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THE SYNTHESIS, STRUCTURAL AND SPECTROSCOPIC CHARACTERIZATION OF $Ph_3PAuRuCo_{3-x}Rh_x(CO)_{12}$ (x = 1–3) MIXED METAL CLUSTERS

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Summary

New trimetallic $HRuCo_{3-x}Rh_x(CO)_{12}$ ($x = 1, 2$) mixed metal clusters have been obtained from the reaction of $Rh(CO)_4^-$ with $RuCo_2(CO)_{11}$. The mixture of clusters formed was treated with Ph_3PAuCl to give gold phosphine derivatives. The latter compounds were characterized in solution by ^{31}P NMR spectroscopy and in the solid state by X-ray crystallography. The $Ph_3PAuRuCo_{3-x}Rh_x(CO)_{12}$ ($x = 1$–3) form crystals with mixed composition: triclinic, space group $P\bar{1}$, a 8.968(1), b 14.374(2), c 14.948(2) Å, α 116.51(1), β 94.99(1), γ 87.98(1)^0, $Z = 2$. The molecular structure closely resembles that of the $Ph_3PAuRuCo_3(CO)_{12}$ cluster, with the gold ligand capping the Co–Rh triangle. The ^{31}P spectrum of the mixture is consistent with the mixed metal cluster formulation.

Introduction

The tetrahedral mixed metal clusters of the iron and cobalt groups form one of the most studied mixed metal systems. The formula of these clusters can be generalized as $H_xM_xM'_{4-x}(CO)_{12}$, $x = 0$–4, where M is an iron group metal (Fe, Ru or Os) and M′ is a cobalt group metal (Co, Rh, Ir). These clusters, their ions, and derivatives offer useful systems for studying the properties of a well defined mixed metal system of a variable composition. Clusters of bimetallic composition have been studied extensively in this class for several pairs of elements, but corresponding studies for clusters with three different metals are rare. This may be due to the difficulties in separation and characterization.

In the present study clusters of the composition $HRuCo_{3-x}Rh_x(CO)_{12}$ ($x = 0$–3) were synthesized, and their properties be correlated with those of the corresponding Ru–Rh, Ru–Co and Rh–Co clusters. Related structurally characterized clusters are $HFeCo_3(CO)_{12}$ [1], $HRuCo_3(CO)_{12}$ [2], $HOsCo_3(CO)_{12}$ [3], $HRuRh_3(CO)_{12}$ [4], and the gold phosphine derivatives $Ph_3PAuFeCo_3(CO)_{12}$ [5] and $Ph_3PAuRuCo_3(CO)_{12}$

[6]. The cluster $HRuCo_{3-x}Rh_x(CO)_{12}$ was characterized via the gold phosphine derivatives, which were studied by X-ray diffraction and ^{31}P NMR spectroscopy.

Experimental

Reagents

Literature methods were used to synthesize $Rh(CO)_4^-$ [7], $Co(CO)_4$ [8], $RuCo_2(CO)_{11}$ [9] and Ph_3PAuCl [10]. Other reagents were obtained from commercial sources. Tetrahydrofuran (THF) was dried and deoxygenated by stirring over Na/benzophenone ketyl and freshly distilled before use. Reactions and manipulations were carried out under N_2 up to the stage of chromatographic separations.

Synthesis

The mixture of $HRuCo_{3-x}Rh_x(CO)_{12}$ ($x = 0-3$) was made by stirring $Rh(CO)_4^-$ (from 74 mg $Rh_2(CO)_4Cl_2$) with $RuCo_2(CO)_{11}$ (94 mg) in THF for 1 h, and treating the anionic mixture with 85% H_3PO_4 (eq. 1). The neutral hydride clusters were then extracted by hexane from the acid phase. The components could not be separated from each other by chromatography on silica gel using hexane as eluent. As previously reported $HRuRh_3(CO)_{12}$ decomposes during the separation [4], and ca. 30% of the original ruthenium was isolated as $HRuCo_{3-x}Rh_x(CO)_{12}$ ($x = 0-3$) (35 mg). The gold triphenyl phosphine compounds were prepared in THF by the sequence shown in eq. 2, the hydride ligand was first removed by KH, followed by chromatography (hexane/CH_2Cl_2 = 1/4).

