C(6)	0.3243 (13)	−0.2115 (14)	−0.1704 (11)	0.0428 (6)
C(7)	0.0209 (14)	0.5580 (11)	0.4711 (9)	0.0284 (5)
C(8)	0.3367 (13)	0.5665 (14)	0.4517 (11)	0.0412 (6)
C(9)	0.1623 (14)	0.6694 (11)	0.3088 (11)	0.0366 (5)
C(10)	−0.4058 (14)	0.6757 (13)	0.1859 (10)	0.0427 (6)

Table 2. *Geometric parameters* (Å, °)

Cu(1)—Cl(1)	2.405 (4)	P(2)—C(2)	1.826 (9)
Cu(1)—P(1)	2.264 (4)	P(2)—C(5)	1.832 (15)
Cu(1)—P(3)	2.251 (3)	P(2)—C(6)	1.839 (13)
Cu(1)—P(2^i)	2.268 (4)	P(2)—Cu(1^i)	2.268 (4)
Cl(2)—C(10)	1.742 (14)	P(3)—C(7)	1.827 (12)
Cl(3)—C(10)	1.787 (14)	P(3)—C(8)	1.844 (12)
P(1)—C(1)	1.822 (9)	P(3)—C(9)	1.839 (14)
P(1)—C(3)	1.828 (14)	C(1)—C(2)	1.534 (17)
P(1)—C(4)	1.816 (13)	C(7)—C(7^i)	1.548 (26)
Cl(1)—Cu(1)—P(1)	104.8 (1)	C(5)—P(2)—C(6)	101.5 (7)
Cl(1)—Cu(1)—P(3)	97.4 (1)	C(2)—P(2)—Cu(1^i)	116.8 (4)
P(1)—Cu(1)—P(3)	116.1 (1)	C(5)—P(2)—Cu(1^i)	115.3 (4)
Cl(1)—Cu(1)—P(2^i)	109.0 (1)	C(6)—P(2)—Cu(1^i)	116.8 (4)
P(1)—Cu(1)—P(2^i)	114.6 (1)	Cu(1)—P(3)—C(7)	119.9 (3)
P(3)—Cu(1)—P(2^i)	112.8 (1)	Cu(1)—P(3)—C(8)	115.1 (4)
Cu(1)—P(1)—C(1)	117.0 (4)	C(7)—P(3)—C(8)	102.4 (5)
Cu(1)—P(1)—C(3)	117.6 (5)	Cu(1)—P(3)—C(9)	115.1 (4)
C(1)—P(1)—C(3)	101.0 (5)	C(7)—P(3)—C(9)	100.3 (6)
Cu(1)—P(1)—C(4)	116.9 (4)	C(8)—P(3)—C(9)	101.3 (6)
C(1)—P(1)—C(4)	101.3 (5)	P(1)—C(1)—C(2)	114.4 (7)
C(3)—P(1)—C(4)	100.1 (6)	P(2)—C(2)—C(1)	112.6 (7)
C(2)—P(2)—C(5)	101.8 (5)	P(3)—C(7)—C(7^i)	113.4 (11)
C(2)—P(2)—C(6)	102.3 (5)	Cl(2)—C(10)—Cl(3)	110.8 (6)

Symmetry code: (i) $-x, -y, -z$.

