Synthesis and structural characterization of [N(PPh$_3$)$_2$][H$_2$Ru$_3$Rh(CO)$_{12}$]

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Abstract

The new anionic mixed metal cluster [N(PPh$_3$)$_2$][H$_2$Ru$_3$Rh(CO)$_{12}$] was made in high yield by reaction between [N(PPh$_3$)$_2$][HRu$_3$(CO)$_{11}$] and Rh$_2$(CO)$_4$Cl$_2$. An X-ray diffraction study shows that in [H$_2$Ru$_3$Rh(CO)$_{12}$]$^-$ anion the metal framework is made up of an apical ruthenium atom and a basal Ru$_2$Rh plane. Both hydride ligands are bonded to the apical ruthenium atom and bridge the Ru–Ru edges of the Ru$_3$Rh tetrahedron.

Key words: Ruthenium; Rhodium; Cluster; Carbonyl; Crystal structure

1. Introduction

The tetranuclear mixed-metal dodecacarbonyl clusters of ruthenium, rhodium and cobalt have been studied extensively, and their structures found to depend on the composition of the metal core and the number of the hydride ligands. Some structural trends have been identified. In the mixed metal clusters H$_x$M$_4$-(CO)$_{12}$ (M = Ru, Co or Rh) containing fewer than three ruthenium atoms, three carbonyls bridge the metals of one face of the metal tetrahedron. Rhodium and cobalt have a greater tendency to be involved in the carbonyl bridges, and the ruthenium atom prefers the apical position [1]. Hydrogens tend to bridge either Ru–Ru or Ru–Rh edges or the basal face of metals.

Although the chemistry of Ru$_3$Rh cluster compounds containing cyclopentadienyl ligands is known fairly well [2], little information is available on the corresponding parent compounds containing only carbonyl and hydride ligands. We have previously reported a low yield synthesis and the crystal structure of H$_3$Ru$_3$Rh(CO)$_{12}$ [3], but preparation of this compound was complicated by the preferred formation of H$_2$Ru$_2$Rh$_2$(CO)$_{12}$ [4,5]. This outcome differs signifi-

cantly from that of the corresponding reaction of [Co(CO)$_4$]$^-$ with Ru$_3$(CO)$_{12}$, which finally gives H$_3$Ru$_3$Co(CO)$_{12}$ [6].

The cluster anion [H$_2$Ru$_3$Rh(CO)$_{11}$(PPh$_3$)]$^-$ containing a phosphine ligand was obtained previously by demethylation of [H$_2$Ru$_3$Rh(CO)$_{10}$(PPh$_3$)(μ-COMe)] with K[BHBu$_3$] [7,8], but up to now there has been no report of the parent cluster anion [H$_2$Ru$_3$Rh(CO)$_{12}$]$^-$.

We now report a high yield synthesis of the tetranuclear anionic cluster [H$_2$Ru$_3$Rh(CO)$_{12}$]$^-$ (in its salt with [N(PPh$_3$)$_2$]$^+$) and its characterization by X-ray crystallography and ^{1}H NMR spectroscopy.

2. Results and discussion

Reaction of [N(PPh$_3$)$_2$][HRu$_3$(CO)$_{11}$] with Rh$_2$-(CO)$_4$Cl$_2$ in CH$_2$Cl$_2$ at ambient temperature produced a mixture of cluster compounds that could partly separated by chromatography on silica. The main product was [N(PPh$_3$)$_2$][H$_2$Ru$_3$Rh(CO)$_{12}$] (1).

The anionic Ru$_3$Co cluster species [H$_2$Ru$_3$-Co(CO)$_{12}$]$^-$, containing two hydride ligands, is also known. This anion is formed in the reaction between [Ru$_3$Co(CO)$_{13}$]$^-$ and H$_2$ [9], where the [Ru$_3$Co-(CO)$_{13}$]$^-$ anion was produced by the reaction of [Co-(CO)$_4$]$^-$ with Ru$_3$(CO)$_{12}$. The [Ru$_3$Co(CO)$_{13}$]$^-$ anion can also be protonated to give HRu$_3$Co(CO)$_{13}$ [10], which reacts with H$_2$ to produce H$_3$Ru$_3$Co(CO)$_{12}$.

