Mixed-metal Carbido Carbonyl Clusters. Part 4.[1] Synthesis and Structural Characterization of $[Rh_6C(CO)_{13}\{Au_2(PPh_3)_2\}]$ ‡

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The new mixed-metal carbido-carbonyl cluster species $[Rh_6C(CO)_{13}\{Au_2(PPh_3)_2\}]$ has been obtained by reaction of $[Rh_6C(CO)_{13}]^{2-}$ with $[Au(PPh_3)Cl]$. The molecular structure has been determined by single-crystal *X*-ray diffractometry: orthorhombic, space group *Fdd*2, a = 22.335(4), b = 31.710(6), c = 14.947(7) Å, Z = 8, R = 0.045, and R' = 0.047. The cluster is a distorted Rh_6 octahedron with two adjacent triangular faces capped by $Au(PPh_3)$ moieties which also establish an Au–Au bond; the CO-ligand stereogeometry is related to that of the parent dianion. The ^{31}P and ^{13}C solution n.m.r. spectra are consistent with a fluxional behaviour of both the CO groups and the two $Au(PPh_3)$ moieties over the Rh_6 core. The compound reacts easily with CO (1 atm, 101 325 Pa; room temperature) yielding the bicapped trigonal prism $[Rh_6C(CO)_{15}\{Au(PPh_3)\}_2]$.

In previous papers we reported the synthesis and structural characterization in solution and/or solid state of several high-nuclearity mixed-metal clusters derived from reaction of the trigonal prismatic dianion $[Rh_6C(CO)_{15}]^{2-}$ [2] with electrophilic metal fragments such as $M(PPh_3)^+$ (M = Cu, Ag, or Au),[1] $M(NCMe)^+$ (M = Cu or Ag),[1,3] and Ag^+.[4] In all these species the original trigonal prism of Rh atoms is preserved and capping by the heteroatoms occurs exclusively on one or both triangular faces.

In order to extend these studies we attempted the same kind of reactions with the octahedral species $[Rh_6C(CO)_{13}]^{2-}$ [5,6] which is obtained by mild pyrolysis of the prismatic $[Rh_6C(CO)_{15}]^{2-}$. In particular, with $[Au(PPh_3)Cl]$, we obtained $[Rh_6C(CO)_{13}\{Au_2(PPh_3)_2\}]$ the synthesis and crystallographic characterization of which are now reported.

Results and Discussion

Synthesis and Chemical Characterization.—The reaction of $[Rh_6C(CO)_{13}]^{2-}$ with $[Au(PPh_3)Cl]$ is best described by the equilibria (1) and (2). The neutral species (**2**) can be obtained

$$[Rh_6C(CO)_{13}]^{2-} \xrightleftharpoons[Cl^-]{[Au(PPh_3)Cl]} \underset{\textbf{(1)}}{[Rh_6C(CO)_{13}\{Au(PPh_3)\}]^-} \quad (1)$$

$$\textbf{(1)} \xrightleftharpoons[Cl^-]{[Au(PPh_3)Cl]} \underset{\textbf{(2)}}{[Rh_6C(CO)_{13}\{Au_2(PPh_3)_2\}]} \quad (2)$$

as a brick-red fine precipitate when $[Au(PPh_3)Cl]$ is added, in slight excess of the molar ratio 2:1, to a solution of $[KL_{ca.3}]_2[Rh_6C(CO)_{13}]$ (L = diglyme = 2,5,8-trioxanonane) in propan-2-ol. Close i.r. monitoring of the stepwise addition of the gold(I) complex revealed the presence in solution, besides the starting dianion and while some (**2**) had already precipitated, of an intermediate product the concentration of which was almost constant. The i.r. absorptions reasonably suggest it to be the monoanion $[Rh_6C(CO)_{13}\{Au(PPh_3)\}]^-$ (**1**). Clearly the precipitation of (**2**) shifts both equilibria to the right, making competitive the reactions of both (**1**) and the dianion with $[Au(PPh_3)Cl]$.

