Reaction of $[H_2Ru_3Rh(CO)_{12}]^-$ cluster anion with $AuPPh_3Cl$ and structural characterization of $AuHRh_2Ru_3(CO)_{13}(PPh_3)_2$ by X-ray diffraction and ^{31}P and ^1H NMR spectroscopy

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Abstract

A novel hexanuclear cluster of Au, Ru and Rh was obtained by reaction of $[H_2Ru_3Rh(CO)_{12}]^-$ with $[AuPPh_3]^+$. The $AuHRh_2Ru_3(CO)_{13}(PPh_3)_2$ cluster was characterized by X-ray crystallography and ^{31}P and ^1H NMR spectroscopy. The molecule consist of a bicapped tetrahedral metal framework with the Rh atoms adjacent to each other and the Ru atoms forming a trigonal plane. The $AuPPh_3$ ligand is coordinated to the Rh_2Ru face, the μ_3-H ligand to a Ru_2Rh face and the other PPh_3 ligand to a rhodium atom.

Keywords: Gold; Ruthenium; Rhodium; Carbonyl; Cluster; Crystal structure

1. Introduction

Mixed-metal clusters of Ru, Rh and Co and their phosphine derivatives have been extensively studied. In particular the tetranuclear compounds have been well characterized [1]. Some pentanuclear clusters are also known, one of which we recently synthesized and characterized [2].

Gold phosphine derivatives of the mixed-metal clusters of Ru, Rh and Co are mainly based on a $Ru_{4-x}Co_x$ ($x = 1–3$) metal framework [3–8]. Of the clusters with a Ru–Rh–Au framework, $AuRuRh_3(CO)_{12}(PPh_3)$, $AuRuRh_3(CO)_{12}(PPh_3) \cdot \frac{1}{2}Ru_3(CO)_{12}$ and $AuHRu_3Rh(CO)_{10}(PPh_3)_2(\mu_3$-COMe) have been crystallographically characterized [9–11]. No gold phosphine derivatives containing a pentanuclear Ru–Rh metal framework were known before the present work.

Gold-containing mixed-metal clusters can generally be efficiently prepared by the reaction of a preformed cluster anion with an appropriate aurating agent, such as the halogeno complex $AuPPh_3Cl$ or the cation $[AuPPh_3]^+$. Rearrangement of the metal framework is rarely observed when one hydride ligand is replaced by a gold phosphine ligand, and so the structures of complexes containing one Au atom often can be predicted from the geometry of the corresponding hydrido derivative.

In the present work we describe a hexanuclear mixed-metal cluster of Ru, Rh and Au. This is the cluster $AuHRh_2Ru_3(CO)_{13}(PPh_3)_2$ (1), formed in the reaction of the mixed-metal cluster anion $[H_2Ru_3Rh-(CO)_{12}]^-$ with the cation $[AuPPh_3]^+$, and its characterization by ^1H and ^{31}P NMR spectroscopy and single crystal X-ray diffraction.

2. Results and discussion

We previously reported the synthesis and structural characterization of the mixed-metal cluster anion $[H_2Ru_3Rh(CO)_{12}]^-$ [12] and its reaction with PPh_3 to yield $H_2Ru_3Rh_2(CO)_{13}(PPh_3)$ and $H_2Ru_3Rh_2(CO)_{12}-(PPh_3)_2$ [2]. In the reaction with PPh_3 the originally tetranuclear metal framework was converted into a pentanuclear framework, the number of metal atoms being increased by one Rh atom.