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TABLE 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{Å}^2 \times 10^3$) for [N(PPh₃)₂][H₂Ru₃Rh-(CO)₁₂] (1)

Atom	x	y	z	$U_{(eq)}$
Ru(1)	3156(1)	1526(1)	4589(1)	38(1)
Ru(2)	1741(1)	1224(1)	5596(1)	36(1)
Ru(3)	3440(1)	581(1)	5945(1)	36(1)
Rh	2271(1)	287(1)	4569(1)	37(1)
P(1)	2470(2)	6791(2)	5719(2)	33(1)
P(2)	2537(2)	5474(2)	4893(2)	29(1)
N	2759(7)	6048(6)	5547(6)	38(4)
O(1)	1890(8)	1947(7)	3072(7)	83(6)
O(2)	4472(8)	895(6)	3587(8)	85(6)
O(3)	4205(10)	2853(7)	4861(9)	117(7)
O(4)	579(8)	2380(6)	5991(8)	86(6)
O(5)	621(9)	347(6)	6536(7)	89(6)
O(6)	5370(7)	634(6)	6867(6)	70(5)
O(7)	2802(8)	−557(6)	6912(7)	74(5)
O(8)	2246(11)	−87(7)	2856(7)	114(7)
O(9)	1342(9)	−975(6)	5042(9)	97(6)
O(12)	2924(7)	1605(7)	7196(7)	84(5)
O(13)	394(7)	988(6)	4036(6)	73(5)
O(23)	4126(7)	−496(6)	4854(6)	68(5)
C(1)	2365(10)	1788(9)	3641(10)	58(6)
C(2)	3987(10)	1112(8)	3973(8)	52(6)
C(3)	3800(12)	2365(8)	4763(10)	66(7)
C(4)	1011(9)	1967(8)	5816(9)	48(6)
C(5)	1059(10)	676(8)	6170(9)	54(6)
C(6)	4649(11)	623(8)	6516(8)	49(6)
C(7)	3070(10)	−133(8)	6564(9)	48(6)
C(8)	2271(12)	58(8)	3488(9)	64(7)
C(9)	1677(11)	−512(8)	4860(9)	52(6)
C(12)	2791(9)	1308(8)	6578(9)	49(6)
C(13)	1059(11)	922(8)	4496(9)	52(6)
C(23)	3677(10)	−79(8)	5083(8)	49(6)
C(41)	3162(6)	7743(5)	6850(6)	67(5)
C(42)	3858	8029	7398	73(5)
C(43)	4707	7708	7568	78(5)
C(44)	4858	7100	7189	78(5)
C(45)	4162	6814	6641	62(4)
C(46)	3313	7136	6471	36(3)
C(51)	841(6)	7391(4)	6047(5)	56(4)
C(52)	39	7378	6379	57(4)
C(53)	−210	6790	6747	57(4)
C(54)	342	6214	6782	54(4)
C(55)	1144	6227	6449	41(3)
C(56)	1394	6815	6082	32(3)
C(61)	1596(5)	7361(5)	4304(5)	54(4)
C(62)	1574	7751	3617	60(4)
C(63)	2345	8119	3497	70(5)
C(64)	3137	8099	4064	73(5)
C(65)	3158	7709	4750	55(4)
C(66)	2388	7340	4871	39(3)
C(71)	3497(5)	4791(4)	3870(5)	49(4)
C(72)	4224	4706	3450	47(4)
C(73)	4936	5178	3535	54(4)
C(74)	4921	5733	4040	51(4)
C(75)	4193	5817	4460	41(3)
C(76)	3481	5346	4375	37(3)
C(81)	1634(5)	5800(5)	3390(5)	43(4)
C(82)	860	5940	2832	61(4)
C(83)	−8	5901	3049	69(5)
C(84)	−102	5721	3823	64(5)
C(85)	672	5581	4382	48(4)

TABLE 1 (continued)