The same reaction performed in tetrahydrofuran (thf) with $[PPh_3(CH_2Ph)]_2[Rh_6C(CO)_{13}]$ gives, even with an excess of $[Au(PPh_3)Cl]$ (molar ratio 3:1 with respect to the dianion), essentially the monoanion (**1**) which shows i.r. absorptions at 2 040w, 2 002s, and 1 853m cm^{-1}. The lack of precipitation and the build-up of Cl^- hinder further reaction to give (**2**). This is consistent with the observation that pure (**2**) reacts with excess of $[NEt_4]X$ ($X = Cl^-$ or I^-) in thf to give the monoanionic species (**1**), releasing $[Au(PPh_3)X]$. Unfortunately the stability of species (**1**) is very poor and in solution it decomposes within hours giving unknown brown products, thus preventing isolation and full characterization.

The red species (**2**) is also rather unstable and in solution (thf, CH_2Cl_2, $CHCl_3$, acetone, or toluene) at room temperature it is in any case mostly decomposed within 1 or 2 d with formation of brown unidentified products, along with considerable amounts of the bicapped prismatic species $[Rh_6C(CO)_{15}\{Au(PPh_3)\}_2]$.[1] This product is very likely generated by reaction of (**2**) with the small amount of CO set free after partial decomposition to the brown species. The red compound (**2**) is completely converted, by carbon monoxide at room temperature within 1–2 h, into the yellow bicapped trigonal prism $[Rh_6C(CO)_{15}\{Au(PPh_3)\}_2]$ with a non-trivial molecular rearrangement.

Spectroscopic Measurements.—The i.r. spectrum of $[Rh_6C(CO)_{13}\{Au_2(PPh_3)_2\}]$ in thf, Figure 1, shows bands in the carbonyl stretching region at 2 068mw, 2 032s, 1 890(sh), 1 875m, and 1 848mw ± 1 cm^{-1}. Very similar spectra are obtained in other solvents.

The ^{31}P n.m.r. spectrum in thf with 10% $[^2H_8]$thf shows a single signal, a septet with J(P–Rh) = 3.81 ± 0.63 Hz, at 58.4

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* For correspondence on synthesis and chemical characterization.

† For correspondence on structural characterization.

‡ μ_4-{[Bis(triphenylphosphineaurio)(*Au*–*Au*)]-*Au*^{1}(Rh^{1-3})*Au*^{2}-($Rh^{2,3,6}$)}-μ_6-carbido-1,2;1,4;2,5;3,4;3,6;4,5;5,6-hepta-μ-carbonyl-1,2,3,4,5,6-hexacarbonyl-*octahedro*-hexarhodium.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

