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Synthesis and X-ray crystal structure analysis of the triruthenium-rhodium carbonyl cluster $[Ru_3Rh(\mu\text{-}H)_2(CO)_{10}(\eta^5\text{-}C_5H_5)]$

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Abstract

The pyrolysis of a mixture of the labile dimer $[(Rh(CO)_2Cl)_2]$ and the hydrido-cluster $[Ru_4H_2(CO)_{13}]$ in the presence of $Tl(C_5H_5)$, in hexane, gives the mixed metal complex $[Ru_3Rh(\mu\text{-}H)_2(CO)_{10}\ (\eta^5\text{-}C_5H_5)]$ as the major product. An X-ray diffraction study of this complex shows that it contains a distorted Ru_3Rh tetrahedron, two Ru–Ru edges of which are bridged by hydrides and one Ru–Rh edge of which is asymmetrically bridged by a carbonyl ligand. The remaining nine carbonyl ligands are terminal, with three bound to each Ru atom, while the cyclopentadienyl ligand is co-ordinated to the Rh atom. The complex crystallises in the monoclinic space group $P2_1/n$ with a 8.186(1), b 15.061(1), c 16.302(1) Å, β 91.06(1)°, $Z = 4$; 2737 observed data with $F > 4\sigma(F)$ were refined by blocked-cascade least squares to $R = 0.040$, $R_w = 0.033$. At low temperature, the ^1H NMR spectrum of the cluster shows two signals, in the hydride region, consistent with the inequivalent hydride positions in the ground state structure, but at higher temperatures coalescence occurs, and the activation energy for this process has been found to be 38 kJ/mol at $-80\,°C$.

Introduction

The chemistry of mixed-metal cluster carbonyls containing elements from the iron and cobalt sub-groups has been extensively investigated. However, much of this work has centred on the iron–cobalt and ruthenium–cobalt bimetallic systems [1], and there have been relatively few studies on ruthenium–rhodium clusters [2]. The

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third row element, osmium, may be incorporated into bimatallic systems by use of the co-ordinatively unsaturated cluster $[Os_3H_2(CO)_{10}]$ in reactions with mononuclear complexes of the cobalt sub-group [3,4], and clusters with the general formula $[Os_3M(\mu\text{-}H)_2(CO)_{10}(\eta^5\text{-}C_5H_5)]$ (M = Co, Rh, Ir) may be prepared [5] by the reaction

$$[Os_3H_2(CO)_{10}] + [M(CO)_2(C_5H_5)] \xrightarrow{368\ K} [Os_3MH_2(CO)_{10}(C_5H_5)]$$

The introduction of ruthenium into a mixed system presents somewhat more of a problem, since there are no readily available unsaturated clusters of ruthenium which can undergo reactions similar to those described above. However, hydrido-containing ruthenium clusters have been shown to be more reactive under mild pyrolytic conditions than the parent binary carbonyl $[Ru_3(CO)_{12}]$. Here, we report the reaction of the hydrido-carbonyl $[Ru_4H_2(CO)_{13}]$ with the dimer $[(Rh(CO)_2Cl)_2]$, in the presence of $Tl(C_5H_5)$, to afford the mixed-metal cluster $[Ru_3Rh(\mu\text{-}H)_2(CO)_{10}(\eta^5\text{-}C_5H_5)]$.