The title compound was isolated upon recrystallization of a (dmpe)copper(I) acetate species by slow diffusion of hexane into a CH_2Cl_2 solution of the complex at room temperature under a nitrogen atmosphere. The (dmpe)copper(I) acetate species was synthesized from the reaction of copper(I) acetate (2.04 mmol) with 1,2-bis(dimethylphosphino)ethane (2.04 mmol) in 40 ml of benzene under nitrogen atmosphere. The presence of chloride was not observed in the starting materials. The synthesis of the $[Cu_2(dmpe)_3Cl_2]_n$ polymer in the absence of chloride ions in the starting material is proposed to proceed from the reaction of CH_2Cl_2 with the (dmpe)copper(I) acetate species, by an undetermined pathway, during recrystallization from CH_2Cl_2/hexane. A suitable crystal of $[Cu_2(dmpe)_3Cl_2]_n.2CH_2Cl_2$ was chosen and mounted on a glass fiber at room temperature with epoxy cement. Inspection of axial photographs about each of the three axes confirmed axis length and Laue symmetry. ω scans of several intense reflections indicated acceptable crystal quality. The Wyckoff scan mode was employed (Siemens, 1990). The ω scan width was 0.6° with a θ variable scan rate between 2.0 and 29.6° min^{-1}. Background measurements were made by stationary crystal and stationary counter technique at the beginning and end of each reflection for half of the total scan time. C-bound H atoms were placed in idealized positions [C—H = 0.96 Å, U(H) = 0.08 Å^2 (fixed)]. The H-atom parameters were not refined.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55966 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1042]

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Structures of the Monoclinic Form of $Ph_3PAuRuRh_3(CO)_{12}$ (I) and its Cubic Form with $Ru_3(CO)_{12}$ (II)

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Abstract

$C_{30}H_{15}AuO_{12}PRh_3Ru$ crystallizes in the monoclinic form (I), penta-μ-carbonyl-1:2κ^2C;1:3κ^2C;2:3κ^2C;2:4κ^2C;3:4κ^2C-heptacarbonyl-1κ^3C,2κC,3κC,4κ^2C-triphenylphosphine-5κP-goldtrirhodiumruthenium-(3*Au*—*Rh*)(3*Rh*—*Rh*)(3*Rh*—*Ru*), and the cubic form (II), tri-μ-carbonyl-2:3κ^2C;2:4κ^2C;3:4κ^2C-nonacarbonyl-1κ^3C,2κ^2C,3κ^2C,4κ^2C-triphenylphosphine-5κP-goldtrirhodiumruthenium(3*Au*—*Rh*)(3*Rh*—*Rh*)-

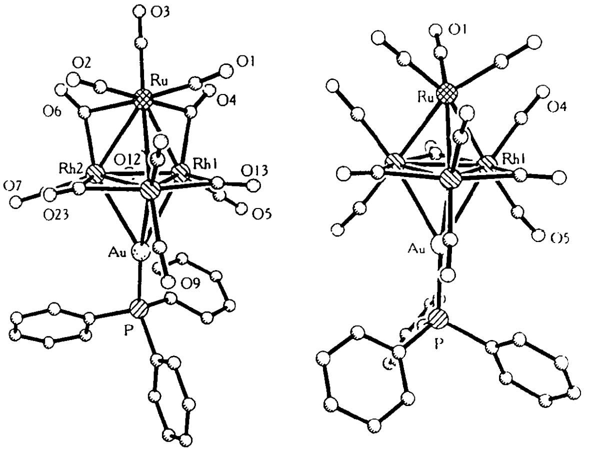
0108-2701/93/061142-05$06.00

(3*Rh—Ru*), in (II) with $Ru_3(CO)_{12}$. In both forms the metal core of the $Ph_3PAuRh_3Ru(CO)_{12}$ molecule is a trigonal bipyramid with the Au and Rh atoms in the apical positions. In (II) three of the twelve carbonyl ligands are symmetrically bridging the basal Rh atoms while the rest are terminal, three being bonded to the Ru atom and two to each of the Rh atoms. In (I) the arrangement of the carbonyl ligands is similar except that two additional semibridges are formed from basal Rh atoms to the apical Ru atom. This difference is also reflected in the metal–metal interactions.

