The Reactivity of $HRu_3(CO)_9C_2Bu^t$. The Synthesis and Crystal Structure of $(PPh_3)AuRu_3(CO)_9C_2Bu^t$, a New Ruthenium-Gold Cluster

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The $(PPh_3)AuRu_3(CO)_9C_2Bu^t$ complex has been obtained by reacting $(PPh_3)AuCl$ with the anionic complex $[Ru_3(CO)_9C_2Bu^t]^-$, prepared from the hydride $HRu_3(CO)_9C_2Bu^t$ with a new procedure. The crystal structure of this heterometallic complex, as acetone solvate, has been determined by X-ray methods: it crystallizes in the orthorhombic space group Fdd2, *with 16 molecules in a unit cell of dimensions $a = 33.64(2)$, $b = 48.38(2)$, $c = 9.23(1)$ Å. The structure has been solved from diffractometer data by direct and Patterson methods, and refined by full-matrix least-squares to $R = 0.068$ for 1628 observed reflections.*

The complex consists of a $AuRu_3$ cluster in a butterfly arrangement with the Au atom on a wingtip. The Au atom of the $Au(PPh_3)$ group bridges one side of the ruthenium triangle and practically substitutes the hydride ligand of the $HRu_3(CO)_9C_2Bu^t$ complex, maintaining the basic features of the $Ru_3(CO)_9C_2Bu^t$ framework virtually unchanged.

Introduction

The chemistry of the hydride $HRu_3(CO)_9C_2Bu^t$ (complex I) [1] has been extensively investigated. It has been shown that the reactivity of this cluster is remarkably influenced by the acetylide coordination, *i.e.* by the presence of a nucleophilic C(σ) atom and of a Ru–C(σ) bond.

Thus the phosphines substitute regiospecifically on the ruthenium atom involved in the σ bond with the acetylide [2]; alkynes easily insert into the Ru–C(σ) bond or give addition on the C(σ) [3]; finally, electron-rich metal fragments give addition on C(σ) forming heterometallic species [4].

The hydridic hydrogen also shows an interesting reactivity; indeed, when I is reacted with alkynes, the hydride is shifted on the new formed organic moiety [3] and in the reactions with nickel derivatives an hydride shift to originate a vinylidene ligand is observed [4]. Both these processes were confirmed 'via' deuteration experiments [3, 5].

'Abstraction' of the hydride was also found possible in presence of Ph_2PCl [6]: the open $Ru_3(CO)_9(C_2Bu^t)(PPh_2)$ cluster [7] is formed in small yields.

The hydride I can also be deprotonated; the $[Ph_4As][Ru_3(CO)_9C_2Bu^t]$ salt was obtained by treating a THF solution of I with ethanolic KOH, then adding $Ph_4AsCl\cdot 2H_2O$ [8]. The anion $[Ru_3(CO)_9C_2Bu^t]^-$ (II) reacts with mercury salts to give the mercury-bridged complexes $[Ru_3(CO)_9(C_2Bu^t)(HgBr)]_2$ (III) [9] and $[Ru_3(CO)_9(C_2Bu^t)]_2Hg$(IV) [10].

As part of a general study of the reactivity of the hydridic bridge in I, and of the use of metal carbonylates in cluster syntheses [11], we now report a new procedure for obtaining the anion II and the *in situ* reactions of this anion with $(PPh_3)AuCl$ to form the new mixed-metal cluster $[(PPh_3)AuRu_3(CO)_9C_2Bu^t]$ (V).

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TABLE I. Infrared Bands (cm^{-1}) in the Carbonyl Region.

