

Reaction of the $[\text{H}_2\text{Ru}_3\text{Rh}(\text{CO})_{12}]^-$ cluster anion with PPh_3 : synthesis and structural characterization of $\text{H}_2\text{Ru}_3\text{Rh}_2(\text{CO})_{13}(\text{PPh}_3)$

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Received 1 September 1994

Abstract

A new pentanuclear phosphine-substituted mixed-metal cluster of Ru and Rh has been obtained from the reaction between $[\text{H}_2\text{Ru}_3\text{Rh}(\text{CO})_{12}]^-$ anion and PPh_3 . The product, $\text{H}_2\text{Ru}_3\text{Rh}_2(\text{CO})_{13}(\text{PPh}_3)$, was characterized by X-ray crystallography and NMR spectroscopy, which showed the molecule to have a pentanuclear trigonal bipyramidal metal framework with the rhodium atoms in apical positions and the ruthenium atoms in equatorial sites. The phosphine ligand is coordinated to an apical rhodium atom.

Keywords: Ruthenium; Rhodium; Clusters; Crystal structure

1. Introduction

The tetranuclear clusters of Ru and Rh and their phosphine derivatives constitute a fairly well-known group of cluster compounds [1]. Pentanuclear Rh-containing compounds are relatively rare, and there are very few examples of the pentanuclear phosphine-substituted Ru–Rh clusters. The crystallographically characterized pentanuclear RhM ($\text{M} = \text{Ru}$ or Rh) clusters are based on a metal framework that contains 2–5 Rh atoms. Among these clusters; $[\text{RuRh}_4(\text{CO})_{15}]^{2-}$ has a trigonal bipyramid structure which in many respects resembles that in $[\text{Rh}_5(\text{CO})_{15}]^-$ and $[\text{Rh}_5(\text{CO})_{14}\text{I}]^{2-}$ [2–4]. The cluster $\text{Ru}_3\text{Rh}_2(\mu_4\text{-PPh})(\text{CO})_{13}(\text{PET}_3)$ is structurally completely different, containing a square pyramidal metal framework [5]. $\text{H}_2\text{Ru}_3\text{Rh}_2(\text{CO})_{12}(\text{PPh}_3)_2$, another example of a neutral pentanuclear phosphine-substituted Ru–Rh cluster, is based on a trigonal bipyramidal structure [6].

Some of these clusters, such as $[\text{Rh}_5(\text{CO})_{15}]^-$ and the iodide-substituted derivative $[\text{Rh}_5(\text{CO})_{14}\text{I}]^{2-}$ (produced in a reaction between $\text{Rh}_4(\text{CO})_{12}$ and I^-) have

been found to be unstable being converted into compounds of different nuclearity.

Previously we described the synthesis and structural characterization of the tetrahedral cluster anion $[\text{H}_2\text{Ru}_3\text{Rh}(\text{CO})_{12}]^-$ [7]. Here we report a reaction between $[\text{H}_2\text{Ru}_3\text{Rh}(\text{CO})_{12}]^-$ anion and PPh_3 ligand, which produces two phosphine-substituted compounds, viz. $\text{H}_2\text{Ru}_3\text{Rh}_2(\text{CO})_{13}(\text{PPh}_3)$ (**1**) and the previously mentioned $\text{H}_2\text{Ru}_3\text{Rh}_2(\text{CO})_{12}(\text{PPh}_3)_2$ (**2**) [6].

2. Results and discussion

Although the reactions of the clusters $\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}$, and $[\text{H}_2\text{Ru}_3\text{Rh}(\text{CO})_{12}]^-$ are in some respects similar, they give different types of cluster on treatment with triphenylphosphine. In the reaction between $\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}$ and PPh_3 , the cluster core remains tetranuclear [8], whereas the reaction of $[\text{H}_2\text{Ru}_3\text{Rh}(\text{CO})_{12}]^-$ with PPh_3 yields two pentanuclear phosphine derivatives, which are separable by chromatography. Separation gives a fraction that crystallizes as the monosubstituted pentanuclear compound $\text{H}_2\text{Ru}_3\text{Rh}_2(\text{CO})_{13}(\text{PPh}_3)$ (**1**). According to the ^1H and ^{31}P NMR spectra, however, (**1**) is not the only compound present. Further separation of the fraction by thin layer chromatography gives another cluster species, which crystallizes as the disubstituted pentanuclear

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complex $\text{H}_2\text{Ru}_3\text{Rh}_2(\text{CO})_{12}(\text{PPh}_3)_2$ (**2**). This compound has previously been observed from a reaction in which the bridging $\mu\text{-CO}$ Me ligand in $\text{H}_2\text{Ru}_3\text{Rh}(\text{CO})_{10}(\text{PPh}_3)(\mu\text{-CO})$ was demethylated by $\text{K}(\text{BHBu}_3)$ in THF, the solvent was evaporated to dryness, and the anionic reaction product $[\text{H}_2\text{Ru}_3\text{Rh}(\text{CO})_{11}(\text{PPh}_3)]^-$ was treated with $[\text{Rh}(\text{CO})_3(\text{PPh}_3)_2][\text{PF}_6]$ in CH_2Cl_2 at -90°C . With solely THF as solvent, the final reaction did not occur. It has also been found possible, with $\text{K}(\text{BHBu}_3)$, to revert $\text{H}_2\text{Ru}_3\text{Rh}_2(\text{CO})_{12}(\text{PPh}_3)_2$ to the cluster $[\text{Ru}_3\text{RhH}_2(\text{CO})_{11}(\text{PPh}_3)]^-$ [6]. This cluster corresponds to our anionic starting material that the apical PPh_3 ligand has replaced the carbonyl ligand present in our complex. Compound **2** is also formed, probably as a decomposition product, in the reaction between $\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}$ and CuPPh_3 [9].