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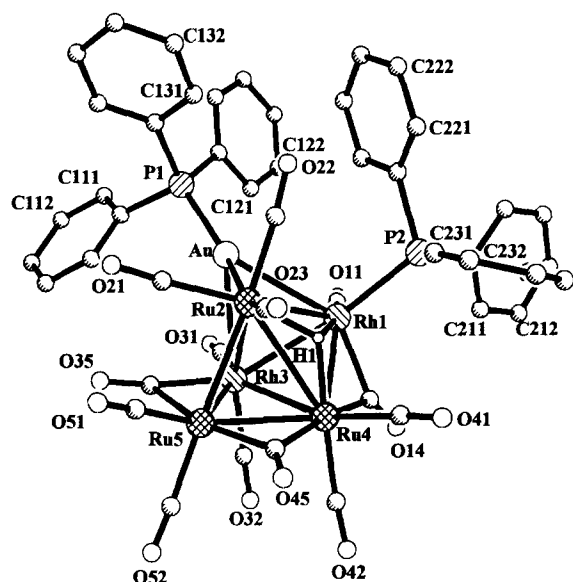
Fig. 1. The molecular structure of $AuHRh_2Ru_3(CO)_{13}(PPh_3)_2$ (1).

The novel hexanuclear cluster now reported was made by a reaction between the $[H_2Ru_3Rh(CO)_{12}]^-$ anion and $[AuPPh_3]^+$ cation. The product was shown by an X-ray diffraction study and ^1H and ^{31}P NMR spectroscopy to be $AuHRh_2Ru_3(CO)_{13}(PPh_3)_2$ (1), in which one hydride ligand of the original anion has been replaced by a gold phosphine ligand (Fig. 1). In this, as in the earlier structure [2] there is one more Rh atom than in the starting structure.

Atomic coordinates and selected geometric parameters for 1 are given in Tables 1 and 2 respectively.

In 1, the originally tetranuclear Ru_3Rh metal framework has been converted into a bicapped tetrahedral $AuRh_2Ru_3$ metal core, in which the Rh(1) atom caps the Ru(2)–Ru(4)–Rh(3) face of the tetrahedral $[H_2Ru_3Rh(CO)_{12}]^-$ precursor. The Ru(2)–Rh(3)–Rh(1) and Ru(2)–Ru(4)–Rh(1) faces so formed are further capped by the $AuPPh_3$ ligand and the μ_3-H ligand. The μ_3-H ligand was located from the electron density map. The other PPh_3 ligand, generated by decomposition of $AuPPh_3$, is coordinated to the Rh(1) atom. Correspondingly in $H_2Ru_3Rh_2(CO)_{13}(PPh_3)$ and $H_2Ru_3Rh_2$-$(CO)_{12}(PPh_3)_2$ [2] the phosphine ligand is coordinated to an Rh atom and the hydride ligands to an Ru_2Rh face.

In 1 the Rh atoms are adjacent to each other. In $H_2Ru_3Rh_2(CO)_{13}(PPh_3)$ and $H_2Ru_3Rh_2(CO)_{12}(PPh_3)_2$, which were produced from the same anionic starting material as 1, they lie on opposite sides of the trigonal Ru_3 plane. The difference between the coordination of the Rh atoms in the structures of $H_2Ru_3Rh_2(CO)_{13}$-(PPh_3) and $H_2Ru_3Rh_2(CO)_{12}(PPh_3)_2$ on the one hand and $AuHRh_2Ru_3(CO)_{13}(PPh_3)_2$ (1) on the other hand probably arises from the preference of the $AuPPh_3$

Table 1
Atomic coordinates and equivalent isotropic displacement coefficients for 1