Complex	Medium	Frequencies	Reference
I	CCl_4	2097m, 2070vs, 2054vs, 2022vs, 1992m	1
	THF	2100mw, 2072vs, 2050vs, 2020vs, 1983m	this work
	KBr	2095m, 2056vs, 2026sh, 2003vs, 1980vs, 1951m	this work
II	THF	2048m, 2018ms, 2000vs, 1992vs, 1967vs, 1943s	this work
III	KBr	2090w, 2050s, 2000s, 1995w	9
V	Hexane	2074m, 2051s, 2036vs, 1996vs, 1968m	this work
	KBr	2067m, 2025vs, 1989vs, 1980sh, 1965s	this work

In view of the isolobal relationship between $AuPPh_3$ and H, it is particularly important to recognize that the exact location of the $AuPPh_3$ group from X-ray studies of a cluster may serve to assess or confirm the location of the H atom in the corresponding hydrido cluster. Thus, it has recently been shown that $AuPPh_3$ can bind to three cobalt atoms in a triply-bridging manner in the two clusters $FeCo_3(CO)_{12}AuPPh_3$ [12] and $RuCo_3(CO)_{12}AuPPh_3$ [13]. This supports the view that the H atom is μ_3-bonded to the Co_3 face in the corresponding $HFeCo_3(CO)_{12}$ an $HRuCo_3(CO)_{12}$ clusters. Complex V is the first acetylide-substituted ruthenium–gold derivative and, to our knowledge, $AuRu_3(\mu_2\text{-COMe})(CO)_{10}(PPh_3)$ [14] is the only other reported Au–Ru mixed cluster. V shows a butterfly arrangement of the metal atoms and the $(PPh_3)Au$ group replaces the hydride-bridge of I, the $Ru_3(CO)_9C_2Bu^t$ group remaining almost unaltered.

Recently Johnson and Lewis [15] reported the synthesis of $AuOs_3$ clusters *via* the reaction of the $[HOs_3(CO)_{11}]^-$ anion with $(PPh_3)AuCl$; the complexes $HOs_3Au(CO)_{10}(PPh_3)$ (VI) and $Os_3Au(CO)_{10}(PPh_3)(SCN)$ (VII) were obtained in good yields. Heterometallic complexes containing gold are particularly interesting because of the versatility of the gold coordination. Examples are now known where gold is linearly bonded to one metal atom, *e.g.* as in Ph_3PAu–M (M = $Mn(CO)_5$, $Co(CO)_4$, $Mo(CO)_3Cp$), [16], linearly bonded to two metal atoms as in the $[M–Au–M]^-$ complexes [17], tricoordinated to two metal atoms and one phosphine ligand as in V and the above mentioned $AuRu_3$ and $AuOs_3$ clusters, and tetracoordinated to three or four metal atoms as in Fe(or Ru)$Co_3(CO)_{12}AuPPh_3$ [12, 13] or $[Os_6Au(CO)_{20}H_2]^-$ [18], respectively.

Experimental

The reactions were performed in Schlenk-type flasks under dry nitrogen. Solvents were distilled under nitrogen from sodium benzophenone-ketyl prior to use. Nitrogen was passed through BASF R3-11 catalyst and molecular sieve columns to remove residual oxygen and water.

Complex I was prepared and purified by procedures already reported.

Synthesis and Crystallization of V

Solid sodium hydride (10 mmol) was added to a yellow THF solution (25 ml) of I (0.4 mmol). The suspension was stirred for 24 hours at room temperature, until the i.r. spectrum underwent significant change (see Table I) and the colour changed to brown.

The reaction mixture containing II was filtered and added to a THF solution (10 ml) of $(PPh_3)AuCl$ (0.4 mmol). The solution was stirred for 3 hours at 0 °C, the progress of the reaction being followed by means of i.r. spectroscopy (ν(CO) region). The solution was then evaporated to dryness under reduced pressure. The resulting powder was extracted with hexane, giving an orange solution which was reduced to small volume. Upon cooling at −78 °C it afforded a yellow microcrystalline product, which by slow recrystallization from acetone at room temperature gave crystals of V, as acetone solvate, suitable for X-ray structural analysis.

The complex was analyzed by means of a Perkin-Elmer mod. 240 elemental analyzer giving satisfactory C, H values. Infrared spectra were recorded on a Perkin-Elmer 398 double beam spectrophotometer.