The arrangement of the metal atoms in (**1**) (Fig. 1), as in (**2**) (Fig. 2), is trigonal bipyramidal, as usually observed in $72e^-$ clusters. The main difference between the structures is in the number and orientation of the phosphine and carbonyl ligands.

The two Rh atoms are in apical positions and the three Ru atoms form a trigonal plane. The nature of the coordination sphere of the rhodium atoms is confirmed by the ^{31}P NMR spectra, as described below. In (**1**), one terminal carbonyl ligand of the apical rhodium atom is replaced by a phosphine ligand. In (**2**), one

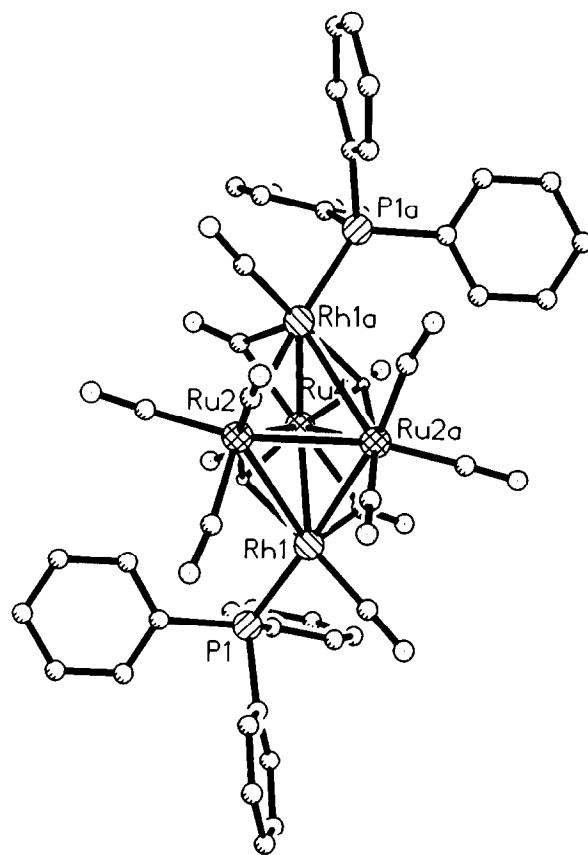


Fig. 2. The molecular structure of (**2**) [6].

terminal CO ligand of each apical rhodium atom is replaced by a phosphine ligand.

The arrangement of the metals differs from that in previously known pentanuclear Ru–Rh clusters, such as $[\text{RuRh}_4(\text{CO})_{15}]^{2-}$, in which the Ru atom occupies an apical position [2]. Also, in $\text{Ru}_3\text{Rh}_2(\mu_4\text{-PPh})(\text{CO})_{13}(\text{PEt}_3)$, where the metal framework is based on a pentanuclear square-pyramid, one of the ruthenium atoms is in the apical position [5].

Two independent molecules A and B are present in the asymmetric unit of (**1**). Atomic coordinates and selected bond lengths and angles in molecules A and B of $\text{H}_2\text{Ru}_3\text{Rh}_2(\text{CO})_{13}(\text{PPh}_3)$ (**1**) are listed in Tables 1 and 2.

Complex (**1**) contains three ($\mu\text{-CO}$) bridges, all in Ru–Rh edges. Two of the carbonyl bridges are slightly unsymmetrical. The bond lengths Rh(5)–C(45), Ru(4)–C(45), Rh(1)–C(14) and Ru(4)–C(14) are 2.034(16) Å, 2.092(13) Å, 1.992(14) Å and 2.113(14) Å in molecule A and 2.041(12) Å, 2.120(13) Å, 2.016(17) Å and 2.087(14) Å in molecule B. The carbonyl ligand CO(32) semi-bridges the Ru(3)–Rh(5) edge, and the bond lengths Rh(5)–C(32) and Ru(3)–C(32) are 2.514(16) Å and 1.935(18) Å in molecule A and 2.496(14) Å and 1.965(18) Å in molecule B. The formal electron deficiency of the Ru(3) atom accounts well for the ob-

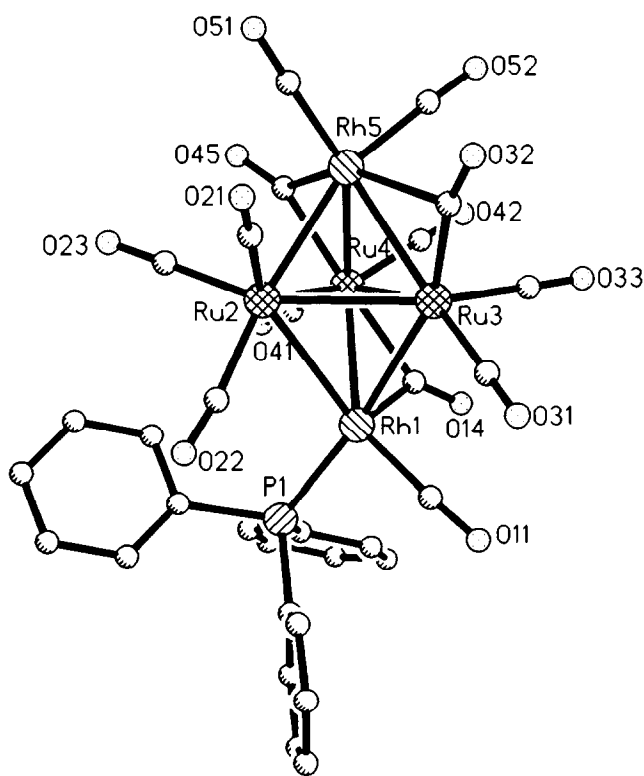


Fig. 1. The molecular structure and numbering scheme of (**1**).