Atom	x ($\times 10^{-4}$)	y ($\times 10^{-4}$)	z ($\times 10^{-4}$)	U_{eq} ($\times 10^{-3}$ Å^2)
Au	2460(1)	31(1)	1587(1)	41(1)
Rh(1)	2598(1)	2147(1)	1337(1)	33(1)
Ru(2)	1032(1)	977(1)	1005(1)	34(1)
Rh(3)	1832(1)	1521(1)	2196(1)	37(1)
Ru(4)	1104(1)	3085(1)	1390(1)	38(1)
Ru(5)	152(1)	1683(1)	1786(1)	38(1)
P(1)	3167(3)	−1440(3)	1736(2)	44(2)
P(2)	3122(3)	2454(3)	493(2)	42(2)
C(11)	3654(10)	1920(12)	1774(7)	43(6)
O(11)	4292(7)	1836(10)	2065(6)	70(5)
C(14)	2367(11)	3455(14)	1630(8)	51(7)
O(14)	2749(7)	4109(9)	1874(7)	77(6)
C(21)	592(10)	−249(13)	1205(7)	48(7)
O(21)	300(9)	−985(10)	1275(6)	85(7)
C(22)	1586(11)	394(12)	452(8)	46(7)
O(22)	1768(8)	3(10)	66(6)	71(6)
C(23)	108(11)	1335(12)	405(8)	49(7)
O(23)	−421(8)	1508(11)	33(6)	80(6)
C(31)	2829(10)	971(12)	2670(7)	47(6)
O(31)	3356(7)	682(10)	2998(5)	72(5)
C(32)	1854(10)	2486(13)	2784(7)	47(6)
O(32)	1883(8)	3059(9)	3135(6)	74(6)
C(35)	1104(9)	574(12)	2456(7)	37(6)
O(35)	907(8)	−105(9)	2691(6)	61(5)
C(41)	891(10)	3941(13)	721(8)	51(7)
O(41)	683(10)	4419(11)	336(7)	97(7)
C(42)	951(11)	4118(14)	1892(9)	61(8)
O(42)	929(9)	4777(10)	2187(7)	90(7)
C(45)	−163(10)	2839(14)	1245(8)	52(7)
O(45)	−786(7)	3214(10)	1022(6)	68(5)
C(51)	−814(12)	857(16)	1538(8)	64(8)
O(51)	−1378(9)	423(12)	1389(7)	104(8)
C(52)	−184(12)	2184(16)	2463(8)	66(9)
O(52)	−392(9)	2449(14)	2856(7)	103(8)
C(111)	3737(6)	−2559(9)	2769(5)	65(5)
C(112)	3659	−2934	3308	88(7)
C(113)	2957	−2727	3519	68(6)
C(114)	2334	−2147	3192	75(6)
C(115)	2412	−1773	2654	76(6)
C(116)	3113	−1979	2442	42(4)
C(121)	4723(8)	−680(8)	2043(5)	70(6)
C(122)	5568	−640	2078	84(7)
C(123)	5953	−1379	1823	88(7)
C(124)	5493	−2159	1533	87(7)
C(125)	4648	−2199	1498	78(6)
C(126)	4263	−1459	1753	54(5)
C(131)	2618(8)	−2076(8)	619(6)	62(5)
C(132)	2265	−2743	185	80(6)
C(133)	2051	−3686	336	148(12)
C(134)	2190	−3962	921	235(20)
C(135)	2543	−3296	1356	147(12)
C(136)	2757	−2353	1204	53(5)
C(211)	4243(7)	3872(9)	1054(5)	68(6)
C(212)	4954	4443	1140	97(8)
C(213)	5513	4311	782	91(7)
C(214)	5359	3610	338	90(7)
C(215)	4647	3039	251	69(6)
C(216)	4089	3171	609	49(4)
C(221)	3150(6)	1088(8)	−437(4)	60(5)
C(222)	3387	205	−655	64(5)

Table 1 (continued)

Atom	x $(\times 10^{-4})$	y $(\times 10^{-4})$	z $(\times 10^{-4})$	U_{eq} $(\times 10^{-3} \text{Å}^2)$
C(223)	3875	−463	−281	62(5)
C(224)	4125	−247	312	59(5)
C(225)	3887	637	530	56(5)
C(226)	3400	1304	156	41(4)
C(231)	1657(7)	2671(7)	−321(5)	60(5)
C(232)	1094	3144	−762	70(6)
C(233)	1301	4035	−990	87(7)
C(234)	2072	4452	−777	92(7)
C(235)	2635	3979	−336	70(6)
C(236)	2428	3088	−108	51(5)

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

ligand for coordination to the Rh atom. In **1**, the incoming RhL_2 (L = CO or PPh_3) unit coordinates to an Ru_2Rh face of the original Ru_3Rh precursor and the $AuPPh_3$ ligand can coordinate to both Rh atoms. In $H_2Ru_3Rh_2(CO)_{13}(PPh_3)$ and $H_2Ru_3Rh_2(CO)_{12}(PPh_3)_2$, an RhL_2 unit is coordinated to the Ru_3 face.