Atom	x	y	z	$U_{(eq)}$
C(86)	1540	5620	4165	29(3)
C(91)	2720(5)	4604(3)	6171(4)	29(3)
C(92)	2722	3969	6531	45(4)
C(93)	2366	3407	6087	61(4)
C(94)	2009	3481	5283	63(4)
C(95)	2007	4117	4922	47(4)
C(96)	2363	4678	5366	27(3)

Among the Ru₃Rh core clusters, H₃Ru₃Rh(CO)₁₂ is the only previously known analogue of this Ru₃Co system. However, whereas the Ru–Co compound [N(PPh₃)₂][H₂Ru₃Co(CO)₁₂] can be protonated to give the neutral parent cluster H₃Ru₃Co(CO)₁₂, treatment of (1) with concentrated aqueous H₃PO₄ or H₂SO₄ does not give the corresponding parent cluster H₃Ru₃Rh(CO)₁₂. Instead, acidification with a small amount of concentrated aqueous H₂SO₄ (5 drops in 25 ml of CH₂Cl₂) gave a mixture of H₂Ru₂Rh₂(CO)₁₂ and other unidentified compounds. The reactions of (1) to some extent resemble those of H₂Ru₂Rh₂(CO)₁₂; thus (1) readily reacts with phosphine and gold phosphine ligands to give penta- and hexanuclear Ru–Rh and Ru–Rh–Au compounds [11].

Treatment of the salt (1) with CH₃OH converted it in part to the hexanuclear species [N(PPh₃)₂][RuRh₅-(CO)₁₆][12], which was identified by IR spectroscopy.

The crystal structure of [N(PPh₃)₂][H₂Ru₃Rh-(CO)₁₂] consists of discrete cations and anions (Tables 1–3). The structure of the [H₂Ru₃Rh(CO)₁₂]⁻ anion is shown in Fig. 1 and selected bond lengths and angles are given in Table 2.

The hydride ligands bridge two of the Ru–Ru edges, in good agreement with observations on other Ru–Rh mixed metal clusters. However, the arrangement to carbonyl ligands is different from that in the hydride clusters [H₃Ru₃Rh(CO)₁₂] and [H₃Ru₃Co(CO)₁₂]: in (1), the basal metal triangle (Rh and two Ru) is bridged by the three carbonyl ligands, that there is one Ru(μ-CO)Ru bridging carbonyl, which is uncommon in tetranuclear clusters of these metals.

The hydride positions were inferred from the structural parameters. Hydride ligands cause lengthening of the corresponding metal–metal bonds and the hydride-bridged Ru(1)–Ru(2) and Ru(1)–Ru(3) bonds have lengths of 2.972(2) Å and 2.945(2) Å. In H₂Ru₂Rh₂(CO)₁₂, whose structure is very similar, the corresponding hydride-bridged ruthenium–ruthenium bond length is only 2.920(1) Å, and in H₃Ru₃Rh(CO)₁₂ the lengths of the basal Ru–Ru bonds, which are hydride bridged, average 2.931 Å. In (1), the length of
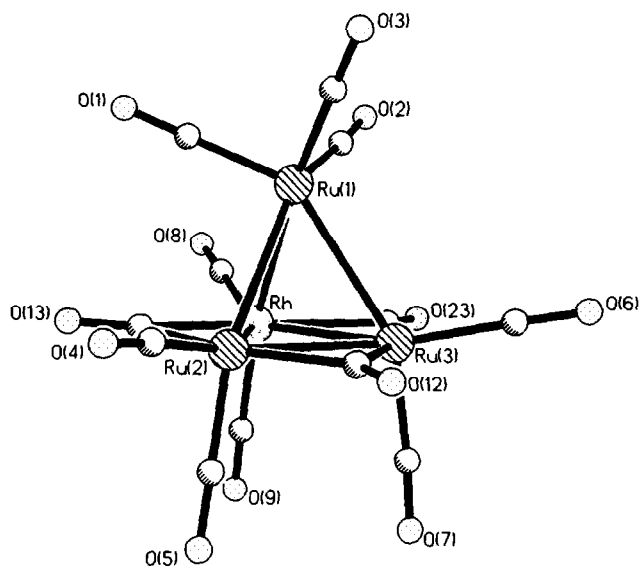
Fig. 1. The schematic presentation and numbering scheme of $[H_2Ru_3Rh(CO)_{12}]^-$.