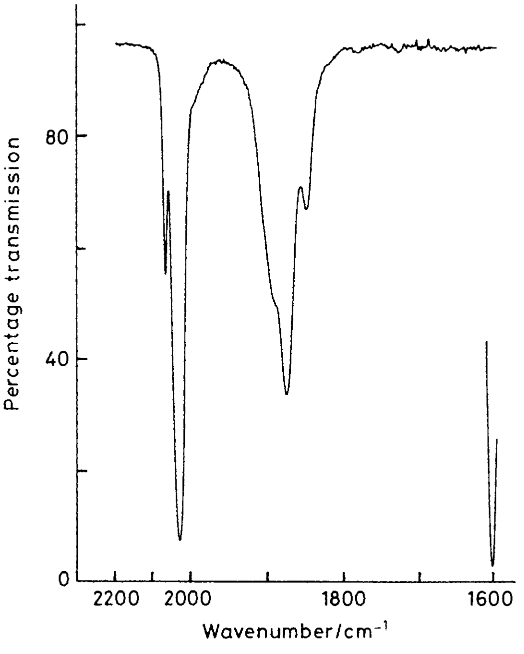

Figure 1. I.r. spectrum of $[Rh_6C(CO)_{13}\{Au_2(PPh_3)_2\}]$ in thf solution

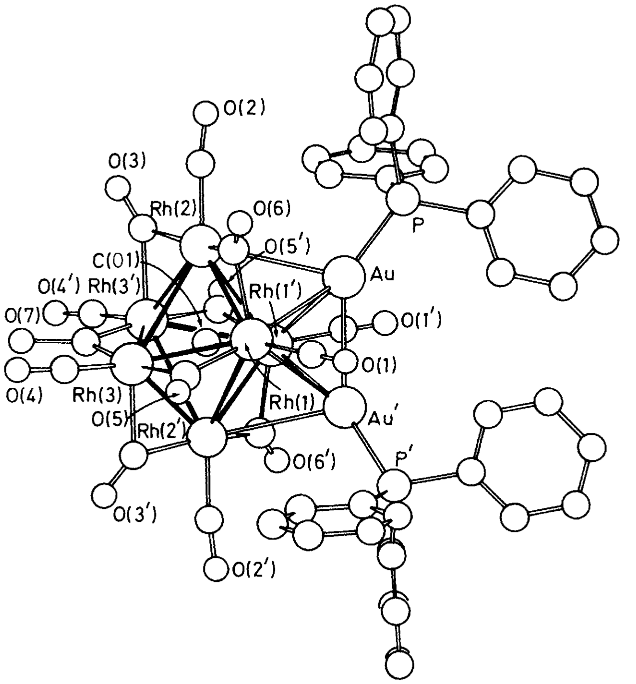

Figure 2. The structure of $[Rh_6C(CO)_{13}\{Au_2(PPh_3)_2\}]$. The C atoms of the CO groups bear the same numbering as the O atoms. The crystallographic two-fold axis bisects the Au–Au bond and comprises the carbide atom and the C(7)–O(7) carbonyl group

p.p.m. The resonance is preserved down to −90 °C with broadening and a slight temperature-dependent shift to 56.3 p.p.m. Analysis of this spectrum is the most convenient way to check the purity of the compound, because the most recurrent impurities, $[Rh_6C(CO)_{15}\{Au(PPh_3)\}_2]$ and excess of $[Au(PPh_3)Cl]$, can easily be detected having resonances at 48.6 [q, J(P–Rh) = 5.0 ± 0.6 Hz] and 33.9 p.p.m. (s), respectively.

Natural-abundance ^{13}C n.m.r. spectra of a nearly saturated solution in thf with 30% $[^2H_8]$thf (450 mg in 2 cm^3) give at room temperature, in the carbonyl region, just a septet at 209.2 p.p.m. with J(C–Rh) of 13.1 ± 3 Hz, typical of a time-averaged interaction. The carbido resonance occurs at very low field, at 452.5 p.p.m., and although at low intensity (one thirteenth of the former) shows the fine structure of a multiplet with spacing between the lines of 16.8 Hz. These values compare well with those found for the parent dianion $[Rh_6C(CO)_{13}]^{2-}$ (217.7 and 470.0 p.p.m., at room temperature),[6] and the monoanionic hydrido derivative $[Rh_6H(C)(CO)_{13}]^-$ (209.7 and 460.4 p.p.m. at −20 °C).[7]

Description of the Structure.—The molecular structure of $[Rh_6C(CO)_{13}\{Au_2(PPh_3)_2\}]$ (**2**) is shown in Figure 2 together with the labelling scheme. Relevant bond distances and angles are reported in Table 1. The molecular geometry clearly shows its parentage to the octahedral $[Rh_6C(CO)_{13}]^{2-}$ and can be described in terms of dicapping of adjacent octahedron faces by an $Au_2(PPh_3)_2$ unit.

The molecule is located around a crystallographic two-fold axis which bisects the Au–Au′, Rh(1)–Rh(1′), and Rh(3)–Rh(3′) edges. The interstitial carbide atom and the C(7)–O(7) bridging ligand lie on the axis. The idealized molecular symmetry is coincident with the crystallographic one, therefore the molecule is chiral.