Complex **1** contains three μ-CO bridges, two on Ru–Rh edges and one on an Ru–Ru edge. The carbonyl ligands CO(45) and CO(14) bridge the Ru–Ru and Ru–Rh edges asymmetrically, and carbonyl CO(35) semibridges the Rh(3)–Ru(5) edge. The bond lengths Rh(3)–C(35) and Ru(5)–C(35) are 1.956(17) Å and 2.487(15) Å respectively. The semibridging connection to Ru(5) is unexpected because Ru(5) is formally electron deficient. All other carbonyl ligands are terminal. The Rh(3), Ru(4) and Ru(5) atoms are each coordinated to two terminal carbonyl ligands, while the Rh(1) atom is coordinated to one terminal carbonyl ligand and the Ru(2) atom to three terminal carbonyl ligands.

The gold phosphine ligand bridges the Rh_2Ru face asymmetrically, the longest bond (Au–Rh(1)) being 2.950(2) Å and the shortest bond (Au–Ru(2)) 2.789(2) Å. The carbonyl ligands CO(22) and CO(31) show a semibridging coordination to Au, the non-bonding Au–C distances being 2.791 Å for Au · · · C(22) and 2.793 Å for Au · · · C(31). The corresponding non-linear M–C–O angles are 171.4(16)° for Rh(3)–C(31)–O(31) and 166.9(14)° for Ru(2)–C(22)–O(22).

As in the reaction between $[H_2Ru_3Rh(CO)_{12}]^-$ and $[AuPPh_3]^+$, **1** can also be produced by reaction between $H_2Ru_2Rh_2(CO)_{12}$ [13] and $[AuPPh_3]^+$ in the presence of $TlPF_6$ with tetrahydrofuran (THF) as solvent. This mode of reaction is quite different from that of reactions of $[H_2Ru_3Rh(CO)_{12}]^-$ and $H_2Ru_2Rh_2(CO)_{12}$ with PPh_3. Reaction between $H_2Ru_2Rh_2(CO)_{12}$ and PPh_3 gives the tetrahedral phosphine derivative $H_2Ru_2Rh_2(CO)_{11}(PPh_3)$ [14], whereas reaction between $[H_2Ru_3Rh(CO)_{12}]^-$ and PPh_3 yields two trigonal bipyramidal compounds $H_2Ru_3Rh_2(CO)_{13}(PPh_3)$ and $H_2Ru_3Rh_2(CO)_{12}(PPh_3)_2$. The latter complex has also

Table 2
Selected bond lengths (Å) and angles (°) in **1**

Bond lengths

Au–Rh(1)	2.950(2)	Au–Ru(2)	2.789(2)
Au–Rh(3)	2.807(2)	Au–P(1)	2.307(5)
Rh(1)–Ru(2)	3.012(2)	Rh(1)–Rh(3)	2.745(2)
Rh(1)–Ru(4)	2.826(2)	Rh(1)–P(2)	2.370(5)
Rh(1)–C(11)	1.861(15)	Rh(1)–C(14)	1.972(19)
Ru(2)–Rh(3)	2.920(2)	Ru(2)–Ru(4)	2.995(2)
Ru(2)–Ru(5)	2.759(2)	Ru(2)–C(21)	1.917(18)
Ru(2)–C(22)	1.920(19)	Ru(2)–C(23)	1.912(16)
Rh(3)–Ru(4)	2.926(2)	Rh(3)–Ru(5)	2.769(2)
Rh(3)–C(31)	1.940(16)	Rh(3)–C(32)	1.898(18)
Rh(3)–C(35)	1.956(17)	Ru(4)–Ru(5)	2.765(2)
Ru(4)–C(14)	2.121(17)	Ru(4)–C(41)	1.924(18)
Ru(4)–C(42)	1.885(20)	Ru(4)–C(45)	2.094(17)
Ru(5)–C(35)	2.487(15)	Ru(5)–C(45)	2.015(18)
Ru(5)–C(51)	1.945(19)	Ru(5)–C(52)	1.920(21)