$$Rh(CO)_4^- + RuCo_2(CO)_{11} \xrightarrow[2.\ 85\%\ H_3PO_4]{1.\ THF,\ 1\ h,\ 25^\circ C} \underset{(30\%)}{HRuCo_{3-x}Rh_x(CO)_{12}} \quad (1)$$

$$HRuCo_{3-x}Rh_x(CO)_{12} \xrightarrow[2.\ AuPPh_3Cl]{1.\ KH} \underset{(30\%)}{Ph_3PAuRuCo_{3-x}Rh_x(CO)_{12}} \quad (2)$$

X-ray diffraction

Brown crystals of $Ph_3PAuRuCo_{3-x}Rh_x(CO)_{12}$ suitable for the X-ray analysis were obtained by slow evaporation of a hexane/CH_2Cl_2 solution at 10°C. A flat crystal of dimensions 0.08 × 0.35 × 0.40 mm was selected and mounted on a Nicolet R3m diffractometer. Unit cell parameters were obtained by least-squares refinement of 2θ-angles of 25 carefully centered reflections in the range $15 < 2\theta < 25$. Intensities were collected at 295 K in the range $3 < 2\theta < 55$. Of the total 7915 independent reflections 5749 ($I > 3\sigma(I)$) were used for the refinement of the structure. Intensities were corrected for background, polarisation, and Lorenz effects. Empirical absorption corrections were made for ψ-scan data.

Crystal data. $Ph_3PAuRuCo_{1.6}Rh_{1.4}(CO)_{12}$, triclinic, a 8.968(1), b 14.374(2), c 14.948(2) Å, α 116.51(1), β 94.99(1), γ 87.98(1)°, V 1717.7(4) Å^3, $Z = 2$, space group $P\bar{1}$, Mo-K_α radiation, μ(Mo-K_α) 57.3 cm^{-1}.

The structure was solved by direct and Fourier methods and refined by least-squares calculations of the SHELXTL program package [11] with initially isotropic and then anisotropic thermal parameters for non-hydrogen atoms. The hydrogen atoms were placed at their geometrically calculated positions (C–H 0.96 Å) and refined with isotropic thermal parameters ($U(H) = 1.2 \times U$(parent C)). The structure

TABLE 1

INFRARED SPECTRA (hexane solution)

	ν(CO) (cm^{-1})
$HRuCo_3(CO)_{12}$	2065vs, 2058vs, 2025s, 1887s
$HRuRh_3(CO)_{12}$	2106w, 2077s, 2067vs, 2036m, 2012m, 1917m, 1898m, 1883m
$HRuCo_{3-x}Rh_x(CO)_{12}$	2110w, 2082s, 2076s, 2065vs, 2056vs, 2035s, 2024m, 2015w, 1917m 1895w, 1885m, 1867m, 1860sh
$Ph_3PAuRuCo_3(CO)_{12}$	2082m, 2055vs, 2030s, 2020s, 1992s, 1960vs, 1865m
$Ph_3PAuRuRh_3(CO)_{12}$	2080m, 2062w, 2038vs, 2010w, 1990s, 1885s
$Ph_3PAuRuCo_{3-x}Rh_x(CO)_{12}$	2080m, 2055vs, 2038s, 2025s, 2015s, 2000vw, 1990s, 1960vs, 1885w, 1868w, 1857m

consists of a trigonal bipyramidal $AuRuCo_xRh_{3-x}$ core with the Ru and Au atoms in apical positions. The metal atoms in the equatorial positions are disordered and the crystal evidently contains separate $Ph_3PAuRuCo_3(CO)_{12}$, $Ph_3PAuRuCo_2Rh(CO)_{12}$, $Ph_3PAuRuCoRh_2(CO)_{12}$ and $Ph_3PAuRuRh_3(CO)_{12}$ molecules. All possible combinations of the rhodium and cobalt atoms in the equatorial plane were included in the structure determination. In every ordered model the electron density map calculations revealed either considerable residual electron density or negative wells in equatorial metal sites. The best model ($R = 0.051$ and $R_w = 0.054$) was achieved when both rhodium and cobalt atoms were placed in every equatorial metal atom position with site occupancy factors of 0.35, 0.20, 0.85 for Rh and 0.65, 0.80, 0.15 for Co atom in metal sites 1, 2 and 3, respectively. The final difference electron density map in the equatorial plane was featureless. The disordered model is also supported by the observed metal–metal distances.