Results and discussion

Treatment of a hexane solution of $[(Rh(CO)_2Cl)_2]$ with $[Ru_4H_2(CO)_{13}]$, in the presence of $Tl(C_5H_5)$, which acts both as a chloride abstractor and as a source of $(C_5H_5)^-$ to give $Rh(CO)_2(C_5H_5)$ as the precursor, under reflux, for a 12-h period, affords a brown solution, from which three bands were isolated by TLC. The major product, obtained in 25% yield, was isolated as an orange-red solid, together with $[Ru_4H_4(CO)_{12}]$, and unreacted starting material. The orange-red product was recrystallised from a hexane/dichloromethane mixture, and initially characterised by means of IR and ^1H NMR spectroscopy (Table 1). The IR spectrum showed five bands in the terminal carbonyl region as well as a weak band in the bridging region. The general pattern and intensity of the bands is similar to that observed in the spectra of $[Os_3Rh(\mu\text{-}H)_2(CO)_{10}(\eta^5\text{-}C_5Me_5)]$ [6] and $[Os_3Co(\mu\text{-}H)_2(CO)_{10}(\eta^5\text{-}C_5Me_4Et)]$ [7]. At −80 °C the ^1H NMR spectrum of the product exhibited a sharp singlet of relative intensity five in the aromatic region of the spectrum, which may be assigned to the protons on the cyclopentadienyl ring, and two singlets of equal intensity in the hydride region, consistent with the presence of two inequivalent bridging hydrides. The position of these hydride signals is similar to those observed for $[Ru_2Rh_2(\mu\text{-}H)_2(CO)_{12}]$ [8] where the hydrides bridge Ru–Ru and Ru–Rh edges of the metal tetrahedron. Upon warming to room temperature coalescence of the hydride signals occurred to give a singlet of intensity two, while the signal assigned to the cyclopentadienyl protons remained unchanged. A similar process is observed in the ^1H NMR spectrum of $[Os_3Rh(\mu\text{-}H)_2(CO)_{10}(\eta^5\text{-}C_5H_5)]$ [5]. On the basis of

Table 1

Spectroscopic data for $[Ru_3Rh(\mu\text{-}H)_2(CO)_{10}(\eta^5\text{-}C_5H_5)]$

IR ν(CO) (cm^{-1}) (in CH_2Cl_2): 2081w, 2066s, 2047s, 2012s, 1978w, 1814br,w	
^1H NMR δ(ppm) (in CD_2Cl_2):	
room temperature:	5.75 (s, 5H), −17.3 (s, 2H)
−80 °C	5.75 (s, 5H), −16.5 (s, 1H), −18.2 (s, 1H)

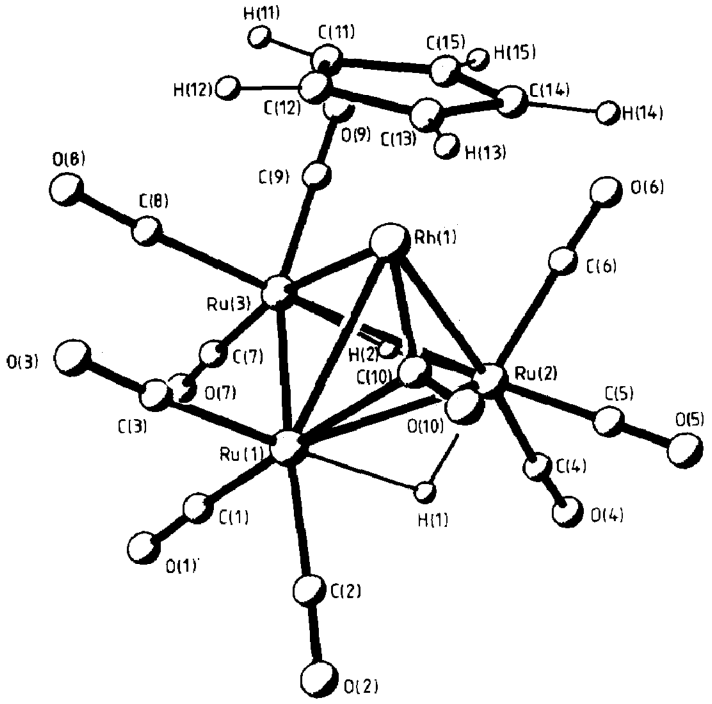

Fig. 1. The molecular structure of $[Ru_3Rh(\mu\text{-}H)_2(CO)_{10}(\eta^5\text{-}C_5H_5)]$ showing the atom numbering scheme.

this spectroscopic evidence the orange-red product was characterised as $[Ru_3Rh(\mu\text{-}H)_2(CO)_{10}(\eta^5\text{-}C_5H_5)]$. From repeated variable temperature NMR measurements on this complex it has been possible to estimate the activation energy, $\Delta G^{\#}$, for the hydride exchange process, and this has been assigned a value of 38 kJ/mol at −80 °C.