Bond angles

Rh(1)–Au–Ru(2)	63.2(1)	Rh(1)–Au–Rh(3)	56.9(1)
Ru(2)–Au–Rh(3)	62.9(1)	Rh(1)–Au–P(1)	144.4(1)
Ru(2)–Au–P(1)	145.9(1)	Rh(3)–Au–P(1)	141.3(1)
Au–Rh(1)–Ru(2)	55.8(1)	Au–Rh(1)–Rh(3)	58.9(1)
Ru(2)–Rh(1)–Rh(3)	60.8(1)	Au–Rh(1)–Ru(4)	108.8(1)
Ru(2)–Rh(1)–Ru(4)	61.6(1)	Rh(3)–Rh(1)–Ru(4)	63.4(1)
Au–Rh(1)–P(2)	113.4(1)	Ru(2)–Rh(1)–P(2)	109.4(1)
Rh(3)–Rh(1)–P(2)	169.5(1)	Ru(4)–Rh(1)–P(2)	116.5(1)
Au–Rh(1)–C(11)	80.5(5)	Ru(2)–Rh(1)–C(11)	136.0(5)
Rh(3)–Rh(1)–C(11)	94.6(6)	Ru(4)–Rh(1)–C(11)	142.1(5)
P(2)–Rh(1)–C(11)	90.8(6)	Au–Rh(1)–C(14)	141.1(6)
Ru(2)–Rh(1)–C(14)	109.9(5)	Rh(3)–Rh(1)–C(14)	82.3(6)
Ru(4)–Rh(1)–C(14)	48.5(5)	P(2)–Rh(1)–C(14)	105.5(6)
C(11)–Rh(1)–C(14)	101.0(7)	Au–Ru(2)–Rh(1)	61.0(1)
Au–Ru(2)–Rh(3)	58.8(1)	Rh(1)–Ru(2)–Rh(3)	55.1(1)
Au–Ru(2)–Ru(4)	108.5(1)	Rh(1)–Ru(2)–Ru(4)	56.1(1)
Rh(3)–Ru(2)–Ru(4)	59.3(1)	Au–Ru(2)–Ru(5)	110.8(1)
Rh(1)–Ru(2)–Ru(5)	101.6(1)	Rh(3)–Ru(2)–Ru(5)	58.3(1)
Ru(4)–Ru(2)–Ru(5)	57.3(1)	Au–Ru(2)–C(21)	79.2(5)
Rh(1)–Ru(2)–C(21)	138.6(5)	Rh(3)–Ru(2)–C(21)	96.0(5)
Ru(4)–Ru(2)–C(21)	138.3(6)	Ru(5)–Ru(2)–C(21)	81.4(6)
Au–Ru(2)–C(22)	69.9(5)	Rh(1)–Ru(2)–C(22)	82.8(5)
Rh(3)–Ru(2)–C(22)	124.4(5)	Ru(4)–Ru(2)–C(22)	127.2(5)
Ru(5)–Ru(2)–C(22)	175.3(5)	C(21)–Ru(2)–C(22)	94.3(8)
Au–Ru(2)–C(23)	160.9(5)	Rh(1)–Ru(2)–C(23)	124.9(5)
Rh(3)–Ru(2)–C(23)	140.3(5)	Ru(4)–Ru(2)–C(23)	87.3(5)
Ru(5)–Ru(2)–C(23)	86.6(6)	C(21)–Ru(2)–C(23)	96.3(7)
C(22)–Ru(2)–C(23)	92.1(7)	Au–Rh(3)–Rh(1)	64.2(1)
Au–Rh(3)–Ru(2)	58.2(1)	Rh(1)–Rh(3)–Ru(2)	64.2(1)
Au–Rh(3)–Ru(4)	110.0(1)	Rh(1)–Rh(3)–Ru(4)	59.7(1)
Ru(2)–Rh(3)–Ru(4)	61.6(1)	Au–Rh(3)–Ru(5)	110.0(1)
Rh(1)–Rh(3)–Ru(5)	108.6(1)	Ru(2)–Rh(3)–Ru(5)	57.9(1)
Ru(4)–Rh(3)–Ru(5)	58.0(1)	Au–Rh(3)–C(31)	69.4(5)
Rh(1)–Rh(3)–C(31)	93.6(5)	Ru(2)–Rh(3)–C(31)	127.6(5)
Ru(4)–Rh(3)–C(31)	146.5(5)	Ru(5)–Rh(3)–C(31)	155.2(5)
Au–Rh(3)–C(32)	156.5(5)	Rh(1)–Rh(3)–C(32)	112.5(6)
Ru(2)–Rh(3)–C(32)	143.5(5)	Ru(4)–Rh(3)–C(32)	84.8(5)
Ru(5)–Rh(3)–C(32)	93.2(5)	C(31)–Rh(3)–C(32)	88.2(7)
Au–Rh(3)–C(35)	90.7(5)	Rh(1)–Rh(3)–C(35)	148.5(5)
Ru(2)–Rh(3)–C(35)	87.0(4)	Ru(4)–Rh(3)–C(35)	118.7(4)
Ru(5)–Rh(3)–C(35)	60.7(4)	C(31)–Rh(3)–C(35)	94.6(7)
C(32)–Rh(3)–C(35)	98.1(7)	Rh(1)–Ru(4)–Ru(2)	62.2(1)
Rh(1)–Ru(4)–Rh(3)	57.0(1)	Ru(2)–Ru(4)–Rh(3)	59.1(1)
Rh(1)–Ru(4)–Ru(5)	106.4(1)	Ru(2)–Ru(4)–Ru(5)	57.1(1)
Rh(3)–Ru(4)–Ru(5)	58.1(1)	Rh(1)–Ru(4)–C(14)	44.2(5)
Ru(2)–Ru(4)–C(14)	106.2(5)	Rh(3)–Ru(4)–C(14)	75.6(5)