Comment

This work is part of structural and reactivity studies of tetrahedral $H_xRu_xCo_yRh_z(CO)_{12}$ ($x + y + z = 4$) clusters. Several $[AuPPh_3]^+$ derivatives have been prepared with the corresponding anionic clusters $[Ru_xCo_yRh_z(CO)_{12}]^{x-}$. In the $Ph_3PAuRuCo_xRh_{3-x}(CO)_{12}$ clusters (Pursiainen, Ahlgrén & Pakkanen, 1985) the Au atom coordinates on the basal face of Co and Rh atoms. The title compounds can be synthesized by treating a tetrahydrofuran solution (30 ml) of $HRuRh_3(CO)_{12}$ (76 mg, 0.1 mmol) (Pursiainen, Pakkanen & Jääskeläinen, 1985) with one equivalent of KH (4 mg, 0.1 mmol), followed by the addition of one equivalent of $AuPPh_3Cl$ (50.3 mg, 0.1 mmol in 10 ml tetrahydrofuran) (Mann, Wells & Purdie, 1937). Quite unexpectedly $Ph_3PAuRuRh_3(CO)_{12}$ crystallized from a chromatographically purified fraction in two different air-stable forms: monoclinic (I), which is not isomorphic with $Ph_3PAuRuCo_3(CO)_{12}$ (Braunstein, Rosé, Dedieu, Dusausoy, Mangeot, Tiripicchio & Tiripicchio Camellini, 1986), and cubic (II). The latter form crystallized together with $Ru_3(CO)_{12}$, which probably was formed in decomposition reactions during the crystallization.

The structure of $Ph_3PAuRuRh_3(CO)_{12}$ in (I) and (II) has the common bipyramidal metal frame with the Au and Ru atoms being at apical positions as shown in Fig. 1. This metal arrangement is confirmed also by a ^{31}P NMR spectrum which consists of a quartet at 62.3 p.p.m. with $^2J(Rh—P) = 2.7$ Hz at ambient temperature. In (II), the PPh_3 ligand is bound to the apical Au atom, each Rh—Rh edge is bridged by a carbonyl group and of the nine terminal carbonyl groups, three are attached to the apical Ru atom and two to each Rh atom. The carbonyl arrangement of (I) is similar to that of (II) except that the carbonyls CO(4) and CO(6) form bent semibridges (Crabtree & Lavin, 1986) between basal Rh atoms and the apical Ru atom: Rh(1)—C(4) = 1.963 (7), Ru—C(4) = 2.280 (9), Rh(2)—C(6) = 1.957 (8) and Ru—C(6) = 2.236 (8) Å. This is also reflected in the metal–metal bond lengths.



(I) (II)

Fig. 1. A view of the molecular structures of $Ph_3PAuRuRh_3(CO)_{12}$ in (I) and (II).

The Ru—Rh interactions of 2.722 (1) Å in (II) are significantly shorter than those of 2.868 (1)–2.947 (1) Å in (I) (Table 3). In contrast, the Rh—Rh interactions of 2.806 (2) Å in (II) are somewhat longer than those of 2.731 (1)–2.746 (1) Å in (I). In $HRuRh_3(CO)_{10}(PPh_3)_2$ (Pursiainen, Pakkanen & Jääskeläinen, 1985), where also the Ru—Rh edges are not bridged by ligands, the corresponding Ru—Rh (mean 2.72 Å) and Rh—Rh (mean 2.78 Å) distances are quite comparable to those of (II). The valence-electron count on the metals reveals that $Ph_3PAuRh_3Ru(CO)_{12}$ in (I) and (II) is a 60 electron *closo* cluster where the $AuPPh_3^+$ ligand is the isolobal analogy to H (Owen, 1988). The $Ru(CO)_3$ centre in (II) is formally electron deficient (17 electrons) and the Rh centres are electron rich. In (I) the electron deficiency of the apical $Ru(CO)_3$ centre is balanced by the CO(4) and CO(6) semibridges which compensate the electron-rich nature of two basal Rh atoms. These electronic differences and metal–ligand π bonding explain well the differences in the observed metal–metal and metal–ligand distances.