In order to confirm the spectroscopic characterisation a single-crystal X-ray analysis of $[Ru_3Rh(\mu\text{-}H)_2(CO)_{10}(\eta^5\text{-}C_5H_5)]$ was undertaken. The structure is isomorphous and isostructural with the related osmium containing cluster $[Os_3Co(\mu\text{-}H)_2(CO)_{10}(\eta^5\text{-}C_5H_5)]$ [4]. The structure is shown in Fig. 1, and bond parameter data is presented in Table 2. The metal framework geometry may be described either as a distorted Ru_3Rh tetrahedron or as a Ru_3 triangle capped by a Rh atom which lies 2.16 Å above the triruthenium plane. The metal–metal distances within this framework follow the same trends as in $[Os_3Co(\mu\text{-}H)_2(CO)_{10}(\eta^5\text{-}C_5H_5)]$ [4], except that the carbonyl bridged Ru(1)–Rh(1) edge is equivalent in length to the unbridged edge Ru(2)–Rh(1), whereas in the osmium complex the carbonyl bridged Os–Co edge is ca. 0.03 Å shorter than the other two Os–Co edges. The two hydride bridged Ru–Ru edges are significantly longer than the Ru(1)–Ru(3) unbridged edge, consistent with the bond lengthening influence of the hydrides. These two bridged edges differ from each other by ca. 0.07 Å, which may reflect the different co-ordination environments at Ru(1) and Ru(3). The Ru(1)–Ru(3) edge is similar in length to the unbridged Ru–Ru edge in $[Ru_3FeH_2(CO)_{13}]$ [9] (2.780(1) Å), and the two bridged Ru–Ru edges in the latter complex with metal–metal separations of 2.876(1) and 2.906(1) Å, are also similar to the equivalent distances in the title

Table 2

Bond lengths (Å) and bond angles (°) for $[Ru_3Rh(\mu\text{-}H)_2(CO)_{10}(\eta^5\text{-}C_5H_5)]$ (Å)