NMR-spectroscopy

^{31}P NMR spectra were recorded on a Bruker AM-250 spectrometer in 10 mm NMR tubes using $CDCl_3$ as a solvent at ambient temperature. Broad-band decoupling was used to remove the $^1H-^{31}P$ couplings. The shifts are relative to 85% H_3PO_4 placed in a coaxial tube.

IR spectroscopy

Infrared spectra were recorded in n-hexane solution on a Perkin–Elmer 297 infrared spectrophotometer using ZnS solution cells. The data are given in Table 1.

Results and discussion

The synthesis of $HRuCo_{3-x}Rh_x(CO)_{12}$ and their gold phosphine derivatives confirms that the standard metallate anion method also provides a synthetic route to heterometallic clusters of three different elements, as was demonstrated previously by Vahrenkamp [18]. The difficulties in the separation of the individual clusters were circumvented by using the gold phosphine derivatives.

The crystal structure of $Ph_3PAuRuCo_{3-x}Rh_x(CO)_{12}$ shows the common bipyramidal metal frame, Fig. 1. The coordinates of the atoms and the selected bond lengths and angles are given in Tables 2 and 3. All observed Ru–M_i ($i = 1, 2, 3$) distances (Table 4) are longer than the Ru–Co distances in the comparable $RuCo_3M$

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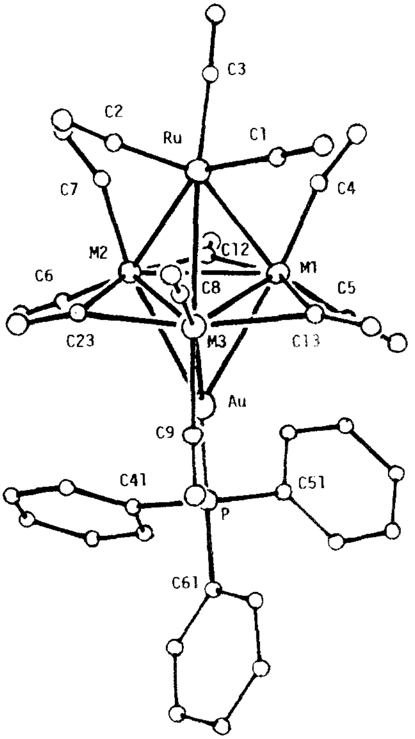

Fig. 1. Numbering scheme for $Ph_3PAuRuM_3(CO)_{12}$ (M = Rh or Co).