Table 2 (continued)

Bond angles			
Ru(5)–Ru(4)–C(14)	133.2(5)	Rh(1)–Ru(4)–C(41)	104.2(6)
Ru(2)–Ru(4)–C(41)	110.0(5)	Rh(3)–Ru(4)–C(41)	160.6(6)
Ru(5)–Ru(4)–C(41)	132.2(5)	C(14)–Ru(4)–C(41)	94.0(7)
Rh(1)–Ru(4)–C(42)	127.1(5)	Ru(2)–Ru(4)–C(42)	153.9(6)
Rh(3)–Ru(4)–C(42)	103.2(6)	Ru(5)–Ru(4)–C(42)	97.8(6)
C(14)–Ru(4)–C(42)	85.4(8)	C(41)–Ru(4)–C(42)	92.0(8)
Rh(1)–Ru(4)–C(45)	142.2(5)	Ru(2)–Ru(4)–C(45)	80.0(5)
Rh(3)–Ru(4)–C(45)	104.6(5)	Ru(5)–Ru(4)–C(45)	46.5(5)
C(14)–Ru(4)–C(45)	172.4(7)	C(41)–Ru(4)–C(45)	87.8(7)
C(42)–Ru(4)–C(45)	87.2(8)	Ru(2)–Ru(5)–Rh(3)	63.8(1)
Ru(2)–Ru(5)–Ru(4)	65.7(1)	Rh(3)–Ru(5)–Ru(4)	63.8(1)
Ru(2)–Ru(5)–C(35)	81.5(4)	Rh(3)–Ru(5)–C(35)	43.3(4)
Ru(4)–Ru(5)–C(35)	107.1(4)	Ru(2)–Ru(5)–C(45)	87.4(6)
Rh(3)–Ru(5)–C(45)	112.8(5)	Ru(4)–Ru(5)–C(45)	48.9(5)
C(35)–Ru(5)–C(45)	156.1(6)	Ru(2)–Ru(5)–C(51)	97.3(6)
Rh(3)–Ru(5)–C(51)	140.2(6)	Ru(4)–Ru(5)–C(51)	142.6(6)
C(35)–Ru(5)–C(51)	102.4(7)	C(45)–Ru(5)–C(51)	100.0(7)
Ru(2)–Ru(5)–C(52)	165.0(5)	Rh(3)–Ru(5)–C(52)	101.3(5)
Ru(4)–Ru(5)–C(52)	109.1(6)	C(35)–Ru(5)–C(52)	87.2(7)
C(45)–Ru(5)–C(52)	99.4(8)	C(51)–Ru(5)–C(52)	94.6(9)
Rh(1)–C(14)–Ru(4)	87.3(7)	Rh(3)–C(35)–Ru(5)	76.0(5)
Ru(4)–C(45)–Ru(5)	84.6(6)		