Table 1
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^{-3}$) for (1)

Atom	x	y	z	U_{eq}
Rh(1)	6238(1)	4055(1)	-2997(1)	44(1)
Ru(2)	4307(1)	4634(1)	-3016(1)	45(1)
Ru(3)	4955(1)	2983(1)	-3137(1)	47(1)
Ru(4)	4699(1)	3282(1)	-1470(1)	49(1)
Rh(5)	3170(1)	3120(1)	-1997(1)	52(1)
P(1)	7193(2)	5117(2)	-2917(2)	44(1)
O(11)	7881(8)	3569(8)	-4302(9)	112(7)
O(14)	6667(8)	2507(7)	-1735(8)	108(6)
O(21)	2941(8)	4807(7)	-4043(8)	99(7)
O(22)	5611(8)	6206(7)	-4415(8)	106(6)
O(23)	3156(8)	5717(7)	-1934(8)	100(7)
O(31)	6268(9)	3113(7)	-4980(7)	106(6)
O(32)	3339(7)	2433(8)	-3643(7)	97(6)
O(33)	5398(10)	1132(7)	-2297(9)	118(8)
O(41)	5053(12)	3952(8)	-122(8)	152(10)
O(42)	4404(8)	1425(7)	-224(7)	101(6)
O(45)	2717(8)	3754(6)	-468(6)	86(5)
O(51)	1223(9)	3662(9)	-2061(10)	135(9)
O(52)	2557(10)	1199(7)	-987(7)	110(7)
C(11)	7268(10)	3767(8)	-3809(10)	68(7)
C(14)	6142(10)	3011(9)	-1943(10)	76(7)
C(21)	3432(10)	4728(9)	-3636(9)	65(7)
C(22)	5193(11)	5601(10)	-3869(9)	75(7)
C(23)	3572(10)	5311(9)	-2334(9)	64(7)
C(31)	5813(10)	3050(8)	-4291(10)	67(7)
C(32)	3831(11)	2663(9)	-3338(9)	70(7)
C(33)	5242(10)	1818(10)	-2611(10)	72(7)
C(41)	4917(13)	3706(10)	-630(9)	89(9)
C(42)	4511(10)	2119(9)	-685(9)	66(6)
C(45)	3257(9)	3517(8)	-1009(8)	55(6)
C(51)	1959(11)	3477(11)	-2060(11)	89(9)
C(52)	2755(11)	1906(10)	-1365(9)	72(7)
C(61)	8153(5)	5727(5)	-4724(5)	65(4)
C(62)	8936	6074	-5491	68(4)
C(63)	9811	6270	-5431	73(4)
C(64)	9904	6118	-4604	78(4)
C(65)	9121	5771	-3837	64(4)
C(66)	8246	5575	-3898	47(3)
C(71)	7608(6)	5135(4)	-1397(5)	55(3)
C(72)	8051	4821	-757	77(4)
C(73)	8585	4095	-735	70(4)
C(74)	8675	3684	-1354	73(4)
C(75)	8232	3998	-1994	66(4)
C(76)	7699	4724	-2015	48(3)
C(81)	5738(5)	5981(4)	-2074(5)	57(3)
C(82)	5251	6703	-1959	60(3)
C(83)	5614	7534	-2546	68(4)
C(84)	6465	7643	-3248	78(4)
C(85)	6953	6921	-3364	68(4)
C(86)	6589	6090	-2777	47(3)
Rh(1')	-1148(1)	312(1)	3026(1)	42(1)
Ru(2')	673(1)	942(1)	3038(1)	44(1)
Ru(3')	309(1)	-797(1)	3125(1)	47(1)
Ru(4')	422(1)	580(1)	1482(1)	46(1)
Rh(5')	2014(1)	192(1)	1994(1)	51(1)
P(1')	-2208(2)	1421(2)	2921(2)	46(1)
O(11')	-2707(8)	-1038(7)	4295(8)	99(6)
O(14')	-1390(8)	-523(7)	1807(7)	95(6)
O(21')	2007(8)	491(7)	4110(7)	92(6)
O(22')	-814(8)	1481(11)	4484(8)	135(9)
O(23')	1591(10)	2785(6)	2096(9)	125(8)
O(31')	-935(8)	-1863(7)	4977(6)	91(5)

Table 1 (continued)