The carbonyl distribution is related to that observed in $[Rh_6C(CO)_{13}]^{2-}$. Two equatorial planes contain six CO (four terminal and two bridging *consecutive* edges), and the third contains seven CO (obviously 'sharing' some terminal CO with the other equators). The main difference from the parent dianion is in the latter equator; while in $[Rh_6C(CO)_{13}]^{2-}$ two edges are bridged by CO (CO_b) and the remaining ligands are terminally bound (although some short Rh • • • CO_t contacts are present), in (**2**) three edges bear CO_b. It is enough to 'push' one CO_t of the former towards a bridging position to attain the triply bridged equator of the latter. This task is accomplished by the $Au_2(PPh_3)_2$ unit which is positioned perpendicularly to the unbridged Rh–Rh bond. The seven-carbonyl equatorial plane is reminiscent of the analogous equatorial planes in $[Co_6C(CO)_{13}]^{2-}$ (one bridging and six terminal ligands, two of which are bent towards bridging positions)[8] and of $[Co_2Rh_4C(CO)_{13}]^{2-}$ (one bridging, two semibridging, and four terminal ligands).[9]

The Rh_6 octahedron is heavily distorted, and the Rh–Rh bond lengths fall in the range 2.726(3)—3.246(4) Å. These values can be compared with what is found in the parent dianion $[Rh_6C(CO)_{13}]^{2-}$: in both species short bonds are associated with the presence of bridging CO ligands [2.781(3) and 2.78(1) Å, respectively] while unbridged distances are longer [3.211(3) and 3.04(1) Å]. The distortion of the Rh_6 octahedron is reflected in the Rh–C(carbide) distances, which fall in the range 2.02—2.18(2) Å. This atom is slightly displaced from the centre of the cavity towards the Rh(1)–Rh(1′) edge. The two Au atoms establish two sets of bond distances with the Rh atoms: short bonds [mean 2.830(2) Å] with the atoms Rh(1) and Rh(1′) and 'long' bonds [3.147(2) Å] with the two apical Rh atoms Rh(2) and Rh(2′). Interestingly the Rh(1)–Rh(1′) bond, whose Rh atoms are involved in a total of six metal–metal interactions (two with Au and four with Rh) and of three metal–ligand interactions, shows the longest value [3.246(4) Å].

The Au–Au bond length [2.929(2) Å] can be compared with the values observed in other mixed-metal clusters containing the Au–Au unit such as $[Ru_5WC(CO)_{17}\{Au(PEt_3)\}_2]$ [2.808(3) Å],[10] $[Au_2Ru_4H_2(CO)_{12}(PPh_3)_2]$ [2.791(1) Å],[11] and $[Ru_3(\mu_3\text{-}S)(CO)_9\{Au(PPh_3)\}_2]$ [2.967(2) Å].[12] This comparison shows that Au–Au bond lengths can cover a fairly large range, which does not seem to depend very much on the actual metal framework stereogeometry or nuclearity.

It is to be noted that there are three ways to achieve dicapping of octahedral frameworks: (*i*) on two opposite triangular faces,

Table 1. Relevant bond distances (Å) and angles (°) for compound (**2**), with standard deviations in parentheses

Rh(1)–Rh(2)	2.726(3)	Rh(1)–C(1)	2.02(2)
Rh(1)–Rh(3)	2.796(3)	Rh(2)–C(2)	1.86(4)
Rh(1)–Rh(1′)	3.246(4)	Rh(2)–C(3)	2.02(3)
Rh(1)–Rh(2′)	3.231(3)	Rh(3′)–C(3)	2.08(3)
Rh(2)–Rh(3)	3.156(3)	Rh(3)–C(4)	1.89(4)
Rh(2′)–Rh(3)	2.792(3)	Rh(1)–C(5)	2.07(3)
Rh(3)–Rh(3′)	2.808(4)	Rh(3)–C(5)	2.19(3)
Rh(1)–Au	2.800(2)	Rh(1)–C(6)	2.10(3)
Rh(2)–Au	3.147(2)	Rh(2)–C(6)	2.01(4)
Rh(1)–Au′	2.860(2)	Rh(3)–C(7)	2.05(7)
Au–Au′	2.929(2)	C(1)–O(1)	1.14(4)
C(01)–Rh(1)	2.02(2)	C(2)–O(2)	1.14(5)
C(01)–Rh(2)	2.18(2)	C(3)–O(3)	1.14(4)
C(01)–Rh(3)	2.08(2)	C(4)–O(4)	1.18(5)
P–Au	2.256(7)	C(5)–O(5)	1.12(4)
P–C(8)	1.81(3)	C(6)–O(6)	1.13(4)
P–C(14)	1.83(2)	C(7)–O(7)	1.25(11)
P–C(20)	1.75(3)		
P–Au–Au′	140(3)	Rh(1)–C(5)–O(5)	140(3)
Rh(1)–C(1)–O(1)	177(3)	Rh(3)–C(5)–O(5)	138(3)
Rh(2)–C(2)–O(2)	174(4)	Rh(1)–C(6)–O(6)	133(3)
Rh(2)–C(3)–O(3)	142(3)	Rh(2)–C(6)–O(6)	144(3)
Rh(3′)–C(3)–O(3)	132(3)	Rh(3)–C(7)–O(7)	137(2)
Rh(3)–C(4)–O(4)	175(3)		