The crystal structure of (II) consists of $Ph_3PAuRh_3Ru(CO)_{12}$ and $Ru_3(CO)_{12}$ molecules in the ratio of 2:1. The $Ru_3(CO)_{12}$ cluster is disordered on the triad inversion axis. The metal core is best described as two Ru_3 triangles related by a 60° rotation about a vector normal to the M_3 plane forming a 'Star-of-David' arrangement. The Ru—Ru distances of 2.835 (3) Å are quite comparable to those of 2.8512 (4)–2.8595 (4) Å found in the ordered structure of $Ru_3(CO)_{12}$ (Churchill, Hollander & Hutchinson, 1977). Since the carbonyl atoms are found in the average positions the other bond lengths and angles deviate from expected values. The O atoms of the CO ligands form a distorted icosahedron around the metal core (Fig. 2) instead of the anticuboctahedron found in $Ru_3(CO)_{12}$ (Churchill, Hollander & Hutchinson, 1977). This arrangement is consistent with a model in which the peripheral O atoms of the CO ligands occupy the same sites while the M_3 triangle takes up two orientations related by a 60° rotation (Bruce, Nicholson & White, 1982).

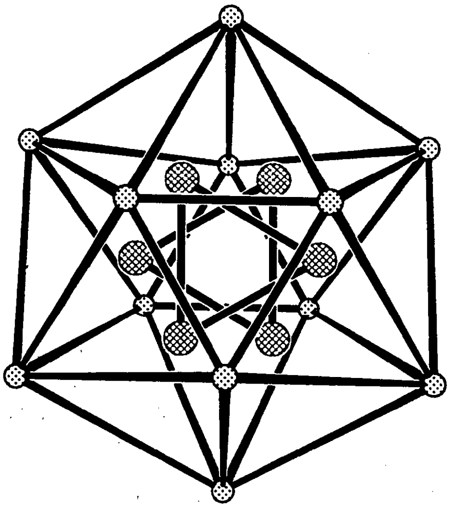


Fig. 2. A view of the distorted icosahedron constructed of the carbonyl O atoms of $Ru_3(CO)_{12}$ and the location of a disordered Ru_3 metal core inside it.

Experimental

Compound (I)

Crystal data

$[AuRh_3Ru(C_{28}H_{15}P)(CO)_{12}]$
$M_r = 1205.17$
Monoclinic
$P2_1/c$
$a = 8.971$ (1) Å
$b = 22.501$ (3) Å
$c = 17.191$ (3) Å
$\beta = 102.97°$
$V = 3381.6$ Å^3
$Z = 4$
$D_x = 2.37$ Mg m^{-3}
Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9$–$11°$
$\mu = 6.26$ mm^{-1}
$T = 293$ K
Needle
0.25 × 0.20 × 0.20 mm
Dark brown
Crystal source: slow evaporation of hexane/CH_2Cl_2 solution at 283 K

Data collection

Enraf-Nonius CAD-4 diffractometer
ω-2θ scans
Absorption correction: empirical (*DIFABS*; Walker & Stuart, 1983)
$T_{min} = 0.822$, $T_{max} = 1.040$
10082 measured reflections
9836 independent reflections

6371 observed reflections [$I > 3\sigma(I)$]
$\theta_{max} = 30°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 31$
$l = -24 \rightarrow 24$
3 standard reflections monitored every 97 reflections intensity variation: insignificant

Refinement

Refinement on F
Final $R = 0.027$
$wR = 0.027$
6371 reflections
433 parameters
H-atom parameters not refined

Unit weights applied
$(\Delta/\sigma)_{max} = 0.05$
$\Delta\rho_{max} = 0.93$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Compound (II)

Crystal data

$[AuRh_3Ru(C_{28}H_{15}P)(CO)_{12}].0.5[Ru_3(CO)_{12}]$
$M_r = 1524.84$
Cubic
$Pa\bar{3}$
$a = 20.647$ (3) Å
$V = 8801.3$ Å^3
$Z = 8$
$D_x = 2.30$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Cell parameters from 25 reflections
$\theta = 9$–$12°$
$\mu = 5.32$ mm^{-1}
$T = 293$ K
Square bipyramidal
0.25 × 0.15 × 0.15 mm
Black
Crystal source: slow evaporation of hexane/CH_2Cl_2 solution at 283 K