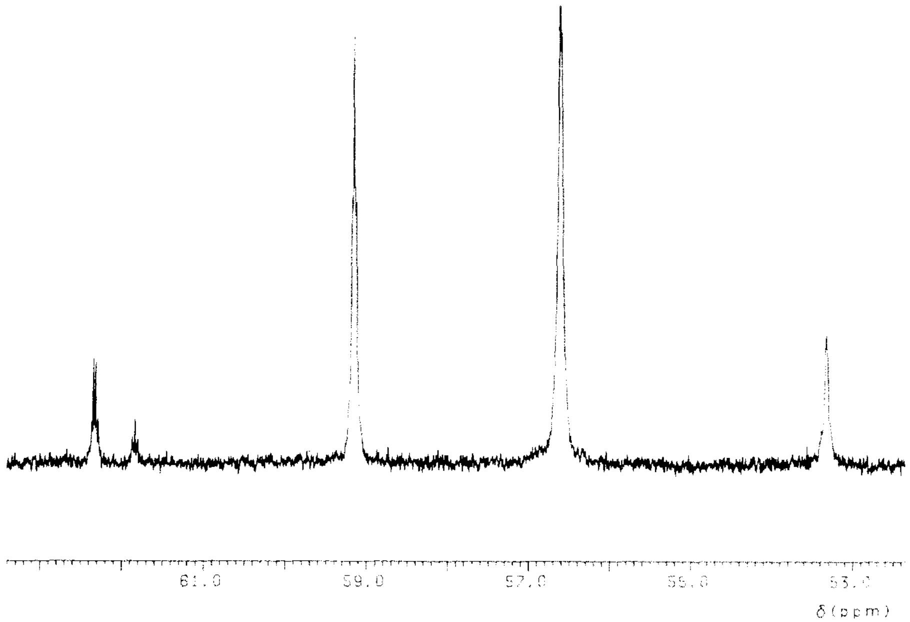

Fig. 2. 101.2 MHz ^{31}P-NMR spectrum of $Ph_3PAuRuCo_{3-x}Rh_x(CO)_{12}$ where $x = 0, 1, 2$ and 3. The resonance at 61.8 ppm is due to an impurity.

TABLE 2

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) AND TEMPERATURE FACTORS ($Å^2 \times 10^3$) FOR $Ph_3PAuRuCo_{1.6}Rh_{1.4}(CO)_{12}$

Atom	x	y	z	U [a]
Au	3391(1)	4321(1)	2303(1)	46(1)
Ru	2940(1)	7882(1)	3917(1)	43(1)
M(1) [b]	4846(1)	6233(1)	3490(1)	42(1)
M(2) [b]	2644(1)	6114(1)	2139(1)	39(1)
M(3) [b]	1999(1)	5994(1)	3790(1)	35(1)
P	4016(2)	2631(2)	1333(2)	40(1)
O(1)	3392(11)	8740(7)	6190(5)	84(4)
O(2)	−138(10)	8876(8)	4021(8)	101(5)
O(3)	4452(11)	9726(7)	3885(6)	87(4)
O(4)	6761(10)	8064(8)	4364(8)	98(5)
O(5)	7513(9)	4965(8)	3533(8)	98(5)
O(6)	1866(12)	5013(10)	7(6)	116(6)
O(7)	2260(11)	7920(6)	1773(6)	87(4)
O(8)	−22(12)	7363(7)	5364(8)	109(5)
O(9)	877(11)	4086(6)	3890(8)	93(5)
O(12)	5700(9)	5975(10)	1502(7)	107(6)
O(13)	4423(9)	6186(7)	5438(6)	77(4)
O(23)	−585(7)	5905(8)	2282(7)	86(5)
C(1)	3253(11)	8407(7)	5351(7)	54(4)
C(2)	1004(11)	8471(8)	3963(8)	62(4)
C(3)	3930(12)	9002(8)	3878(7)	60(4)
C(4)	5810(16)	7448(10)	4049(9)	80(5)
C(5)	6443(11)	5385(9)	3446(8)	63(5)
C(6)	2176(13)	5396(9)	832(8)	70(5)
C(7)	2492(11)	7374(8)	2180(8)	62(4)
C(8)	755(11)	6858(8)	4769(9)	64(5)
C(9)	1318(11)	4739(8)	3791(8)	60(4)
C(12)	4852(10)	6052(8)	2054(7)	59(4)
C(13)	4055(11)	6152(8)	4669(6)	53(4)
C(23)	668(10)	5955(7)	2512(7)	53(4)
C(41)	3504(9)	2165(7)	2(6)	46(3)
C(42)	4385(12)	1408(9)	−706(7)	66(5)
C(43)	3988(15)	1043(12)	−1686(8)	85(6)
C(44)	2724(19)	1395(13)	−2017(10)	99(7)
C(45)	1849(18)	2089(15)	−1371(11)	113(9)
C(46)	2240(12)	2509(10)	−311(9)	75(5)
C(51)	6026(9)	2470(7)	1416(6)	50(3)
C(52)	6715(12)	1794(11)	1741(9)	75(6)
C(53)	8261(14)	1732(15)	1831(12)	115(9)
C(54)	9112(12)	2335(14)	1575(12)	118(8)
C(55)	8446(12)	2985(11)	1224(13)	114(8)
C(56)	6882(11)	3076(9)	1145(11)	81(6)
C(61)	3219(8)	1692(6)	1655(6)	43(3)
C(62)	3095(10)	1946(8)	2657(7)	55(4)
C(63)	2461(13)	1293(10)	2948(9)	72(5)
C(64)	1897(14)	339(10)	2227(11)	79(6)
C(65)	1984(14)	74(9)	1221(10)	80(5)
C(66)	2638(12)	746(8)	948(8)	62(4)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U tensor. [b] The metal atom M(1), M(2) and M(3) sites are occupied by the Co and Rh atoms with occupancy factors of 0.65, 0.80, 0.15 for Co and 0.35, 0.20, 0.85 for Rh.