Rh(1)–Ru(1)	2.726(1)	Rh(1)–Ru(2)	2.724(1)
Rh(1)–Ru(3)	2.707(1)	Rh(1)–C(10)	1.924(7)
Rh(1)–C(11)	2.261(9)	Rh(1)–C(12)	2.246(11)
Rh(1)–C(13)	2.194(12)	Rh(1)–C(14)	2.207(9)
Rh(1)–C(15)	2.199(9)	Ru(1)–Ru(2)	2.937(2)
Ru(1)–Ru(3)	2.763(1)	Ru(1)–H(1)	2.02(7)
Ru(1)–C(1)	1.927(8)	Ru(1)–C(2)	1.930(8)
Ru(1)–C(3)	1.882(8)	Ru(1)–C(10)	2.215(7)
Ru(2)–Ru(3)	2.869(1)	Ru(2)–H(1)	1.66(7)
Ru(2)–H(2)	1.81(12)	Ru(2)–C(4)	1.914(8)
Ru(2)–C(5)	1.916(7)	Ru(2)–C(6)	1.892(7)
Ru(3)–H(2)	1.73(13)	Ru(3)–C(7)	1.911(9)
Ru(3)–C(8)	1.904(8)	Ru(3)–C(9)	1.886(9)
C(1)–O(1)	1.121(10)	C(2)–O(2)	1.122(11)
C(3)–O(3)	1.142(10)	C(4)–O(4)	1.138(9)
C(5)–O(5)	1.131(9)	C(6)–O(6)	1.152(9)
C(7)–O(7)	1.130(11)	C(8)–O(8)	1.132(10)
C(9)–O(9)	1.139(11)	C(10)–O(10)	1.160(9)
C(11)–C(12)	1.351(17)	C(11)–C(15)	1.408(15)
C(12)–C(13)	1.334(23)	C(13)–C(14)	1.381(20)
C(14)–C(15)	1.422(17)		
Ru(1)–Rh(1)–Ru(2)	65.2(1)	Ru(1)–Rh(1)–Ru(3)	61.1(1)
Ru(1)–Rh(1)–C(10)	53.6(2)	Ru(1)–Rh(1)–C(11)	135.7(2)
Ru(1)–Rh(1)–C(12)	124.8(3)	Ru(1)–Rh(1)–C(13)	133.9(3)
Ru(1)–Rh(1)–C(14)	159.7(3)	Ru(1)–Rh(1)–C(15)	162.2(3)
Ru(2)–Rh(1)–Ru(3)	63.8(1)	Ru(2)–Rh(1)–C(10)	81.1(2)
Ru(2)–Rh(2)–C(11)	135.7(3)	Ru(2)–Rh(1)–C(12)	169.1(3)
Ru(2)–Rh(1)–C(13)	142.8(5)	Ru(2)–Rh(1)–C(14)	112.6(3)
Ru(2)–Rh(1)–C(15)	109.2(2)	Ru(3)–Rh(1)–C(10)	114.1(2)
Ru(3)–Rh(1)–C(11)	91.5(3)	Ru(3)–Rh(1)–C(12)	115.7(4)
Ru(3)–Rh(1)–C(13)	149.7(4)	Ru(3)–Rh(1)–C(14)	137.7(4)
Ru(3)–Rh(1)–C(15)	101.1(3)	C(10)–Rh(1)–C(11)	143.0(4)
C(10)–Rh(1)–C(12)	108.1(4)	C(10)–Rh(1)–C(13)	89.4(4)
C(10)–Rh(1)–C(14)	106.3(4)	C(10)–Rh(1)–C(15)	143.9(4)
C(11)–Rh(1)–C(12)	34.9(4)	C(11)–Rh(1)–C(13)	59.3(5)
C(11)–Rh(1)–C(14)	61.1(4)	C(11)–Rh(1)–C(15)	36.8(4)
C(12)–Rh(1)–C(13)	34.9(6)	C(12)–Rh(1)–C(14)	59.8(5)
C(12)–Rh(1)–C(15)	60.0(4)	C(13)–Rh(1)–C(14)	36.6(6)
C(13)–Rh(1)–C(15)	61.2(4)	C(14)–Rh(1)–C(15)	37.6(5)
Rh(1)–Ru(1)–Ru(2)	57.4(1)	Rh(1)–Ru(1)–Ru(3)	59.1(1)
Rh(1)–Ru(1)–H(1)	89(2)	Rh(1)–Ru(1)–C(1)	135.1(2)
Rh(1)–Ru(1)–C(2)	128.5(2)	Rh(1)–Ru(1)–C(3)	88.3(3)
Rh(1)–Ru(1)–C(10)	44.4(2)	Ru(2)–Ru(1)–Ru(3)	60.4(1)
Ru(2)–Ru(1)–H(1)	33(2)	Ru(2)–Ru(1)–C(1)	104.8(2)
Ru(2)–Ru(1)–C(2)	112.9(2)	Ru(2)–Ru(1)–C(3)	144.4(3)
Ru(2)–Ru(1)–C(10)	71.9(2)	Ru(3)–Ru(1)–H(1)	83(2)
Ru(3)–Ru(1)–C(1)	76.2(2)	Ru(3)–Ru(1)–C(2)	167.0(2)
Ru(3)–Ru(1)–C(3)	95.8(2)	Ru(3)–Ru(1)–C(10)	102.9(2)
H(1)–Ru(1)–C(1)	89(2)	H(1)–Ru(1)–C(2)	87(2)
H(1)–Ru(1)–C(3)	177(2)	H(1)–Ru(1)–C(10)	88(2)
C(1)–Ru(1)–C(2)	96.1(3)	C(1)–Ru(1)–C(3)	93.0(3)
C(1)–Ru(1)–C(10)	176.5(3)	C(2)–Ru(1)–C(3)	95.1(3)
C(2)–Ru(1)–C(10)	84.2(3)	C(3)–Ru(1)–C(10)	90.4(3)