Data collection

Enraf-Nonius CAD-4 diffractometer
ω-2θ scans
Absorption correction: empirical (*DIFABS*; Walker & Stuart, 1983)
$T_{min} = 0.823$, $T_{max} = 1.165$
4884 measured reflections
4262 independent reflections

1119 observed reflections [$I > 3\sigma(I)$]
$\theta_{max} = 30°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 28$
$l = 0 \rightarrow 28$
3 standard reflections monitored every 97 reflections intensity variation: insignificant

Refinement

Refinement on F
Final $R = 0.033$
$wR = 0.033$
1119 reflections
190 parameters
H-atom parameters not refined

Unit weights applied
$(\Delta/\sigma)_{max} = 0.01$
$\Delta\rho_{max} = 0.98$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for* (I)

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Au	0.69679 (2)	0.06313 (1)	0.18636 (2)	2.66 (1)
Rh(1)	0.48673 (5)	0.13367 (2)	0.07540 (3)	2.67 (1)
Rh(2)	0.73173 (6)	0.18806 (2)	0.17229 (3)	2.65 (1)
Rh(3)	0.77563 (5)	0.11313 (2)	0.05332 (3)	2.20 (1)
Ru	0.63129 (6)	0.22996 (2)	0.01147 (3)	2.99 (1)
P	0.6540 (2)	0.00361 (7)	0.28740 (9)	2.46 (3)
O(1)	0.5633 (8)	0.1870 (3)	−0.1620 (3)	5.7 (2)
O(2)	0.9565 (6)	0.2722 (3)	0.0129 (3)	5.0 (1)
O(3)	0.4717 (9)	0.3478 (3)	−0.0323 (5)	8.5 (2)
O(4)	0.2691 (7)	0.2192 (3)	−0.0156 (4)	6.5 (2)
O(5)	0.2104 (7)	0.0609 (3)	0.0870 (4)	6.6 (2)
O(6)	0.6933 (9)	0.3178 (3)	0.1579 (4)	6.8 (2)

O(7)	0.8785 (9)	0.2217 (5)	0.3409 (4)	10.4 (3)
O(8)	0.9348 (7)	0.1339 (3)	−0.0829 (3)	5.8 (1)
O(9)	0.9132 (6)	−0.0105 (3)	0.0775 (3)	4.3 (1)
O(12)	0.4293 (6)	0.1936 (3)	0.2281 (4)	5.4 (1)
O(13)	0.5049 (6)	0.0528 (3)	−0.0646 (3)	4.4 (1)
O(23)	1.0638 (6)	0.1683 (2)	0.1605 (4)	4.4 (1)
C(1)	0.5876 (9)	0.2009 (4)	−0.0973 (4)	3.8 (2)
C(2)	0.8377 (8)	0.2562 (3)	0.0111 (4)	3.2 (1)
C(3)	0.5324 (9)	0.3034 (4)	−0.0168 (6)	5.0 (2)
C(4)	0.3878 (9)	0.2011 (3)	0.0118 (5)	3.9 (2)
C(5)	0.3128 (8)	0.0884 (4)	0.0828 (4)	3.7 (1)
C(6)	0.6911 (9)	0.2696 (4)	0.1338 (5)	4.5 (2)
C(7)	0.8200 (9)	0.2072 (5)	0.2785 (5)	5.4 (2)
C(8)	0.8720 (8)	0.1272 (3)	−0.0336 (4)	3.6 (1)
C(9)	0.8608 (7)	0.0367 (3)	0.0733 (4)	2.9 (1)
C(12)	0.5025 (8)	0.1801 (3)	0.1834 (4)	3.4 (1)
C(13)	0.5486 (7)	0.0831 (3)	−0.0101 (4)	2.9 (1)
C(23)	0.9336 (8)	0.1635 (3)	0.1438 (4)	3.0 (1)
C(101)	0.7388 (7)	0.0318 (3)	0.3866 (4)	2.8 (1)
C(102)	0.6763 (9)	0.0207 (4)	0.4513 (4)	4.3 (2)
C(103)	0.7499 (9)	0.0422 (5)	0.5265 (5)	5.1 (2)
C(104)	0.8854 (9)	0.0726 (4)	0.5372 (5)	4.7 (2)
C(105)	0.9478 (9)	0.0836 (4)	0.4728 (5)	4.7 (2)
C(106)	0.8745 (8)	0.0636 (4)	0.3973 (4)	3.7 (1)
C(201)	0.4506 (7)	0.0009 (3)	0.2835 (3)	2.6 (1)
C(202)	0.3800 (8)	0.0537 (3)	0.2981 (4)	3.6 (1)
C(203)	0.2228 (8)	0.0549 (4)	0.2901 (5)	4.3 (2)
C(204)	0.1368 (8)	0.0063 (5)	0.2664 (5)	4.8 (2)
C(205)	0.2033 (8)	−0.0455 (4)	0.2513 (5)	4.4 (2)
C(206)	0.3619 (8)	−0.0489 (4)	0.2594 (4)	3.5 (1)
C(301)	0.7167 (7)	−0.0731 (3)	0.2863 (4)	2.7 (1)
C(302)	0.7778 (8)	−0.0927 (3)	0.2242 (5)	3.7 (2)
C(303)	0.8280 (9)	−0.1517 (4)	0.2231 (6)	4.9 (2)
C(304)	0.8158 (9)	−0.1898 (4)	0.2835 (6)	5.2 (2)
C(305)	0.7557 (9)	−0.1704 (4)	0.3447 (6)	5.3 (2)
C(306)	0.7055 (9)	−0.1124 (3)	0.3473 (5)	4.2 (2)