Atom	x	y	z	U_{eq}
O(32')	2064(8)	-1553(8)	3593(8)	103(6)
O(33')	103(11)	-2169(7)	2347(8)	135(9)
O(41')	-5(10)	2037(8)	19(8)	115(8)
O(42')	1027(8)	-510(7)	298(7)	93(6)
O(45')	2222(7)	1870(6)	526(6)	82(5)
O(51')	3832(9)	793(9)	2163(10)	124(9)
O(52')	3208(10)	-666(8)	701(8)	125(8)
C(11')	-2116(10)	-538(10)	3832(9)	64(7)
C(14')	-918(10)	-95(9)	1984(9)	65(7)
C(21')	1520(10)	652(8)	3682(9)	61(7)
C(22')	-317(11)	1254(12)	3928(10)	85(9)
C(23')	1239(11)	2104(8)	2427(9)	65(7)
C(31')	-477(11)	-1467(8)	4293(9)	65(7)
C(32')	1527(12)	-1175(11)	3296(10)	81(8)
C(33')	189(12)	-1645(10)	2629(10)	82(8)
C(41')	112(11)	1479(9)	581(9)	66(7)
C(42')	811(10)	-82(9)	737(9)	67(7)
C(45')	1783(9)	1246(8)	1041(8)	54(6)
C(51')	3147(11)	576(10)	2088(9)	75(8)
C(52')	2738(11)	-385(9)	1206(10)	75(8)
C(61')	-3163(5)	825(5)	4747(6)	65(4)
C(62')	-3948	705	5512	76(4)
C(63')	-4811	1045	5450	71(4)
C(64')	-4888	1505	4624	82(4)
C(65')	-4104	1624	3859	66(4)
C(66')	-3241	1285	3921	49(3)
C(71')	-2746(6)	2327(4)	1423(5)	59(3)
C(72')	-3171	2369	791	74(4)
C(73')	-3581	1615	796	78(4)
C(74')	-3565	818	1433	86(5)
C(75')	-3140	776	2065	65(4)
C(76')	-2730	1530	2060	50(3)
C(81')	-1918(5)	2927(5)	3299(4)	67(4)
C(82')	-1455	3725	3121	82(4)
C(83')	-727	4102	2318	83(4)
C(84')	-462	3681	1693	81(4)
C(85')	-924	2883	1872	58(3)
C(86')	-1652	2506	2675	50(3)

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

served differences in the bond lengths for CO(32). The Ru(3) and Ru(4) atoms each have two terminal carbonyls, while Ru(2) bears three terminal carbonyl ligands, this being the preferred coordination to the Ru atom in the cluster compounds of Ru, Rh and Co. In the structure of (2), the μ -CO bridges are slightly unsymmetrical. Bond lengths to the formally electron deficient Rh atoms are 2.005(5) Å and to the Ru atoms 2.146(5) Å, corresponding to the bond lengths around the phosphine-substituted Rh atom in (1). In (2), as in (1), one carbonyl ligand semibridges the Ru–Rh edge, and the M–C distances are Ru–C 1.903(5) Å and Rh \cdots C 2.875(6) Å.

The metal framework is slightly distorted in (1). The bond lengths Rh(1)–Ru(2) and Ru(2)–Ru(4), which are 2.988(2) Å and 3.026(2) Å in molecule A and 2.943(2) Å and 3.030(2) Å in molecule B, are especially long. The length of the third M–M bond of the Rh(1)–

Table 2
 Selected geometric parameters (Å, °) for (1)