(*ii*) on two faces with a common vertex, and (*iii*) on two adjacent faces sharing an edge. The first of these possibilities has been adopted by many homometallic and heterometallic species such as $[Re_8C(CO)_{24}]^{2-}$ [13] and $[Re_7C(CO)_{21}\{Au(PPh_3)\}]^{2-}$ [14] and it certainly optimizes the interligand interactions, particularly when bulky groups such as PPh_3 are to be accommodated. The second choice is adopted in $[Os_8(CO)_{22}]^{2-}$ [15] and is seen as part of the larger multicapped framework of $[Os_{10}C(CO)_{24}]^{2-}$ and derivatives.[16] Capping of adjacent faces might be difficult to attain in the presence of a large number of ligands {as would be the case for an isomeric form of $[Re_8C(CO)_{24}]^{2-}$}. The latter choice is adopted in the species under examination although formation of a 'regular' Au–Au bond is preferred to symmetric capping of the Rh_3 faces which would leave the Au atoms much further apart. An alternative possibility would be that adopted by the $(CuNCMe)_2$ unit in $[Ru_6C(CO)_{16}\{Cu(NCMe)\}_2]$ [17] where the Cu atoms are bonded together but with only one Cu atom actually capping an octahedron face. However, it is worth stressing that the heteroatom positioning adopted in the present case is able to preserve *at the same time* the ligand distribution of the parent species and a highly symmetric bonding of the Au_2 unit. The co-ordination of the Au_2P_2 fragment does not alter the octahedral arrangement of the Rh_6C core. This fact had already been noted for the prismatic $[Rh_6C(CO)_{15}(ML)_2]$ derivatives (M = Cu, Ag, or Au),[3] and explained in terms of no electron-pair contribution to the cluster orbitals by the ML^+ fragments which act as pure electron acceptors.

Finally, of note is the easy reconversion of (**2**) into the bicapped trigonal prism $[Rh_6C(CO)_{15}\{Au(PPh_3)\}_2]$ which is observed upon treatment with CO. At first sight a simple $O_h \longleftrightarrow D_{3h}$ interconversion around a three-fold axis of the Rh_6 core is ruled out because relocation of the capping atoms, from two edge-sharing faces on the Rh_6 octahedron towards opposite triangular faces on the prism, would also be required. However this is not difficult to achieve since both ^{31}P and ^{13}C n.m.r. data suggest that in solution the $Au(PPh_3)$ fragments move all over the rhodium frame, analogously to the CO ligands, even at very low temperature.

Table 2. Crystal data and details of structure measurement for compound (**2**)

Formula	$C_{50}H_{30}Au_2O_{13}P_2Rh_6$
M_r	1 911.6
Crystal system	Orthorhombic
Space group	*Fdd*2
a/Å	22.335(4)
b/Å	31.710(6)
c/Å	14.947(7)
U/Å^3	10 585
Z	8
λ(Mo-K_α)/Å	0.710 69
F(000)	7 136
D_c/g cm^{-3}	2.40
μ(Mo-K_α)/cm^{-1}	70.9
Crystal dimensions/mm	0.10 × 0.12 × 0.10
Scan mode	ω—2θ
θ Range/°	2—30
Octants of reciprocal space explored	$+h, +k, +l$
No. measured reflections	2 590
No. observed [$I > 2.5\sigma(I)$]	1 787
Final R and R' *	0.045, 0.047
ω Scan width/°	1.20
Prescan speed/° min^{-1}	5
Prescan acceptance $\sigma(I)/(I)$	0.5
Max. scan time/s	140
Requested $\sigma(I)/I$	0.01
No. parameters refined	172

* $R' = \Sigma[(F_o - F_c)w^{\frac{1}{2}}]/\Sigma(F_o w^{\frac{1}{2}})$ where $w = K/[\sigma^2(F) + |g|F^2]$.