Table 2. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for* (II)

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Au	0.3405	0.3405	0.3405	3.85 (1)
Rh	0.2310 (1)	0.3383 (1)	0.2601 (1)	3.31 (2)
Ru	0.2153 (2)	0.2153	0.2153	4.08 (4)
P	0.4043 (6)	0.4043	0.4043	3.1 (1)
O(1)	0.2009 (7)	0.2399 (9)	0.0718 (6)	9.0 (5)
O(4)	0.1146 (6)	0.3615 (7)	0.1763 (7)	7.6 (4)
O(5)	0.2333 (7)	0.4771 (6)	0.3131 (7)	8.3 (4)
O(12)	0.3094 (6)	0.3723 (6)	0.1383 (6)	7.4 (3)
C(1)	0.2053 (8)	0.2317 (9)	0.1253 (9)	5.8 (5)
C(4)	0.1585 (8)	0.3498 (9)	0.2071 (8)	5.2 (4)
C(5)	0.2368 (9)	0.4255 (8)	0.2941 (9)	5.2 (4)
C(12)	0.2981 (8)	0.3417 (9)	0.1834 (8)	5.0 (4)
C(101)	0.4510 (8)	0.4617 (7)	0.3580 (7)	3.7 (3)
C(102)	0.5147 (9)	0.4767 (8)	0.3740 (8)	4.5 (4)
C(103)	0.5479 (8)	0.5235 (9)	0.3395 (9)	5.8 (4)
C(104)	0.5169 (9)	0.5537 (8)	0.2881 (9)	6.2 (5)
C(105)	0.4551 (9)	0.5392 (9)	0.2729 (9)	6.3 (5)
C(106)	0.4224 (8)	0.4935 (9)	0.3074 (8)	4.8 (4)
Ru(2)*	0.0001 (2)	0.0545 (2)	−0.0576 (2)	4.88 (7)
O(21)	0.0693 (7)	0.0616 (8)	−0.1837 (7)	9.2 (4)
O(22)	0.1194 (7)	0.1161 (7)	0.0066 (7)	8.0 (4)
C(21)	0.053 (1)	0.049 (1)	−0.1361 (8)	7.1 (5)
C(22)	0.081 (1)	0.074 (2)	−0.010 (1)	13 (1)

* Site-occupation factor 0.5.