Table 2 (continued)

Rh(1)–Ru(2)–Ru(1)	57.4(1)	Rh(1)–Ru(2)–Ru(3)	57.8(1)
Rh(1)–Ru(2)–H(1)	97(2)	Rh(1)–Ru(2)–H(2)	91(4)
Rh(1)–Ru(2)–C(4)	173.6(2)	Rh(1)–Ru(2)–C(5)	91.4(2)
Rh(1)–Ru(2)–C(6)	86.2(2)	Ru(1)–Ru(2)–Ru(3)	56.8(1)
Ru(1)–Ru(2)–H(1)	42(2)	Ru(1)–Ru(2)–H(2)	82(4)
Ru(1)–Ru(2)–C(4)	119.5(2)	Ru(1)–Ru(2)–C(5)	99.0(2)
Ru(1)–Ru(2)–C(6)	141.6(2)	Ru(3)–Ru(2)–H(1)	86(2)
Ru(3)–Ru(2)–H(2)	35(4)	Ru(3)–Ru(2)–C(4)	115.8(2)
Ru(3)–Ru(2)–C(5)	147.3(2)	Ru(3)–Ru(2)–C(6)	94.7(2)
H(1)–Ru(2)–H(2)	92(5)	H(1)–Ru(2)–C(4)	81(2)
H(1)–Ru(2)–C(5)	87(2)	H(1)–Ru(2)–C(6)	176(3)
H(2)–Ru(2)–C(4)	83(4)	H(2)–Ru(2)–C(5)	178(5)
H(2)–Ru(2)–C(6)	87(4)	C(4)–Ru(2)–C(5)	94.7(3)
C(4)–Ru(2)–C(6)	95.3(3)	C(5)–Ru(2)–C(6)	93.7(3)
Rh(1)–Ru(3)–Ru(1)	59.8(1)	Rh(1)–Ru(3)–Ru(2)	58.4(1)
Rh(1)–Ru(3)–H(2)	94(4)	Rh(1)–Ru(3)–C(7)	167.3(3)
Rh(1)–Ru(3)–C(8)	89.5(2)	Rh(1)–Ru(3)–C(9)	96.9(3)
Ru(1)–Ru(3)–Ru(2)	62.8(1)	Ru(1)–Ru(3)–H(2)	89(4)
Ru(1)–Ru(3)–C(7)	108.1(3)	Ru(1)–Ru(3)–C(8)	92.0(2)
Ru(1)–Ru(3)–C(9)	155.9(2)	Ru(2)–Ru(3)–H(2)	37(4)
Ru(2)–Ru(3)–C(7)	114.2(2)	Ru(2)–Ru(3)–C(8)	145.8(2)
Ru(2)–Ru(3)–C(7)	114.2(20	Ru(2)–Ru(3)–C(8)	145.8(2)
Ru(2)–Ru(3)–C(9)	101.1(2)	H(2)–Ru(3)–C(7)	82(4)
H(2)–Ru(3)–C(8)	177(5)	H(2)–Ru(3)–C(9)	87(4)
C(7)–Ru(3)–C(8)	93.8(3)	C(7)–Ru(3)–C(9)	94.7(4)
C(8)–Ru(3)–C(9)	93.8(4)	Ru(1)–H(1)–Ru(2)	106(4)
Ru(2)–H(2)–Ru(3)	108(6)	Ru(1)–C(1)–O(1)	172.2(7)
Ru(1)–C(2)–O(2)	178.2(7)	Ru(1)–C(3)–O(3)	177.1(8)
Ru(2)–C(4)–O(4)	177.0(6)	Ru(2)–C(5)–O(5)	178.5(6)
Ru(2)–C(6)–O(6)	178.6(6)	Ru(3)–C(7)–O(7)	177.1(7)
Ru(3)–C(8)–O(8)	177.4(7)	Ru(3)–C(9)–O(9)	179.1(8)
Rh(1)–C(10)–Ru(1)	82.0(3)	Rh(1)–C(10–O(10)	143.8(6)
Ru(1)–C(10)–O(10)	134.0(6)	Rh(1)–C(11)–C(12)	71.9(6)
Rh(1)–C(11)–C(15)	69.2(5)	C(12)–C(11)–C(15)	107.2(10)
Rh(1)–C(12)–C(11)	73.2(6)	Rh(1)–C(12)–C(13)	70.4(7)
C(11)–C(12)–C(13)	110.4(12)	Rh(1)–C(13)–C(12)	74.6(8)
Rh(1)–C(13)–C(14)	72.2(7)	C(12)–C(13)–C(14)	109.7(12)
Rh(1)–C(14)–C(13)	71.2(7)	Rh(1)–C(14)–C(15)	70.9(6)
C(13)–C(14)–C(15)	105.8(10)	Rh(1)–C(15)–C(11)	74.0(5)
Rh(1)–C(15)–C(14)	71.5(5)	C(11)–C(15)–C(14)	106.8(9)