Rh(1)–Ru(2)	2.988(2)	Rh(1)–Ru(3)	2.760(2)
Rh(1)–Ru(4)	2.784(1)	Rh(1)–P(1)	2.355(4)
Rh(1)–C(11)	1.859(14)	Rh(1)–C(14)	1.992(14)
Ru(2)–Ru(3)	2.878(2)	Ru(2)–Ru(4)	3.026(2)
Ru(2)–Rh(5)	2.754(2)	Ru(2)–C(21)	1.894(18)
Ru(2)–C(22)	1.935(13)	Ru(2)–C(23)	1.918(15)
Ru(3)–Ru(4)	2.933(2)	Ru(3)–Rh(5)	2.776(2)
Ru(3)–C(31)	1.928(15)	Ru(3)–C(32)	1.935(18)
Ru(3)–C(33)	1.913(15)	Ru(4)–Rh(5)	2.750(2)
Ru(4)–C(14)	2.113(14)	Ru(4)–C(41)	1.899(20)
Ru(4)–C(42)	1.895(13)	Ru(4)–C(45)	2.092(13)
Rh(5)–C(32)	2.514(16)	Rh(5)–C(45)	2.034(16)
Rh(5)–C(51)	1.891(18)	Rh(5)–C(52)	1.931(15)
Rh(1')–Ru(2')	2.943(2)	Rh(1')–Ru(3')	2.774(2)
Rh(1')–Ru(4')	2.800(1)	Rh(1')–P(1')	2.350(3)
Rh(1')–C(11')	1.870(12)	Rh(1')–C(14')	2.016(17)
Ru(2')–Ru(3')	2.864(2)	Ru(2')–Ru(4')	3.030(2)
Ru(2')–Rh(5')	2.747(2)	Ru(2')–C(21')	1.871(17)
Ru(2')–C(22')	1.925(16)	Ru(2')–C(23')	1.913(12)
Ru(3')–Ru(4')	2.905(2)	Ru(3')–Rh(5')	2.797(1)
Ru(3')–C(31')	1.911(12)	Ru(3')–C(32')	1.965(18)
Ru(3')–C(33')	1.889(19)	Ru(4')–Rh(5')	2.755(2)
Ru(4')–C(14')	2.087(14)	Ru(4')–C(41')	1.903(14)
Ru(4')–C(42')	1.869(16)	Ru(4')–C(45')	2.120(13)
Rh(5')–C(32')	2.496(14)	Rh(5')–C(45')	2.041(12)
Rh(5')–C(51')	1.893(18)	Rh(5')–C(52')	1.910(17)
Ru(2)–Rh(1)–Ru(3)	59.9(1)	Ru(2)–Rh(1)–Ru(4)	63.1(1)
Ru(3)–Rh(1)–Ru(4)	63.9(1)	Ru(2)–Rh(1)–P(1)	112.6(1)
Ru(3)–Rh(1)–P(1)	172.3(1)	Ru(4)–Rh(1)–P(1)	115.2(1)
Ru(2)–Rh(1)–C(11)	133.4(6)	Ru(3)–Rh(1)–C(11)	92.8(5)
Ru(4)–Rh(1)–C(11)	140.9(4)	P(1)–Rh(1)–C(11)	91.9(5)
Ru(2)–Rh(1)–C(14)	111.2(4)	Ru(3)–Rh(1)–C(14)	79.7(5)
Ru(4)–Rh(1)–C(14)	49.2(4)	P(1)–Rh(1)–C(14)	105.6(6)
C(11)–Rh(1)–C(14)	98.3(6)	Rh(1)–Ru(2)–Ru(3)	56.1(1)
Rh(1)–Ru(2)–Ru(4)	55.1(1)	Ru(3)–Ru(2)–Ru(4)	59.5(1)
Rh(1)–Ru(2)–Rh(5)	101.5(1)	Ru(3)–Ru(2)–Rh(5)	59.0(1)
Ru(4)–Ru(2)–Rh(5)	56.6(1)	Rh(1)–Ru(2)–C(21)	142.6(4)
Ru(3)–Ru(2)–C(21)	96.3(5)	Ru(4)–Ru(2)–C(21)	136.2(4)
Rh(5)–Ru(2)–C(21)	79.9(4)	Rh(1)–Ru(2)–C(22)	75.0(5)
Ru(3)–Ru(2)–C(22)	112.7(5)	Ru(4)–Ru(2)–C(22)	124.6(5)
Rh(5)–Ru(2)–C(22)	170.6(5)	C(21)–Ru(2)–C(22)	97.6(6)
Rh(1)–Ru(2)–C(23)	124.4(5)	Ru(3)–Ru(2)–C(23)	150.1(4)
Ru(4)–Ru(2)–C(23)	95.1(4)	Rh(5)–Ru(2)–C(23)	94.7(4)
C(21)–Ru(2)–C(23)	92.4(7)	C(22)–Ru(2)–C(23)	94.4(6)
Rh(1)–Ru(3)–Ru(2)	64.0(1)	Rh(1)–Ru(3)–Ru(4)	58.4(1)
Ru(2)–Ru(3)–Ru(4)	62.8(1)	Rh(1)–Ru(3)–Rh(5)	106.9(1)
Ru(2)–Ru(3)–Rh(5)	58.3(1)	Ru(4)–Ru(3)–Rh(5)	57.5(1)
Rh(1)–Ru(3)–C(31)	90.0(5)	Ru(2)–Ru(3)–C(31)	113.8(4)
Ru(4)–Ru(3)–C(31)	147.2(5)	Rh(5)–Ru(3)–C(31)	151.8(5)
Rh(1)–Ru(3)–C(32)	157.4(4)	Ru(2)–Ru(3)–C(32)	94.1(4)
Ru(4)–Ru(3)–C(32)	118.0(4)	Rh(5)–Ru(3)–C(32)	61.5(4)
C(31)–Ru(3)–C(32)	94.5(7)	Rh(1)–Ru(3)–C(33)	106.4(6)
Ru(2)–Ru(3)–C(33)	151.3(5)	Ru(4)–Ru(3)–C(33)	88.9(6)
Rh(5)–Ru(3)–C(33)	103.8(4)	C(31)–Ru(3)–C(33)	92.3(6)
C(32)–Ru(3)–C(33)	95.6(7)	Rh(1)–Ru(4)–Ru(2)	61.7(1)
Rh(1)–Ru(4)–Ru(3)	57.7(1)	Ru(2)–Ru(4)–Ru(3)	57.7(1)
Rh(1)–Ru(4)–Rh(5)	107.0(1)	Ru(2)–Ru(4)–Rh(5)	56.7(1)
Ru(3)–Ru(4)–Rh(5)	58.4(1)	Rh(1)–Ru(4)–C(14)	45.5(4)
Ru(2)–Ru(4)–C(14)	106.3(4)	Ru(3)–Ru(4)–C(14)	73.9(5)
Rh(5)–Ru(4)–C(14)	131.3(5)	Rh(1)–Ru(4)–C(41)	103.2(4)
Ru(2)–Ru(4)–C(41)	115.7(4)	Ru(3)–Ru(4)–C(41)	160.9(4)
Rh(5)–Ru(4)–C(41)	136.0(6)	C(14)–Ru(4)–C(41)	92.7(8)
Rh(1)–Ru(4)–C(42)	128.4(4)	Ru(2)–Ru(4)–C(42)	148.7(5)
Ru(3)–Ru(4)–C(42)	100.2(5)	Rh(5)–Ru(4)–C(42)	93.6(5)

Table 2 (continued)