The $^{13}C\text{-}\{^1H\}$ NMR data indicate that compound (1) is structurally similar to $[H_2Ru_3Rh(CO)_{11}(PPh_3)]^-$. In the $^{13}C\text{-}\{^1H\}$ NMR spectrum of (1) the two signals at low field (267.9 and 252.9 ppm) arise from the bridging carbonyl groups, with the signal of relative intensity 2

TABLE 2. Selected bond lengths (Å) and angles (°) in $[H_2Ru_3Rh(CO)_{12}]^-$

Ru(1)–Ru(2)	2.972(2)	Ru(1)–Ru(3)	2.945(2)
Ru(1)–Rh	2.769(2)	Ru(1)–C(1)	1.908(15)
Ru(1)–C(2)	1.922(16)	Ru(1)–C(3)	1.907(17)
Ru(2)–Ru(3)	2.795(2)	Ru(2)–Rh	2.743(2)
Ru(2)–C(4)	1.892(15)	Ru(2)–C(5)	1.860(16)
Ru(2)–C(12)	2.100(13)	Ru(2)–C(13)	2.068(15)
Ru(3)–Rh	2.743(1)	Ru(3)–C(6)	1.897(15)
Ru(3)–C(7)	1.892(16)	Ru(3)–C(12)	2.115(15)
Ru(3)–C(23)	2.034(15)	Rh–C(8)	1.897(16)
Rh–C(9)	1.908(17)	Rh–C(13)	2.175(16)
Rh–C(23)	2.245(14)		