X-Ray Data Collection

A yellow-orange, thin, prismatic crystal of the complex V, having approximate dimensions 0.06 × 0.10 × 0.30 mm was used for the X-ray data collection. Unit cell parameters, preliminary determined from rotation and Weissenberg photographs, were refined by a least-squares procedure applied to the 29 θ values of accurately measured reflections on a Siemens AED single-crystal diffractometer, using the nickel-filtered CuKα radiation ($\bar{\lambda}$ = 1.54178 Å). Crystal data are as follows: $C_{33}H_{24}AuO_9PRu_3 \cdot ½(CH_3)_2CO$, M = 1124.73, orthorhombic, a = 33.64(2), b = 48.38(2), c = 9.23(1) Å; V = 15022(19)

TABLE II. Fractional Atomic Coordinates ($\times 10^4$) with e.s.d.s. in Parentheses for the Non-hydrogen Atoms.

	x/a	*y/b*	*z/c*
Au	1023(1)	2012(1)	2857
Ru1	1480(1)	1284(1)	710(5)
Ru2	1318(1)	1493(1)	3460(5)
Ru3	770(1)	1572(1)	1186(5)
P	1016(3)	2478(2)	3192(14)
O1	2002(16)	1745(11)	–496(62)
O2	1309(13)	1001(8)	–2237(56)
O3	2134(12)	879(8)	1591(47)
O4	1049(10)	1720(7)	6256(46)
O5	1828(10)	1058(7)	5022(39)
O6	2049(11)	1853(8)	3073(46)
O7	20(11)	1872(7)	2110(41)
O8	377(11)	1256(7)	–1250(45)
O9	1065(13)	2010(9)	–848(52)
O10	2500	2500	–3682(81)
C1	1863(19)	1549(12)	–59(72)
C2	1348(18)	1113(13)	–1133(83)
C3	1883(15)	1034(10)	1225(61)
C4	1117(14)	1621(9)	5112(57)
C5	1628(15)	1219(10)	4367(57)
C6	1773(17)	1737(11)	3330(63)
C7	316(15)	1762(10)	1880(53)
C8	508(14)	1373(9)	–336(57)
C9	947(19)	1846(15)	82(86)
C10	1046(12)	1187(8)	2013(46)
C11	762(11)	1250(7)	2890(50)
C12	459(13)	1105(9)	3864(54)
C13	177(15)	981(10)	2776(67)
C14	633(15)	876(9)	4685(57)
C15	218(16)	1303(11)	4912(66)
C16	1070(9)	2584(6)	5083(27)
C17	864(9)	2807(6)	5682(27)
C18	934(9)	2885(6)	7116(27)
C19	1210(9)	2740(6)	7950(27)
C20	1416(9)	2517(6)	7351(27)
C21	1346(9)	2439(6)	5918(27)
C22	565(8)	2646(6)	2554(35)
C23	580(8)	2852(6)	1497(35)
C24	230(8)	2974(6)	1001(35)
C25	–135(8)	2890(6)	1561(35)
C26	–151(8)	2684(6)	2617(35)
C27	199(8)	2562(6)	3114(35)
C28	1444(8)	2647(6)	2345(33)
C29	1663(8)	2496(6)	1332(33)
C30	1980(8)	2621(6)	610(33)
C31	2079(8)	2895(6)	899(33)
C32	1860(8)	3046(6)	1912(33)
C33	1542(8)	2922(6)	2635(33)
C34	2500	2500	–5007(82)
C35	2189(20)	2365(16)	–6035(81)

Å^3, $Z = 16$, $D_c = 1.99$ g cm^{-3}, μ(CuKα) = 179.75 cm^{-1}, space group: *Fdd*2 from systematic absences.

The crystal diffracted weakly and showed a significant fall-off of intensities at higher angles. A total of 2937 independent reflections with θ in the range 3–60° were measured on the same diffractometer using the Ni-filtered CuKα radiation and the $\theta/2\theta$ scan technique. 1628 reflections having $I > 2\sigma(I)$ were considered observed, and were used in the analysis. The structure amplitudes were obtained after the usual Lorentz and polarization corrections; no corrections were applied for the absorption effects, because of the small size of the crystal. Data were placed on an approximate absolute scale by means of a Wilson's plot which also provided the average overall temperature factor.