been obtained from the reaction of $[Rh(CO)_3(PPh_3)_2]$ $[PF_6]$ with the anionic cluster compound $[H_2Ru_3Rh-(CO)_{11}(PPh_3)]^-$, generated from $H_2Ru_3Rh(CO)_{10}-(PPh_3)(\mu\text{-COMe})$ and $K(BHBu_3)$ [11]. The corresponding reaction in which the $AuPPh_3$ ligand is used in place of $[Rh(CO)_3(PPh_3)_2][PF_6]$ does not give **1** but instead $AuHRu_3Rh(CO)_{10}(PPh_3)_2(\mu_3\text{-COMe})$ and $AuH_2Ru_3Rh(CO)_{11}(PPh_3)_2$. Both of these clusters have a pentanuclear Ru–Rh–Au metal core and contain one less rhodium atom than **1**. In the crystallographically characterized $AuHRu_3Rh(CO)_{10}(PPh_3)_2(\mu_3\text{-COMe})$, the gold phosphine ligand is coordinated to the Ru_2Rh face, just like the μ_3-H ligand, and the phosphine ligand is coordinated to the Rh atom. From the NMR spectra of $AuH_2Ru_3Rh(CO)_{11}(PPh_3)_2$ the gold phosphine ligand was judged to be coordinated to the Ru_3 face [11].

The ^{31}P NMR spectrum of (1) in solution shows two signals. The phosphine is coordinated to the Rh atom and gives a doublet of doublets signal at 19.0 ppm, with the coupling constants $^1J(Rh-P) = 134$ Hz and $^2J(P-H) = 5.1$ Hz. The triplet at 70.4 ppm is assigned to the $AuPPh_3$ group. The triplet arises from the P–Rh two-bond couplings with $^2J(Rh-P) = 6$ Hz. The data are in good agreement with those for the ^{31}P NMR spectrum of $AuHRu_3Rh(CO)_{10}(PPh_3)_2(\mu_3\text{-COMe})$, in which the signal of $AuPPh_3$ at 67.1 ppm has a $J(Rh-P)$ coupling constant of 5 Hz.

In the ^{1}H NMR spectrum, the unique hydride ligand gives a doublet of doublets signal at -19.7 ppm with coupling constants $^1J(Rh-H) = 14.5$ Hz and $^2J(P-H) = 3.3$ Hz, in good agreement data for the corresponding signal from $AuHRu_3Rh(CO)_{10}(PPh_3)_2(\mu_3\text{-COMe})$ at

-19.2 ppm with coupling constants $^1J(Rh-H) = 14$ Hz and $^2J(P-H) = 4$ Hz [11].

3. Experimental details

3.1. General comments

All manipulations up to the chromatographic separation were carried out under N_2 in deoxygenated solvents. The Fourier transform IR spectrum was recorded on a Nicolet 20SXC spectrometer. The ^{1}H NMR spectrum was recorded on a Bruker AM-250 spectrometer at 273 K in $CDCl_3$ with Me_4Si as reference, and the ^{31}P NMR spectrum at 294 K in $CDCl_3$ with concentrated H_3PO_4 as external reference. Crystals were grown by slow evaporation of the solvent from a saturated hexane–CH_2Cl_2 solution. The complexes $[H_2Ru_3Rh-(CO)_{12}]^-$, $H_2Ru_2Rh_2(CO)_{12}$ and $AuPPh_3$ were prepared by published methods [2,13,15]. Other reagents and solvents were obtained from commercial sources. THF was dried and deoxygenated by stirring over Na–benzophenone ketyl and freshly distilled before use.