Ru(2)–Ru(1)–Ru(3)	56.4(1)	Ru(2)–Ru(1)–Rh	56.9(1)
Ru(3)–Ru(1)–Rh	57.3(1)	Ru(2)–Ru(1)–C(1)	98.5(5)
Ru(3)–Ru(1)–C(1)	145.7(5)	Rh–Ru(1)–C(1)	90.2(5)
Ru(2)–Ru(1)–C(2)	143.3(5)	Ru(3)–Ru(1)–C(2)	97.8(4)
Rh–Ru(1)–C(2)	87.8(5)	C(1)–Ru(1)–C(2)	90.7(6)
Ru(2)–Ru(1)–C(3)	117.7(6)	Ru(3)–Ru(1)–C(3)	114.9(5)
Rh–Ru(1)–C(3)	171.9(5)	C(1)–Ru(1)–C(3)	96.9(7)
C(2)–Ru(1)–C(3)	96.0(7)	Ru(1)–Ru(2)–Ru(3)	61.3(1)
Ru(1)–Ru(2)–Rh	57.8(1)	Ru(3)–Ru(2)–Rh	59.4(1)
Ru(1)–Ru(2)–C(4)	115.8(5)	Ru(3)–Ru(2)–C(4)	146.3(4)
Rh–Ru(2)–C(4)	151.4(4)	Ru(1)–Ru(2)–C(5)	155.7(5)
Ru(3)–Ru(2)–C(5)	99.8(5)	Rh–Ru(2)–C(5)	110.3(5)
C(4)–Ru(2)–C(5)	88.4(7)	Ru(1)–Ru(2)–C(12)	86.7(4)
Ru(3)–Ru(2)–C(12)	48.7(4)	Rh–Ru(2)–C(12)	108.0(4)
C(4)–Ru(2)–C(12)	98.9(6)	C(5)–Ru(2)–C(12)	91.3(6)
Ru(1)–Ru(2)–C(13)	79.7(5)	Ru(3)–Ru(2)–C(13)	110.8(4)
Rh–Ru(2)–C(13)	51.5(4)	C(4)–Ru(2)–C(13)	101.0(6)
C(5)–Ru(2)–C(13)	94.7(6)	C(12)–Ru(2)–C(13)	159.4(6)
Ru(1)–Ru(3)–Ru(2)	62.3(1)	Ru(1)–Ru(3)–Rh	58.1(1)
Ru(2)–Ru(3)–Rh	59.4(1)	Ru(1)–Ru(3)–C(6)	112.3(5)
Ru(2)–Ru(3)–C(6)	146.4(5)	Rh–Ru(3)–C(6)	149.5(5)
Ru(1)–Ru(3)–C(7)	152.9(4)	Ru(2)–Ru(3)–C(7)	97.2(4)
Rh–Ru(3)–C(7)	96.9(4)	C(6)–Ru(3)–C(7)	94.6(6)
Ru(1)–Ru(3)–C(12)	87.2(4)	Ru(2)–Ru(3)–C(12)	48.2(4)
Rh–Ru(3)–C(12)	107.6(4)	C(6)–Ru(3)–C(12)	100.2(6)
C(7)–Ru(3)–C(12)	91.4(6)	Ru(1)–Ru(3)–C(23)	81.9(4)
Ru(2)–Ru(3)–C(23)	113.0(4)	Rh–Ru(3)–C(23)	53.6(4)
C(6)–Ru(3)–C(23)	98.0(6)	C(7)–Ru(3)–C(23)	91.4(6)
C(12)–Ru(3)–C(23)	161.2(5)	Ru(1)–Rh–Ru(2)	65.3(1)
Ru(1)–Rh–Ru(3)	64.6(1)	Ru(2)–Rh–Ru(3)	61.3(1)
Ru(1)–Rh–C(8)	98.6(5)	Ru(2)–Rh–C(8)	145.5(5)
Ru(3)–Rh–C(8)	141.4(5)	Ru(1)–Rh–C(9)	164.1(5)
Ru(2)–Rh–C(9)	101.5(5)	Ru(3)–Rh–C(9)	101.9(4)
C(8)–Rh–C(9)	97.3(7)	Ru(1)–Rh–C(13)	83.0(4)
Ru(2)–Rh–C(13)	48.1(4)	Ru(3)–Rh–C(13)	109.3(4)
C(8)–Rh–C(13)	102.1(7)	C(9)–Rh–C(13)	94.6(6)
Ru(1)–Rh–C(23)	82.6(4)	Ru(2)–Rh–C(23)	108.1(4)
Ru(3)–Rh–C(23)	46.8(4)	C(8)–Rh–C(23)	99.0(6)
C(9)–Rh–C(23)	94.0(6)	C(13)–Rh–C(23)	155.9(5)
Ru(2)–C(12)–Ru(3)	83.1(5)	Ru(2)–C(13)–Rh	80.5(5)
Ru(3)–C(23)–Rh	79.6(5)		

the non-bridged Ru(1)–Rh(1) bond is 2.769(2) Å, and in $H_2Ru_2Rh_2(CO)_{12}$ the corresponding bond length is 2.730(1) Å. In $H_3Ru_3Rh(CO)_{12}$ the lengths of the non-bridged Ru–Rh bonds average 2.759 Å. The hydride-bridged Ru–Rh bond in $H_2Ru_2Rh_2(CO)_{12}$ is significantly longer, at 2.889(1) Å.

There is also repulsion between the hydride ligands and the nearest carbonyl ligands. Thus the bond angles Ru(1)–Ru(2)–C(4) and Ru(1)–Ru(3)–C(6) are 115.8(5)° and 112.3(5)°, respectively, whereas the angle Ru(1)–Rh–C(8) is only 98.6(5)°. In $H_2Ru_2Rh_2(CO)_{12}$, the corresponding angles next to the hydride-bridged metal–metal edges are Ru–Ru–C_{eq} 115.8(1)° and Ru–Rh–C_{eq} 110.7(2)°, whereas the angle next to the non bridged Ru–Rh bond is Ru–Rh–C_{eq} 91.5(1)°.