TABLE 3

SELECTED BOND LENGTHS (A) AND ANGLES (°) FOR $Ph_3PAuRuCo_{1.6}Rh_{1.4}(CO)_{12}$ (occupancy factors for Co and Rh in the metal sites M(1), M(2) and M(3) are 0.65, 0.80, 0.15 and 0.35, 0.20, 0.85, respectively)

Ru–M(1)	2.740(1)	M(1)–C(13)	2.007(11)	C(1)–Ru–M(1)	95.2(3)
Ru–M(2)	2.737(1)	M(3)–C(13)	2.127(9)	C(1)–Ru–M(3)	89.1(3)
Ru–M(3)	2.790(1)	M(2)–C(23)	1.954(10)	C(2)–Ru–M(2)	101.6(3)
M(1)–M(2)	2.652(1)	M(3)–C(23)	2.143(10)	C(2)–Ru–M(3)	96.2(4)
M(1)–M(3)	2.690(1)	Ru–C(1)	1.926(10)	C(3)–Ru–M(1)	110.1(3)
M(2)–M(3)	2.662(1)	Ru–C(2)	1.898(10)	C(3)–Ru–M(2)	115.4(3)
Au–M(1)	2.810(1)	Ru–C(3)	1.891(13)	C(4)–M(1)–Ru	67.6(5)
Au–M(2)	2.749(1)	Ru–C(4)	2.638(13)	C(4)–M(1)–M(2)	113.5(5)
Au–M(3)	2.789(1)	M(1)–C(4)	1.782(13)	C(4)–M(1)–M(3)	123.8(4)
Au–P	2.285(2)	M(1)–C(5)	1.833(11)	C(7)–M(2)–Ru	58.6(3)
P–C(41)	1.814(9)	M(2)–C(6)	1.774(10)	C(7)–M(2)–M(1)	106.4(3)
P–C(51)	1.810(8)	M(2)–C(7)	1.786(12)	C(7)–M(2)–M(3)	115.9(4)
P–C(61)	1.809(11)	Ru–C(7)	2.363(12)	C(8)–M(3)–Ru	82.6(4)
M(1)–C(12)	2.045(12)	M(3)–C(8)	1.869(10)	C(8)–M(3)–M(1)	131.4(3)
M(2)–C(12)	1.992(9)	M(3)–C(9)	1.926(13)	C(8)–M(3)–M(2)	128.3(4)

clusters. They are also somewhat longer than the Ru–Rh distances in $HRuRh_3(CO)_{12}(PPh_3)_2$ [4] but in the same range as those in $HRuRh_3(CO)_{12}$ [4]. The same feature is more clearly seen in the M_i–M_j (i, j = 1, 2, 3) distances (Table 4). Ruthenium atoms could conceivably present in equatorial positions as well, but such models were excluded by the NMR studies. The metal–metal distances and metal–ligand angles do not indicate any hydride ligands, which should be present if there were more than one ruthenium atom in the cluster.

The terminal and bridging carbonyl groups show normal M–C bond lengths except the C(4) and C(7) carbonyl carbons, which semibridge M_1–Ru and M_2–Ru. Similar semibridges are found in $Ph_3PAuRuCo_3(CO)_{12}$ [6] and $(Ph_3PAu)_2CoRu_3H(CO)_{12}$ [12].