3.2. Synthesis

A THF (15 ml) solution of $[N(PPh_3)_2][H_2Ru_3Rh-(CO)_{12}]$ (86.3 mg, 0.067 mmol) was treated with solid $AuPPh_3Cl$ (45.8 mg, 0.093 mmol) in the presence of $TlPF_6$. The mixture was stirred at ambient temperature for 16 h, and the solvent then evaporated off under reduced pressure. The mixture of cluster compounds obtained was separated by chromatography on silica. With 1:1 hexane:CH_2Cl_2 as eluent, **1** was isolated as the third fraction (reddish brown; 22.9 mg, 0.014 mmol). It was identified by X-ray diffraction and ^{1}H and ^{31}P NMR spectroscopy.

An alternative route to **1** involved treating a THF solution of $H_2Ru_2Rh_2(CO)_{12}$ (190.9 mg, 0.256 mmol) with $AuPPh_3Cl$ (128.6 mg, 0.260 mmol) in the presence of $TlPF_6$. The reaction was complete after 4.5 h and the chromatographic separation on silica with 1:1 hexane:CH_2Cl_2 as eluent gave **1** as the third fraction (60.0 mg, 0.038 mmol).

3.3. Spectroscopic data for 1

^{1}H NMR: δ -19.7 (dd, $^1J(Rh-H) = 14.5$ Hz, $^2J(P-H) = 3.3$ Hz) ppm. ^{31}P NMR: δ 70.4 (t, $^2J(Rh-P) = 6$ Hz), 19.0 (dd, $^1J(Rh-P) = 134$ Hz, $^2J(P-H) = 5.1$ Hz) ppm.

IR (CH_2Cl_2): ν 2069 s, 2036 vs, 2013 vs, 1838 m,br cm^{-1}.

3.4. Structure determination

Crystal data and details of data collection and refinement are summarized in Table 3. Diffraction data were

Table 3
Crystal data and collection parameters for **1**

Formula	$AuC_{49}H_{31}O_{13}P_2Rh_2Ru_3$
Formula weight	1595.7
Colour; habit	Brown block
Crystal size (mm)	$0.20 \times 0.20 \times 0.25$
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	16.683(7)
b (Å)	13.572(6)
c (Å)	23.482(7)
β (°)	102.51(3)
V (Å³)	5191(4)
Z	4
Calculated density (g cm^{-3})	2.042
μ (mm^{-1})	4.378
$F(000)$	3040.
Number of centring reflections	25
Centring 2θ (°)	16–22
Scan range 2θ (°)	4–50
Scan speed (° min^{-1})	2.49–29.30
h, k, l range	27, 16, ± 19
Number of reflections collected	9989
Number of unique reflections	9126
Number of observed data $(F > 3\sigma(F))$	4226
Number of parameters	382
R	0.0483
R'	0.0519
G(weight)	0.0007
Goodness of fit	1.11
Largest difference peak (electrons Å^{-3})	1.22
Largest difference hole (electrons Å^{-3})	-0.83

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

recorded on a Nicolet R3m diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710$ 73 Å). ω scan mode with a scan speed of 2.49–29.29° min^{-1} was used. Intensities were corrected for Lorentz, polarization and background effects.

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

[16] program package. Non-hydrogen atoms were refined anisotropically, except for the phenyl carbon atoms which were refined isotropically with the phenyl rings treated as rigid groups. Hydrogen atoms were placed in calculated positions (0.96 Å; $U = 0.08$ Å^2) and not refined.

4. Supplementary material available

Complete lists of bond lengths and angles, and tables of hydrogen atom coordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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