The arrangement of the hydride and carbonyl ligands is similar to that in $H_2Ru_2Rh_2(CO)_{12}$, where the hydrides occupy apical–basal Ru–Ru and Ru–Rh sites, and also to that in the spectroscopically characterized $[H_2Ru_4(CO)_{12}]^{2-}$ [13]. In $[H_2Ru_4(CO)_{12}]^{2-}$ the hydride ligands are thought to bridge basal–apical edges with carbonyl ligands occupying the basal Ru–Ru sites. Although the arrangement of the hydride ligands is similar in neutral $H_2Ru_4(CO)_{13}$, in that case only two of the basal Ru–Ru sites are bridged, with Ru(μ-CO)Ru semibridges [14]. In the corresponding compound containing three hydrides, $[H_3Ru_4(CO)_{12}]^-$, all the carbonyl ligands are terminal [15]. In solution the hydrides of (1) are equivalent, as shown by the sharp singlet at -20.2 ppm in the ^1H NMR spectrum. No coupling to the rhodium atom was observed.

assigned to the carbonyls CO(13) and CO(23) and the signal with relative intensity 1 assigned to the carbonyl CO(12). Although the presence of impurities is clearly indicated by the ^{13}C-{^{1}H} NMR spectrum (see spectroscopic data), no signals from impurities can be seen in the bridging carbonyl regions. Signals analogous to those of (1) are found at 266.7 and 255.5 ppm in the ^{13}C-{^{1}H} NMR spectrum of [H$_2$Ru$_3$Rh(CO)$_{11}$(PPh$_3$)]$^-$. The two high field signals of (1) (191.2 and 182.9 ppm) both show typical ^1J(RhC) couplings for terminal CO groups bound to Rh atom, and must arise from the CO groups CO(8) and CO(9). These signals correspond to the coupled signals at 192.5 and 183.0 ppm in the spectrum of [H$_2$Ru$_3$Rh(CO)$_{11}$(PPh$_3$)]$^-$. Signals at 199.9, 195.9 and 192.9 ppm (relative intensity 2) arise from pairs of the equivalent equatorial and equivalent axial carbonyl ligands bound to the basal ruthenium atoms, and from the two equivalent apical carbonyl ligands. In the spectrum of [H$_2$Ru$_3$Rh(CO)$_{11}$(PPh$_3$)]$^-$, corresponding signals are observed at 201.0, 200.2 and

193.8 ppm. The signal from the remaining apical carbonyl ligand of (1) may be any one of the singlets at 203.0, 198.3, 194.2 or 192.5 ppm (which all have the same intensity; see spectroscopic data). Additional broad signals are present at 204.8 and 211.7 ppm. These signals arise from an impurity, which was present in the ^{13}C-enriched Ru$_3$(CO)$_{12}$ used and could not be separated with silica gel. However, the ^{1}H and ^{13}C-{^{1}H} NMR spectra confirm that no other compounds containing hydride ligands or carbonyl bridges are present.

3. Experimental details

3.1. General

All manipulations except chromatographic separations were carried out under N$_2$ and with deoxygenated solvents. FT-IR spectra were recorded on a Galaxy 6020 spectrometer. The ^{1}H NMR spectrum was recorded on a Bruker AM-250 spectrometer at 273 K in CDCl$_3$ with Me$_4$Si as reference, and the ^{31}P NMR spectrum at 294 K in CDCl$_3$ with concentrated aqueous H$_3$PO$_4$ as an external reference. The ^{13}C-{^{1}H} NMR spectrum was recorded at 233 K in CH$_2$Cl$_2$. Crystals were grown by evaporation of the solvent from a saturated hexane-CH$_2$Cl$_2$ solution.

3.2. Synthesis

The salt [N(PPh$_3$)$_2$][HRu$_3$(CO)$_{11}$] [16] (200 mg, 0.174 mmol) was treated with Rh$_2$(CO)$_4$Cl$_2$ (34 mg, 0.087 mmol) in CH$_2$Cl$_2$ (30 ml) at room temperature to give a mixture of cluster compounds, which were partly separated by column chromatography on silica. Elution with a hexane gave a yellow fraction of HRu$_3$(CO)$_{10}$Cl (30 mg, 0.048 mmol) [17], characterized by IR, followed by a minor unidentified orange fraction (3 mg, CH$_2$Cl$_2$/hexane 1:1 mixture). Elution with CH$_2$Cl$_2$ gave a red fraction which yield the title compound (1), (102 mg, 0.080 mmol) containing some impurities, as mentioned earlier.