Structure Determination and Refinement

The structure was solved by combined direct and Patterson methods. The refinement was carried out by least-squares full-matrix cycles using the SHELX system of computer programs [19], first with isotropic and then anisotropic thermal parameters for the Au, Ru and P atoms only. No attempt was made to localize the hydrogen atoms. The final conventional R factor was 0.068 for the observed reflections only. Atomic scattering factors, corrected for the anomalous dispersion of Au, Ru and P atoms were taken from International Tables [20]. The function minimized in the least-squares calculations was $\Sigma w|\Delta F|^2$; unit weights were used in the first cycles of refinement while in the final cycles the weight used was calculated as $w = K/[\sigma^2(F_o) + gF_o^2]$, with $K = 0.1123$ and $g = 0.005$.

The atomic fractional coordinates for the non-hydrogen atoms are listed in Table II, the thermal parameters and the list of observed and calculated structure factors are available from the authors on request.

All the calculations were performed on the CYBER 76 computer of Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna, with financial support from the University of Parma.

Results and Discussion

The i.r. spectra of the complexes I, II, III and V are given in Table I. Apparently the presence of gold instead of the hydride ligand on the basic structure of I has a considerable influence in lowering the CO stretching frequencies. The more pronounced negative shift, observed for the compound II, is in agreement with its anionic nature.

The X-ray structure of the complex V is represented in Fig. 1; selected bond distances and angles are given in Table III. The complex consists of a tetrametallic cluster of three Ru and one Au atoms, in a butterfly arrangement with the heteroatom on a wingtip. The dihedral angle between the two triangular Au–Ru(2)–Ru(3) and Ru(1)–Ru(2)–Ru(3) wings is 129.3° and the non-bonding Au–Ru(1)

TABLE III. Selected Bond Distances (Å) and Angles (°) with Their Estimated Standard Deviations.

a) In the coordination sphere of the metal atoms

Au–Ru(2)	2.757(1)	Ru(2)–C(4)	1.78(1)
Au–Ru(3)	2.763(1)	Ru(2)–C(5)	1.88(2)
Au–P	2.276(3)	Ru(2)–C(6)	1.94(2)
Ru(1)–Ru(2)	2.786(2)	Ru(2)–C(10)	2.19(1)
Ru(1)–Ru(3)	2.800(1)	Ru(2)–C(11)	2.27(1)
Ru(2)–Ru(3)	2.820(1)	Ru(3)–C(7)	1.89(1)
Ru(1)–C(1)	1.95(2)	Ru(3)–C(8)	1.92(1)
Ru(1)–C(2)	1.94(2)	Ru(3)–C(9)	1.77(2)
Ru(1)–C(3)	1.88(2)	Ru(3)–C(10)	2.22(1)
Ru(1)–C(10)	1.95(1)	Ru(3)–C(11)	2.21(1)

Ru(2)–Au–Ru(3)	61.4(1)	Ru(3)–Ru(2)–C(11)	50.2(3)
Ru(2)–Au–P	151.5(1)	C(10)–Ru(2)–C(11)	33.5(4)
Ru(3)–Au–P	146.7(1)	C(10)–Ru(2)–Au	110.0(3)
Ru(2)–Ru(1)–Ru(3)	60.6(1)	C(10)–Ru(2)–Ru(1)	44.1(3)
Ru(3)–Ru(2)–Au	59.4(1)	C(11)–Ru(2)–Au	97.4(3)
Ru(3)–Ru(2)–Ru(1)	59.9(1)	C(11)–Ru(2)–Ru(1)	76.2(3)
Au–Ru(2)–Ru(1)	102.5(1)	C(10)–Ru(3)–C(11)	33.8(4)
Au–Ru(3)–Ru(1)	102.0(1)	C(10)–Ru(3)–Au	109.0(3)
Au–Ru(3)–Ru(2)	59.2(1)	C(10)–Ru(3)–Ru(1)	43.8(3)
Ru(1)–Ru(3)–Ru(2)	59.4(1)	C(10)–Ru(3)–Ru(2)	49.9(3)
Ru(2)–Ru(1)–C(10)	51.6(4)	C(11)–Ru(3)–Au	98.6(3)
Ru(3)–Ru(1)–C(10)	52.0(4)	C(11)–Ru(3)–Ru(1)	76.8(3)
Ru(3)–Ru(2)–C(10)	50.6(3)	C(11)–Ru(3)–Ru(2)	52.0(3)

b) In the carbonyl groups

O(1)–C(1)	1.13(2)	O(6)–C(6)	1.11(2)
O(2)–C(2)	1.16(2)	O(7)–C(7)	1.15(2)
O(3)–C(3)	1.18(2)	O(8)–C(8)	1.11(2)
O(4)–C(4)	1.18(2)	O(9)–C(9)	1.23(2)
O(5)–C(5)	1.19(2)		