Table 3. *Selected geometric parameters* (Å, °) *for* $Ph_3PAuRuRh_3(CO)_{12}$ *in* (I) *and* (II)

	(I)	(II)
Rh(1)—Au	2.845(1)	2.804(1)
Rh(2)—Au	2.845(1)	
Rh(3)—Au	2.779(1)	
Ru—Rh(1)	2.868(1)	2.722(1)
Ru—Rh(2)	2.868(1)	
Ru—Rh(3)	2.947(1)	
Rh(1)—Rh(2)	2.731(1)	2.806(2)
Rh(1)—Rh(3)	2.742(1)	
Rh(2)—Rh(3)	2.746(1)	
Ru—C(1)	1.936(7)	1.899(18)
Ru—C(2)	1.945(7)	
Ru—C(3)	1.887(9)	
Rh(1)—C(4)	1.963(7)	1.869(17)
Rh(1)—C(5)	1.891(8)	1.935(17)
Rh(2)—C(6)	1.957(8)	
Rh(2)—C(7)	1.870(8)	
Rh(3)—C(8)	1.913(8)	
Rh(3)—C(9)	1.882(7)	
Rh(1)—C(12)	2.106(7)	2.105(17)
Rh(2)—C(12)	2.115(7)	2.120(17)
Rh(1)—C(13)	2.033(7)	
Rh(3)—C(13)	2.191(6)	
Rh(2)—C(23)	2.055(7)	
Rh(3)—C(23)	2.173(6)	
Ru—C(4)	2.280(8)	3.019(17)
Ru—C(6)	2.236(8)	
Au—Rh(1)—C(4)	162.5(2)	171.8(6)
Au—Rh(2)—C(6)	160.0(2)	
Au—Rh(3)—C(8)	162.3(2)	
Au—Rh(1)—C(5)	95.0(2)	73.8(5)
Au—Rh(2)—C(7)	100.1(3)	
Au—Rh(3)—C(9)	69.4(2)	
Ru—Rh(1)—C(5)	152.0(2)	176.4(5)
Ru—Rh(2)—C(7)	146.9(3)	
Ru—Rh(3)—C(9)	176.2(2)	
Ru—Rh(1)—C(4)	52.3(2)	79.9(6)
Ru—Rh(2)—C(6)	51.1(2)	
Ru—Rh(3)—C(8)	85.0(2)	
Rh(1)—Ru—C(1)	95.9(2)	99.1(5)
Rh(2)—Ru—C(3)	124.3(3)	
Rh(3)—Ru—C(2)	84.6(2)	
Rh(1)—Ru—C(2)	138.0(2)	158.1(6)
Rh(2)—Ru—C(1)	140.5(2)	
Rh(3)—Ru—C(3)	178.0(3)	
Rh(1)—Ru—C(3)	122.2(3)	100.3(6)
Rh(2)—Ru—C(2)	90.6(2)	
Rh(3)—Ru—C(1)	85.2(2)	
Rh(1)—C(12)—Rh(2)	80.6(3)	83.2(6)
Rh(1)—C(13)—Rh(3)	80.9(2)	
Rh(2)—C(23)—Rh(3)	81.0(2)	
C(4)—Rh(1)—C(5)	100.2(3)	98.2(8)
C(6)—Rh(2)—C(7)	96.9(4)	
C(8)—Rh(3)—C(9)	93.3(3)	

The metal-atom positions were obtained by direct methods (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). Other calculations were performed with the *SDP* program package (Frenz, 1978).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and bond distances and angle have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55886 (65 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1029]

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Structure of *trans*-[Rh(PPh$_3$)$_2$(CO)(OH$_2$)]-[ClO$_4$].CH$_2$Cl$_2$

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Abstract

In crystals of *trans*-aquacarbonylbis(triphenylphosphine)rhodium(I) perchlorate dichloromethane solvate, the cations and anions are linked through O—H···O hydrogen bonds to form dimeric [Rh(PPh$_3$)$_2$(CO)(OH$_2$)]$_2$[ClO$_4$]$_2$ units characterized by crystallographically imposed C_i symmetry. The cationic complex displays a slightly distorted square-planar geometry around the Rh atom. The water molecule coordinates the Rh^I centre at an Rh—O distance of 2.127 (4) Å.

