourier synthesis located all non-H atoms [12]. All non-H atoms and solvate atoms were refined with anisotropic thermal parameters. Methyl groups were treated as rigid groups, and the H-atoms of the cyclopentadienyl rings in **2** were included at fixed, calculated positions. Atomic coordinates are listed in Tables 3 and 4. Thermal parameters, hydrogen atom coordinates, and structure factors are available from the authors.

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