C(14)–Ru(4)–C(42)	85.4(5)	C(41)–Ru(4)–C(42)	92.0(7)
Rh(1)–Ru(4)–C(45)	135.0(3)	Ru(2)–Ru(4)–C(45)	73.9(3)
Ru(3)–Ru(4)–C(45)	105.0(4)	Rh(5)–Ru(4)–C(45)	47.3(4)
C(14)–Ru(4)–C(45)	178.3(7)	C(41)–Ru(4)–C(45)	88.8(7)
C(42)–Ru(4)–C(45)	93.6(5)	Ru(2)–Rh(5)–Ru(3)	62.7(1)
Ru(2)–Rh(5)–Ru(4)	66.7(1)	Ru(3)–Rh(5)–Ru(4)	64.1(1)
Ru(2)–Rh(5)–C(32)	85.5(3)	Ru(3)–Rh(5)–C(32)	42.5(4)
Ru(4)–Rh(5)–C(32)	105.9(4)	Ru(2)–Rh(5)–C(45)	81.3(3)
Ru(3)–Rh(5)–C(45)	112.4(4)	Ru(4)–Rh(5)–C(45)	49.1(4)
C(32)–Rh(5)–C(45)	154.9(5)	Ru(2)–Rh(5)–C(51)	101.3(4)
Ru(3)–Rh(5)–C(51)	138.4(5)	Ru(4)–Rh(5)–C(51)	148.3(6)
C(32)–Rh(5)–C(51)	102.0(7)	C(45)–Rh(5)–C(51)	101.5(7)
Ru(2)–Rh(5)–C(52)	162.1(4)	Ru(3)–Rh(5)–C(52)	100.5(4)
Ru(4)–Rh(5)–C(52)	101.3(5)	C(32)–Rh(5)–C(52)	85.2(6)
C(45)–Rh(5)–C(52)	101.2(6)	C(51)–Rh(5)–C(52)	95.6(7)
Rh(1)–P(1)–C(66)	115.0(4)	Rh(1)–P(1)–C(76)	114.1(3)
Rh(1)–P(1)–C(85)	115.1(3)	Rh(1)–C(14)–Ru(4)	85.4(6)
Ru(3)–C(32)–Rh(5)	76.0(6)	Ru(4)–C(45)–Rh(5)	83.6(5)
Ru(2')–Rh(1')–Ru(3')	60.0(1)	Ru(2')–Rh(1')–Ru(4')	63.6(1)
Ru(3')–Rh(1')–Ru(4')	62.8(1)	Ru(2')–Rh(1')–P(1')	110.9(1)
Ru(3')–Rh(1')–P(1')	170.9(1)	Ru(4')–Rh(1')–P(1')	113.7(1)
Ru(2')–Rh(1')–C(11')	134.5(5)	Ru(3')–Rh(1')–C(11')	94.3(5)
Ru(4')–Rh(1')–C(11')	140.4(5)	P(1')–Rh(1')–C(11')	93.1(5)
Ru(2')–Rh(1')–C(14')	110.0(4)	Ru(3')–Rh(1')–C(14')	75.9(4)
Ru(4')–Rh(1')–C(14')	48.0(4)	P(1')–Rh(1')–C(14')	108.4(4)
C(11')–Rh(1')–C(14')	97.2(7)	Rh(1')–Ru(2')–Ru(3')	57.1(1)
Rh(1')–Ru(2')–Ru(4')	55.9(1)	Ru(3')–Ru(2')–Ru(4')	59.0(1)
Rh(1')–Ru(2')–Rh(5')	103.3(1)	Ru(3')–Ru(2')–Rh(5')	59.8(1)
Ru(4')–Ru(2')–Rh(5')	56.7(1)	Rh(1')–Ru(2')–C(21')	141.0(4)
Ru(3')–Ru(2')–C(21')	95.4(4)	Ru(4')–Ru(2')–C(21')	136.6(5)
Rh(5')–Ru(2')–C(21')	80.5(5)	Rh(1')–Ru(2')–C(22')	73.9(6)
Ru(3')–Ru(2')–C(22')	111.4(5)	Ru(4')–Ru(2')–C(22')	125.5(6)
Rh(5')–Ru(2')–C(22')	169.4(5)	C(21')–Ru(2')–C(22')	95.3(7)
Rh(1')–Rh(2')–C(23')	124.9(5)	Ru(3')–Ru(2')–C(23')	152.6(5)
Ru(4')–Ru(2')–C(23')	98.1(5)	Rh(5')–Ru(2')–C(23')	96.1(4)
C(21')–Ru(2')–C(23')	92.6(6)	C(22')–Ru(2')–C(23')	93.8(7)
Rh(1')–Ru(3')–Ru(2')	62.9(1)	Rh(1')–Ru(3')–Ru(4')	59.0(1)
Ru(2')–Ru(3')–Ru(4')	63.4(1)	Rh(1')–Ru(3')–Rh(5')	106.5(1)
Ru(2')–Ru(3')–Rh(5')	58.0(1)	Ru(4')–Ru(3')–Rh(5')	57.7(1)
Rh(1')–Ru(3')–C(31')	88.5(4)	Ru(2')–Ru(3')–C(31')	110.0(5)
Ru(4')–Ru(3')–C(31')	146.8(5)	Rh(5')–Ru(3')–C(31')	149.4(5)
Rh(1')–Ru(3')–C(32')	155.9(6)	Ru(2')–Ru(3')–C(32')	93.6(2)
Ru(4')–Ru(3')–C(32')	116.8(4)	Rh(5')–Ru(3')–C(32')	60.2(4)
C(31')–Ru(3')–C(32')	95.5(6)	Rh(1')–Ru(3')–C(33')	109.0(5)
Ru(2')–Ru(3')–C(33')	153.6(4)	Ru(4')–Ru(3')–C(33')	90.6(4)
Rh(5')–Ru(3')–C(33')	105.3(4)	C(31')–Ru(3')–C(33')	94.3(6)
C(32')–Ru(3')–C(33')	94.4(8)	Rh(1')–Ru(4')–Ru(2')	60.5(1)
Rh(1')–Ru(4')–Ru(3')	58.2(1)	Ru(2')–Ru(4')–Ru(3')	57.7(1)
Rh(1')–Ru(4')–Rh(5')	106.9(1)	Ru(2')–Ru(4')–Rh(5')	56.5(1)
Ru(3')–Ru(4')–Rh(5')	59.2(1)	Rh(1')–Ru(4')–C(14')	45.9(4)
Ru(2')–Ru(4')–C(14')	104.9(4)	Ru(3')–Ru(4')–C(14')	71.9(4)
Rh(5')–Ru(4')–C(14')	130.3(4)	Rh(1')–Ru(4')–C(41')	105.8(4)
Ru(2')–Ru(4')–C(41')	120.5(5)	Ru(3')–Ru(4')–C(41')	163.4(4)
Rh(5')–Ru(4')–C(41')	135.7(5)	C(14')–Ru(4')–C(41')	94.0(6)
Rh(1')–Ru(4')–C(42')	130.5(4)	Ru(2')–Ru(4')–C(42')	144.9(5)
Ru(3')–Ru(4')–C(42')	97.4(4)	Rh(5')–Ru(4')–C(42')	90.4(5)
C(14')–Ru(4')–C(42')	87.5(6)	C(41')–Ru(4')–C(42')	90.4(7)
Rh(1')–Ru(4')–C(45')	131.6(4)	Ru(2')–Ru(4')–C(45')	72.3(4)
Ru(3')–Ru(4')–C(45')	105.4(3)	Rh(5')–Ru(4')–C(45')	47.3(3)
C(14')–Ru(4')–C(45')	177.0(6)	C(41')–Ru(4')–C(45')	88.4(6)
C(42')–Ru(4')–C(45')	94.3(6)	Ru(2')–Rh(5')–Ru(3')	62.2(1)
Ru(2')–Rh(5')–Ru(4')	66.8(1)	Ru(3')–Rh(5')–Ru(4')	63.1(1)
Ru(2')–Rh(5')–C(32')	85.8(4)	Ru(3')–Rh(5')–C(32')	43.1(4)