Comment

As part of our investigation of complexes of the platinum-group metals with weakly coordinating anions, we attempted to repeat the preparation of *trans*-[Rh(PPh$_3$)$_2$(CO)(ClO$_4$)] using the recommended aerobic filtration (Peone, Flynn & Vaska, 1974). The product was recrystallized from a CH$_2$Cl$_2$/petroleum ether mixture and identified by an X-ray structure analysis as the title compound, in which the metal atom in the cationic complex is coordinated by an H$_2$O molecule rather than by the ClO_4^- ion (Fig. 1). The relatively high displacement parameters of the atoms in the ClO_4^- ion (Table 1) suggest that it may be slightly disordered.

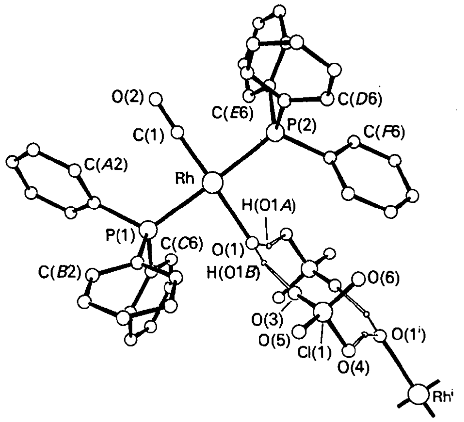

Fig. 1. A view of the structure illustrating hydrogen-bonding interactions of two [Rh(PPh$_3$)$_2$(CO)(OH$_2$)][ClO$_4$] units related by a centre of symmetry, which bisects the O(1)→O(1^i) vector. In the phenyl rings the atoms are numbered cyclically C(n1)···C(n6), where n = *A*, *B*, *C*, *D*, *E* or *F*, and the C(n1) atom is bonded to the P atom; only the C(n2) or C(n6) labels are shown, for clarity.

The aqua complex [Rh(PPh$_3$)$_2$(CO)(OH$_2$)]$^+$ was previously obtained in the form of $SO_3CF_3^-$, BF_4^- and ClO_4^- salts and the crystal structure of [Rh(PPh$_3$)$_2$(CO)(OH$_2$)][BF$_4$].$\frac{1}{2}$H$_2$O.$\frac{1}{4}$C$_6$H$_{12}$ has been determined (Branan, Hoffman, McElroy, Prokopuk, Salazar, Robbins, Hill & Webb, 1991).

In the latter compound, as well as in the ClO_4^- salt reported here, the coordination geometry around the Rh atom is square planar. In the ClO_4^- salt this geometry is subject to a small tetrahedral distortion, which is evident from the bond angles subtended at the Rh centre (Table 2) and from the displacements of the P(1), P(2), O(1) and C(1) atoms by 0.070 (1), 0.068 (1), −0.070 (4) and −0.087 (5) Å, respectively, from the coordination plane of the metal atom. The Rh—P, Rh—O and Rh—C distances (Table 2) are in good agreement with those observed in the BF_4^- salt and in related transition-metal complexes (Alcock, Brown & Jeffery, 1976, 1977; Ceriotti, Ciani & Sironi, 1983; Dahan & Choukroun, 1985; Rheingold & Geib, 1987). The geometrical parameters of the ClO_4^- ion and of the CH$_2$Cl$_2$ solvent molecule are as expected.

In the crystal structure the CH$_2$Cl$_2$ molecules are separated by van der Waals distances from the dimeric [Rh(PPh$_3$)$_2$(CO)(OH$_2$)]$_2$[ClO$_4$]$_2$ units, in which the cations and anions are held together by hydrogen bonding involving H atoms of the coordinated water molecules (Fig. 1, Table 3). The dimeric

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