compound. The hydrides in this Ru_3Rh cluster were located directly, and their co-ordination to the Ru atoms shows some asymmetry, within the limits of the high estimated standard deviations on these bond parameters. The Ru–Rh distances in $[Ru_3Rh(\mu\text{-}H)_2(CO)_{10}(\eta^5\text{-}C_5H_5)]$ are all slightly shorter than the range of distances (2.742(1)–2.901(1) Å) found in other tetranuclear RuRh mixed metal clusters [2,8,10]. The carbonyl ligand, C(10)O(10), asymmetrically bridges the Ru(1)–Rh(1) edge, with the shorter metal–carbon interaction to the Rh atom. The nine remaining carbonyl ligands are all terminal, and show an average deviation from linearity of ca. 3σ. The planar cyclopentadienyl ligand is slightly displaced from a symmetrical co-ordination mode, the Rh–C distances lying in the range 2.194(12)–2.261(9) Å. The Rh–C_5(centroid) distance is 1.887 Å.

Experimental

All reactions were carried out under nitrogen using dry, distilled solvents. Thin-layer chromatography (TLC) and subsequent procedures were carried out in air. IR, and ^1H NMR spectra were recorded on a Perkin–Elmer PE 580 spectrophotometer and a Varian XL-300 spectrometer, respectively. Starting materials were synthesised using literature techniques [11].

Preparation of $[Ru_3RhH_2(CO)_{10}(C_5H_5)]$

The complex $[(Rh(CO)_2Cl)_2]$ (37 mg), in hexane, was stirred with freshly sublimed $Tl(C_5H_5)$ (70 mg) for 1 h. The mixture was then filtered into a flask containing $[Ru_4H_2(CO)_{13}]$ (100 mg), and heated, under reflux, for 12 h, to give a dark brown solution. The mixture was separated by TLC using a 1/1 hexane/dichloromethane mixture as eluent. An orange-red band was obtained together with bands corresponding to $[Ru_4H_4(CO)_{12}]$ and unreacted starting material. Red

Table 3

Atomic co-ordinates ($\times 10^4$)