Table 2 (continued)

Ru(4')–Rh(5')–C(32')	105.3(4)	Ru(2')–Rh(5')–C(45')	80.0(4)
Ru(3')–Rh(5')–C(45')	111.6(4)	Ru(4')–Rh(5')–C(45')	49.8(4)
C(32')–Rh(5')–C(45')	154.7(6)	Ru(2')–Rh(5')–C(51')	100.5(5)
Ru(3')–Rh(5')–C(51')	137.6(4)	Ru(4')–Rh(5')–C(51')	149.3(5)
C(32')–Rh(5')–C(51')	101.3(6)	C(45')–Rh(5')–C(51')	101.8(6)
Ru(2')–Rh(5')–C(52')	168.6(6)	Ru(3')–Rh(5')–C(52')	110.2(5)
Ru(4')–Rh(5')–C(52')	102.4(6)	C(32')–Rh(5')–C(52')	93.7(6)
C(45')–Rh(5')–C(52')	96.1(6)	C(51')–Rh(5')–C(52')	90.7(8)
Rh(1')–P(1')–C(66')	15.5(3)	Rh(1')–P(1')–C(76')	112.4(3)
Rh(1')–P(1')–C(86')	113.8(3)	Rh(1')–C(14')–Ru(4')	86.1(7)
Ru(3')–C(32')–Rh(5')	76.6(5)	Ru(4')–C(45')–Rh(5')	82.9(4)

Ru(2)–Ru(4) face is 2.784(1)–2.800(1) Å in molecules A and B. These values agree well with those found in the hydride-bridged face in (2), for which the corresponding values are 2.939(1) Å, 3.045(1) Å and 2.798(1) Å. In the structure of (2) the two hydrides were located from the electron density map; they are bonded to different rhodium atoms on opposite Ru₂Rh faces. Unfortunately direct location of the hydride ligands in (1) was not possible, but the ¹H NMR spectrum indicated that they were bonded to the Rh atom.

The bond lengths and angles in (1) suggest that another hydride ligand is located in a similar manner to that in (2), the Rh(1)–Ru(2)–Ru(4) face being hydride bridged. A face-bridging hydride ligand repulses the carbonyl ligands next to it, and typically M–M–C angles are larger in these faces; for example, a mean of 118° in HRuCo₃(CO)₁₂ [10].

Angles Ru(2)–Ru(4)–C(41) and Ru(4)–Ru(2)–C(23) are 115.7(4)° and 95.1(4)° in molecule A and 120.5(5)° and 98.1(5)° in molecule B. The corresponding angles in the hydride-bridged face of (2) are 112.7° and 103.7° [11].

In (2) another hydride ligand is located on the face that in (1) corresponds to the face Ru(3)–Ru(4)–Rh(5). In (2) the carbonyl ligands are repulsed by the hydride ligand and Ru–Ru–C bond angles are 103.7° and 112.7°. In (1) the corresponding bond angles Ru(4)–Ru(3)–C(33) and Ru(3)–Ru(4)–C(42) are only 88.9(6)° and 100.2(5)° in molecule A and 90.6(4)° and 97.4(4)° in molecule B. The angles Ru(2)–Ru(3)–C(31) and Ru(3)–Ru(2)–C(22) in the Rh(1)–Ru(2)–Ru(3) face are 113.8(4)° and 112.7(5)° in molecule A, and 110.0(5)° and 111.4(5)° in molecule B. Bond angles are larger than in (2), in which this face is not hydride-bridged and the Ru–Ru–C angles are 84.7° and 103.7°. These values suggest that in (1) the Rh(1)–Ru(2)–Ru(3) face is a probable location for another hydride ligand. Furthermore space-filling representations of (1) show that the hydride ligands have most space in the Rh(1)–Ru(2)–Ru(4) and Rh(1)–Ru(2)–Ru(3) faces.