3.3. Spectroscopic data of (1)

^{1}H NMR (in ppm): −20.2. ^{31}P NMR characteristic of [N(PPh$_3$)$_2$]$^+$. IR (in cm^{-1}): 2073 w, 2038 vs, 2029 vs, 2008 vs, 1976 m, sh, 1830 m, 1815 m, 1797 m, CH$_2$Cl$_2$, all signals broad. ^{13}C NMR (in ppm): 267.9 (m, 1C), 252.9 (m, 2C), 199.9 (s, 2C), 195.9 (s, 2C), 192.9 (s, 2C), 191.2 [d, 1C, J(RhC) = 71.7 Hz], 182.9 [d, J(RhC) = 62.9 Hz].

The following signals may be due to impurities (see text): {203.0 (s, 1C), 198.3 (s, 1C), 194.2 (s, 1C), 192.5 (s, 1C)}, {204.8 (m, br), 211.7 (m, br)}.

The ^{13}C-{^{1}H} NMR spectrum was recorded for a sample prepared from ^{13}C-enriched Ru$_3$(CO)$_{12}$ and

TABLE 3. Crystallographic data for compound (1)

Formula	C$_{48}$H$_{32}$NO$_{12}$P$_2$RhRu$_3$
FW	1282.8
Colour; habit	Dark brown block
Crystal size (mm^3)	0.45×0.45×0.45
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	14.804(2)
b (Å)	19.712(3)
c (Å)	17.031(2)
β (°)	99.210(10)
V (Å^3)	4905.9(12)
Z	4
Calc. density (g cm^{-3})	1.737
μ (mm^{-1})	1.338
F(000)	2512
No. centering reflections	25
Centering 2θ	16–26
Scan range (2θ)	4–50
Scan speed (° min^{-1})	2.49–29.30
h, k, l range	18, 24, ±21
Reflections collected	9105
No. of unique reflections	8581
Obs. data ($F \leq 3\sigma(F)$)]	4227
No. of parameters varied	352
R	0.0561
R'	0.0637
G (weight)	0.0005
Goodness of fit	1.48
Largest diff. peak (e Å^{-3})	0.81
Largest diff. hole (e Å^{-3})	−0.75

$R = (\Sigma \|F_o\| - \|F_c\|)/\Sigma |F_o|$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w |F_o|^2]^{1/2}$, and goodness of fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$ where $N_o =$ number of observed reflections and $N_v =$ number of variables. Weighting scheme used of form $w^{-1} = [\sigma^2(F) + gF^2]$.

chromatographed in the usual manner. The spectrum showed the presence of significant amounts of impurities. However, the spectrum showed that (1) was the only carbonyl-bridged compound present, and Rh–C couplings were observed in the signals belonging to it.

3.4. Structure determination

Diffraction data were recorded on a Nicolet R3m diffractometer with graphite-monochromated Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å). ω (omega) scan mode with scan speed 2.49–29.29° min^{-1} was used. Intensities were corrected for Lorentz, polarization and background effects. No absorption correction was applied.

Metal atom positions were located by direct methods, and coordinates for non-metal atoms were determined from subsequent difference electron density calculations. All calculations were performed with the SHELXTL Plus [18] program package. All nonhydrogen atoms were refined anisotropically, except for the phenyl carbons in N(PPh₃)₂, which were refined isotropically with the phenyl rings as rigid groups. Hydrogen atoms were placed in calculated positions (0.96 Å, $U = 0.06$ Å^2) and not refined.

4. Supplementary material available

A complete list of bond lengths and angles and tables of thermal parameters and hydrogen atom coordinates have been deposited at the Cambridge Crystallographic Data Centre.

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