The ^{31}P NMR spectrum of the $Ph_3PAuRuCo_{3-x}Rh_x(CO)_{12}$ mixture is shown in Fig. 2. There are four almost equally spaced groups of ^{31}P resonances in a sequence: a singlet at 53.3, a broadened doublet at 56.6, a triplet at 59.2, and a quartet at 62.3 ppm. The singlet at 53.5 and the quartet at 62.3 ppm were assigned to $Ph_3PAuRuCo_3(CO)_{12}$ and $Ph_3PAuRuRh_3(CO)_{12}$ by comparison with the spectra of the authentic samples [19]. The quartet is due to the P–Rh two-bond couplings with ^2J(Rh–P) of 2.7 Hz.

The middle two resonances are assigned for $Ph_3PAuRuRh_2Co(CO)_{12}$ and for $Ph_3PAuRuRhCo_2(CO)_{12}$. Their chemical shifts are in a good agreement with the expected values and the multiplicities (triplet and doublet) together with the line broadening agree well with the presence of Rh_2Co and $RhCo_2$ entities in the equatorial plane.

The present results show that ^{31}P NMR is a sensitive probe for determination of the structures of gold phosphine substituted metal clusters.

TABLE 4

COMPARISON OF METAL–METAL BOND LENGTHS IN TRIGONAL BIPYRAMIDAL RuM_3M' CORES, WHERE M IS Co, Rh AND/OR Ru AND M′ IS Au, Hg, Rh or H

Compound	Ru–M(1)	Ru–M(2)	Ru–M(3)	M(1)–M(2)	M(1)–M(3)	M(2)–M(3)	M′–M(1)	M′–M(2)	M′–M(3)	Ref.
$RuCo_3H(CO)_{10}(PPh_3)_2$	2.656(2)	2.643(3)	2.640(2)	2.526(3)	2.512(3)	2.503(2)				4
$RuCo_3Hg(CO)_{12}Co(CO)_4$	2.686(5)	2.686(5)	2.677(6)	2.509(6)	2.519(7)	2.499(7)	2.765(5)	2.706(5)	2.799(5)	12
$RuCo_3Au(CO)_{12}PPh_3$	2.679(4)	2.664(4)	2.687(5)	2.539(6)	2.543(3)	2.497(5)	2.745(4)	2.679(4)	2.740(4)	6
$RuCo_{1.6}Rh_{1.4}Au(CO)_{12}PPh_3$	2.740(1)	2.737(1)	2.790(1)	2.652(1)	2.690(1)	2.662(1)	2.810(1)	2.749(1)	2.789(1)	this work
$RuRh_3(CO)_{12}H$	2.726(6)	2.733(4)	2.878(5)	2.798(5)	2.753(6)	2.748(4)				4
$RuRh_3H(CO)_{10}(PPh_3)_2$	2.722(0)	2.724(0)	2.719(0)	2.802(0)	2.733(0)	2.789(0)				4
$RuRh_3Rh(CO)_{15}{}^{2-}$	2.962(2)	2.998(2)	3.005(2)	2.721(3)	2.728(2)	2.683(2)	2.926(2)	3.061(3)	3.099(2)	13
$RuCo_2RuH(CO)_{12}H$	2.666(1)	2.663(1)	2.904(1)	2.546(1)	2.643(1)	2.653(1)				14
$RuCo_2RuAu(CO)_{12}Au(PPh_3)_2$	2.690(3)	2.675(3)	2.785(2)	2.492(4)	2.954(3)	2.723(2)	2.651(3)	2.866(3)	2.887(2)	15
$RuCoRu_2Au(CO)_{13}PPh_3$	2.710(1)	2.818(1)	2.837(1)	2.631(2)	2.629(2)	3.025(1)	2.868(2)	2.776(1)	2.774(1)	16
$RuCoRu_2Au(CO)_{12}Au(PPh_3)_2$	2.691(3)	2.826(2)	2.833(2)	2.697(3)	2.786(3)	2.989(2)	2.704(3)	2.915(2)	2.953(2)	16
$RuCoRu_2Au(CO)_{12}Au_2(PPh_3)_3$	2.692(4)	2.869(4)	2.844(2)	2.825(4)	2.710(3)	2.992(3)	2.726(4)	2.850(2)	3.054(3)	17

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