The ³¹P NMR spectrum of (1) gives a doublet signal at 21.2 ppm, with coupling constant ¹J(Rh–P) = 138.6 Hz, in agreement with the crystal structure. In the ¹H

NMR spectrum the doublet at –19.4 ppm, with coupling constant 9.8 Hz, indicates that the two hydrides are equivalent in the solution state and are coordinated to the Rh atom. After separation of the first fraction on a silica gel column, additional signals are observed in the ³¹P NMR spectrum at 17.1 d [¹J(Rh–P) = 132.2 Hz] and in the ¹H NMR spectrum at –19.3 d of t [¹J(Rh–H) = 15.0 Hz, ²J(P–H) = 3.3 Hz]. These additional signals are assigned to the disubstituted compound, which can be separated from the monosubstituted compound by thin layer chromatography.

3. Experimental details

3.1. General

All manipulations except chromatographic separations were carried out under N₂ with deoxygenated solvents. FT-IR spectra were recorded on a Galaxy 6020 spectrometer. The ¹H NMR spectra were recorded on a Bruker AM-250 spectrometer at 273 K in CDCl₃ with Me₄Si as reference, and the ³¹P NMR spectra at 294 K in CDCl₃ with concentrated aqueous H₃PO₄ as external reference. Crystals were grown by slow evaporation of the solvent from a saturated hexane–CH₂Cl₂ solution.

3.2. Synthesis

Reaction of [N(PPh₃)₂][H₂Ru₃Rh(CO)₁₂] (193 mg, 0.150 mmol) with PPh₃ (55 mg, 0.210 mmol) in THF (30 ml) (18 h) at ambient temperature, gave a mixture of cluster compounds which were separated by chromatography on silica. Elution with a hexane–CH₂Cl₂ 1:1.4 mixture from the silica column gave a red fraction (60 mg) of phosphine-substituted compounds, which crystallized as H₂Ru₃Rh₂(CO)₁₃(PPh₃). Further elution with CH₂Cl₂ gave a red fraction containing the starting material (66 mg, 0.051 mmol). According to the ³¹P NMR spectrum of the first fraction, the amount of (1) present was 36% and the amount of (2) was 64%. Further separation of this fraction by thin layer chro-

Table 3
Crystal data and collection parameters for (1)

Formula	C ₃₁ H ₁₇ O ₁₃ PRu ₃ Rh ₂
FW	1137.5
Colour; habit	Brown block
Crystal size (mm)	0.45 × 0.45 × 0.45
Crystal system	Triclinic
Space group	<i>P</i> - 1
<i>a</i> (Å)	14.845(3)
<i>b</i> (Å)	16.361(5)
<i>c</i> (Å)	16.992(5)
α (°)	70.58(2)
β (°)	70.94(2)
γ (°)	87.52(2)
<i>V</i> / Å ³	3669(2)
<i>Z</i>	2
Calc. density (g cm ⁻³)	2.056
μ (mm ⁻¹)	2.154
<i>F</i> (000)	2168
No. centering reflections	25
Centering 2θ	12–24
Scan range (2θ)	4–55
Scan speed (° min ⁻¹)	2.49–29.30
<i>h, k, l</i> range	19, ± 21, ± 22
Reflections collected	17139
No. of unique reflections	16789
Obs. data [<i>F</i> > 3 σ (<i>F</i>)]	7007
No. of parameters	649
<i>R</i>	0.0455
<i>R'</i>	0.0435
<i>G</i> (weight)	0.0005
Goodness of fit	1.15
Largest diff. peak (e Å ⁻³)	0.81
Largest diff. hole (e Å ⁻³)	-1.27

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

matography (hexane-CH₂Cl₂ 1:1 mixture) gave a fraction crystallizing as H₂Ru₃Rh₂(CO)₁₂(PPh₃)₂.

3.3. Spectroscopic data for complexes (1) and (2)

¹H NMR (ppm): -19.4 d [¹*J*(Rh-H) = 9.8 Hz, H₂Ru₃Rh₂(CO)₁₃(PPh₃)] and -19.3 d of t [¹*J*(Rh-H) = 15.0 Hz, ²*J*(P-H) = 3.3 Hz, H₂Ru₃Rh₂(CO)₁₂(PPh₃)₂].
³¹P NMR (ppm): 21.2 d [¹*J*(Rh-P) = 138.6 Hz, H₂Ru₃Rh₂(CO)₁₃(PPh₃)] and 17.1 d [¹*J*(Rh-P) = 132.2 Hz, H₂Ru₃Rh₂(CO)₁₂(PPh₃)₂].

IR (cm⁻¹): 2086m, 2061s, 2039vs, 2021s, 1850w, CH₂Cl₂ [mixture of H₂Ru₃Rh₂(CO)₁₃(PPh₃) and H₂Ru₃Rh₂(CO)₁₂(PPh₃)₂].

3.4. Structure determination

Crystal data and details of data collection are summarized in Table 3. Diffraction data were recorded on a Nicolet R3m diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). ω scan mode with scan speed 2.49–29.29° min⁻¹ was used. Intensities were corrected for Lorentz, polarization and background effects. No empirical absorption correction was applied.

The asymmetric unit of (1) contained two identical molecules. For both of these molecules, metal atoms were located by direct methods, and coordinates for non-metal atoms were determined from subsequent difference electron density calculations. All calculations were performed by use of the SHELXTL Plus [12] program package. All non-hydrogen atoms were refined anisotropically, except for the phenyl carbons, which were refined isotropically with the phenyl rings as rigid groups. Hydrogen atoms were placed in calculated positions (0.96 Å, *U* = 0.07 Å²) and were not refined.

Complete lists 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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