Ru(1)–C(1)–O(1)	162(2)	Ru(2)–C(6)–O(6)	169(2)
Ru(1)–C(2)–O(2)	173(2)	Ru(3)–C(7)–O(7)	170(1)
Ru(1)–C(3)–O(3)	178(2)	Ru(3)–C(8)–O(8)	176(1)
Ru(2)–C(4)–O(4)	169(1)	Ru(3)–C(9)–O(9)	171(2)
Ru(2)–C(5)–O(5)	175(1)		

c) In the organic and triphenylphosphine ligands

C(10)–C(11)	1.29(2)	C(12)–C(15)	1.58(2)
C(11)–C(12)	1.53(2)	P–C(16)	1.83(1)
C(12)–C(13)	1.51(2)	P–C(22)	1.82(1)
C(12)–C(14)	1.46(2)	P–C(28)	1.83(1)

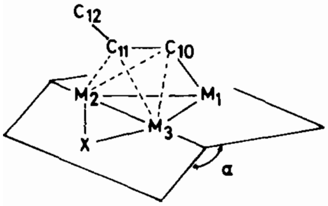
C(16)–P–Au	113.9(3)	C(12)–C(11)–C(10)	139(1)
C(22)–P–Au	114.0(3)	Ru(2)–C(11)–Ru(3)	78(1)
C(28)–P–Au	112.1(3)	Ru(2)–C(11)–C(10)	70(1)

C(11)–C(10)–Ru(1)	152(1)	Ru(3)–C(11)–C(10)	73(1)
C(11)–C(10)–Ru(2)	77(1)	C(13)–C(12)–C(14)	107(1)
C(11)–C(10)–Ru(3)	73(1)	C(13)–C(12)–C(15)	109(1)
Ru(1)–C(10)–Ru(2)	84(1)	C(13)–C(12)–C(11)	102(1)
Ru(1)–C(10)–Ru(3)	84(1)	C(14)–C(12)–C(15)	110(1)
Ru(2)–C(10)–Ru(3)	79(1)	C(14)–C(12)–C(11)	113(1)
C(12)–C(11)–Ru(2)	131(1)	C(15)–C(12)–C(11)	115(1)
C(12)–C(11)–Ru(3)	138(1)		

TABLE IV. Comparison of Bonding Distances (Å) and Angles (°) in the Complexes (I)–(V).[a]

	I [21]	II [8]	III [9]	IV [10]		V
M_1-M_2	2.795(3)	2.800(3)	2.813(3)	2.799(5)	2.812(4)	2.786(2)
M_1-M_3	2.799(3)	2.790(3)	2.806(2)	2.798(5)	2.807(5)	2.800(1)
M_2-M_3	2.792(3)	2.665(3)	2.900(3)	2.855(3)	2.847(3)	2.820(1)
M_2-X	1.798(5)	–	2.733(2)	2.840(6)	2.840(7)	2.757(1)
M_3-X	1.796(5)	–	2.739(2)	2.808(6)	2.819(6)	2.763(1)
M_2-X-M_3	102.3(2)	–	64.0(1)	60.7(1)	60.4(1)	61.4(1)
α (dihedral angle)	115.0	–	127.0	124.4	126.7	129.3
M_1-C_{10}	1.947(3)	1.95(2)	1.96(2)	1.98(3)	1.96(3)	1.95(1)
M_2-C_{10}	2.207(3)	2.18(2)	2.19(2)	2.20(3)	2.17(3)	2.19(1)
M_3-C_{10}	2.214(3)	2.16(2)	2.20(2)	2.16(3)	2.14(3)	2.22(1)
M_2-C_{11}	2.268(3)	2.24(2)	2.25(2)	2.31(4)	2.24(3)	2.27(1)
M_3-C_{11}	2.271(3)	2.24(2)	2.26(2)	2.27(4)	2.21(3)	2.21(1)
$C_{10}-C_{11}$	1.315(3)	1.27(3)	1.31(3)	1.32(4)	1.27(4)	1.29(2)
$M_2-C_{11}-M_3$	75.9(1)	73(1)	80.0(7)	77(1)	79(1)	78(1)
$C_{10}-C_{11}-C_{12}$	141.0(2)	141(2)	140(2)	143(3)	142(3)	139(1)