Atom	*x*	*y*	*z*
Rh(1)	2061(1)	8166(1)	8606(1)
Ru(1)	2659(1)	6570(1)	9340(1)
Ru(2)	200(1)	6798(1)	8022(1)
Ru(3)	−176(1)	7501(1)	9644(1)
H(1)	1247(83)	5982(48)	8469(40)
H(2)	−1155(143)	6889(82)	8886(76)
C(1)	1587(10)	5866(5)	10158(5)
O(1)	1134(7)	5423(4)	10658(3)
C(2)	4300(9)	5700(6)	9079(5)
O(2)	5248(8)	5184(5)	8947(4)
C(3)	3960(9)	7170(6)	10125(4)
O(3)	4740(7)	7567(5)	10583(4)
C(4)	−1206(8)	5828(5)	7732(4)
O(4)	−2067(7)	5272(4)	7532(3)
C(5)	1585(9)	6657(5)	7097(4)
O(5)	2393(7)	6555(4)	6549(3)
C(6)	−1107(9)	7678(5)	7505(4)
O(6)	−1927(7)	8201(4)	7188(4)
C(7)	−1503(11)	6790(6)	10338(5)
O(7)	−2311(8)	6351(5)	10720(4)
C(8)	839(10)	8141(6)	10522(5)
O(8)	1407(8)	8549(5)	11036(3)
C(9)	−1793(10)	8373(5)	9454(5)
O(9)	−2754(8)	8909(5)	9339(4)
C(10)	3780(9)	7348(5)	8344(5)
O(10)	4922(7)	7250(4)	7944(3)
C(11)	1581(14)	9566(6)	9042(6)
C(12)	3215(16)	9458(7)	8988(9)
C(13)	3619(15)	9269(7)	8219(11)
C(14)	2235(20)	9270(6)	7722(6)
C(15)	906(11)	9431(6)	8251(7)

crystals, suitable for an X-ray analysis, were obtained by recrystallisation of the orange-red solid from hexane/dichloromethane.

Structure determination of $[Ru_3Rh(\mu\text{-}H)_2(CO)_{10}(\eta^5\text{-}C_5H_5)]$

Crystal data. $C_{15}H_{17}O_{10}RhRu_3$, M 753.33, monoclinic, a 8.186(1), b 15.061(1), c 16.302(1) Å, β 91.06(1)°, V 2009.5 Å^3 (by least-squares refinement on diffractometer angles for 64 automatically centred reflections in the range $15 < 2\theta < 25°$, λ 0.71 069 Å), space group $P2_1/n$ (alt. setting of $P2_1/c$, No. 14), $Z = 4$, D_x 2.489 g cm^{-3}, $F(000)$ 1416. Red platelets. Crystal dimensions (distance from face to centre): 0.11 (100, $\bar{1}00$) × 0.013 (010, $0\bar{1}0$) × 0.11 (001, $00\bar{1}$) mm, μ(Mo-K_α) 29.87 cm^{-1}.

Data collection and processing. Stoe-Siemens four-circle diffractometer, graphite-monochromated Mo-K_α radiation, 24 step ω–θ scans with step width 0.05°, scan speeds 0.025–0.1° s^{-1}; 7927 reflections measured ($5.0 < 2\theta < 50.0°$, $+h$, $\pm k$, $\pm l$), 3538 unique [merging $R = 0.031$ after numerical absorption correction (max., min. transmission factors = 0.948, 0.676)], giving 2737 with $F > 4\sigma(F)$. No significant variation in intensities of three standard reflections.

Structure analyses and refinement. Automatic centrosymmetric direct methods (SHELX76: EEES) for Ru and Rh atom positions, followed by Fourier difference techniques for C, O, and hydridic H atoms. Cyclopentadienyl H atoms placed in idealised positions and allowed to ride on the relevant C atom with C–H fixed at 1.08 Å; refined with a common isotropic temperature factor. Blocked-cascade least-squares with all non-hydrogen atoms anisotropic, hydridic H refining freely. The weighting scheme $w = [\sigma^2(F_0) + 0.000\,055\ F_0^2]^{-1}$, with $\sigma(F_0)$ from counting statistics gave satisfactory agreement analyses. Final R and R_w values are 0.040 and 0.033. Programs and computers used are given in [12]. Final atomic co-ordinates, are listed in Table 3. Structure factor tables are available from the authors.

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