[a] For the atom labels see the following scheme:



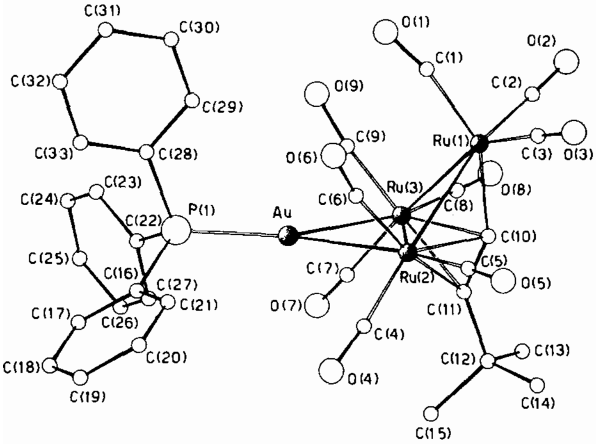


Fig. 1. View of the molecular shape of the complex $(PPh_3)AuRu_3(CO)_9C_2Bu^t$ with the atomic numbering system.

distance is 4.277(1) Å. The Au atom of the $Au(PPh_3)$ group bridges the Ru(2)–Ru(3) side and virtually substitutes the hydride ligand in I, leaving the $Ru_3(CO)_9C_2Bu^t$ framework almost unaltered. In it the three ruthenium atoms define a nearly equilateral triangle [Ru–Ru bonds: 2.786(2), 2.800(1), 2.820(1) Å]; each Ru atom is bound to three terminal carbonyl groups and the t-butylacetylene ligand interacts with all the Ru atoms, *via* one σ-bond with Ru(1) and two π bonds with Ru(2) and Ru(3), with consequent lengthening of the acetylenic bond C(10)–C(11) [1.29(2) Å].

In Table IV the bond distances and angles in the complex $HRu_3(CO)_9C_2Bu^t$ (where the bridging hydride has been precisely localized by neutron diffraction [21]) are compared with those found in the deprotonated complex II, in the complexes III, IV and V where the mercury or gold atom, substituting the hydride ligand in I, bridges one side of the triangular cluster.

The structural parameters of the $Ru_3(CO)_9C_2Bu^t$ framework in all these compounds remain practically unchanged, indicating remarkable rigidity of this framework. The main difference concerns the length of the Ru(2)–Ru(3) bond, involved in the hydride or metal bridge; the removal of the hydride ligand determines a considerable shortening of this bond, in agreement with the increasing metal–metal bonding. However, on substituting the hydride with the mercury atom, a lengthening of this bond is observed, consistent with the picture of a relatively polar Ru–Hg bridge bond, where mercury is more positively charged than the hydride. When gold-bridged, the Ru–Ru bond is only slightly longer than in I showing that the Ru–Au bond is only slightly polar, according to the nucleophilicity ascribed to the Au(PPh$_3$) ligand.

In V, gold is tricoordinated being bonded to two Ru atoms and to the P atom of the triphenylphosphine ligand. Displacements of the Au, Ru(2), Ru(3) and P atoms from the mean plane passing through them are –0.044(3), –0.009(4), –0.011(4) and 0.065(11) respectively. The Au–Ru bonds [2.757(1) and 2.763(1) Å] are comparable with those found in AuRu$_3$(μ_2-COMe)(CO)$_{10}$(PPh$_3$) [2.760(2) and 2.762(2) Å] [14], the only other Au–Ru cluster reported until now, where the Au(PPh$_3$) group is bonded to the Ru$_3$ cluster in a similar way. This last complex has been obtained from HRu$_3$(COMe)(CO)$_{10}$ by replacing the hydride ligand with the isolobal Au(Ph$_3$) group.

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