Experimental

All the operations were carried out under nitrogen; the solvents were purified and stored under nitrogen. The compounds $K_2[Rh_6C(CO)_{15}]$·*ca.* 3 thf,[18] $[PPh_3(CH_2Ph)]_2[Rh_6C(CO)_{13}]$,[5] and $[Au(PPh_3)Cl]$ [19] were prepared according to the literature. I.r. spectra were recorded on a Perkin-Elmer 781 spectrophotometer equipped with a data station, using 0.1-mm CaF_2 cells previously purged with nitrogen. Phosphorus-31 and ^{13}C n.m.r. spectra were obtained on a Bruker AC200 spectrometer at 81.0 and 50.3 MHz respectively.

Synthesis of $[Rh_6C(CO)_{13}\{Au_2(PPh_3)_2\}]$ *from* $K_2[Rh_6C(CO)_{15}]$·*ca.* 3 thf.—This is a two-step preparation, where the red octahedral $[Rh_6C(CO)_{13}]^{2-}$ is obtained '*in situ*' and then treated with the gold complex. In a typical preparation, a solution of $K_2[Rh_6C(CO)_{15}]$·*ca.* 3 thf (723.5 mg, 0.538 mmol) in propan-2-ol (75 cm^3) was refluxed under nitrogen at 100 °C, making a few evacuations to remove the evolved CO. I.r. monitoring showed that within 1 h the starting dianion had completely disappeared with formation of a red-brown solution. Diglyme (L) (1 cm^3) was then added to the hot solution which was allowed to cool at room temperature. This caused precipitation of brown by-products (as $KL_x{}^+$ salts) which were filtered off, yielding a clear red-orange solution containing almost pure $[Rh_6C(CO)_{13}]^{2-}$ whose i.r. spectrum shows bands at 2 028w, 1 984s, 1 832mw, and 1 810 (sh) cm^{-1}. Yields of this first step are generally 70—80%. This solution was treated with a nearly saturated solution of $[Au(PPh_3)Cl]$ in thf (410.2 mg, 0.829 mmol in 10 cm^3), added in portions of 1—2 cm^3, while stirring; a fine brick-red precipitation occurred within minutes after the first additions. After addition of 6 cm^3, the i.r. spectrum of the decanted solution showed the presence of both the starting dianion and the monoanion (**1**), and subsequently, when a total of 9 cm^3 has been added, the presence of only (**1**). Another 1 cm^3 was added and the mixture stirred for about 30 min. The brown-red mother-liquor still containing some (**1**) {it is advisable not to use an excess of $[Au(PPh_3)Cl]$ to avoid

Table 3. Fractional atomic co-ordinates

Atom	x	y	z
Au	0.062 13(4)	0.014 78(3)	0.765 00
Rh(1)	0.025 68(9)	−0.047 88(6)	0.885 26(15)
Rh(2)	0.096 40(9)	0.010 03(7)	0.968 97(16)
Rh(3)	−0.001 99(10)	−0.044 25(7)	1.067 52(16)
P	0.124 0(3)	0.055 3(2)	0.682 4(5)
C(01)	0.0000	0.0000	0.965 3(21)
C(1)	0.029 4(12)	−0.087 2(8)	0.790 0(18)
O(1)	0.034 8(12)	−0.110 8(8)	0.732 8(18)
C(2)	0.178 7(16)	0.018 9(11)	0.966 0(26)
O(2)	0.228 6(15)	0.024 9(10)	0.956 4(27)
C(3)	0.094 2(13)	0.054 4(9)	1.066 1(20)
O(3)	0.124 5(11)	0.075 5(8)	1.108 5(16)
C(4)	0.011 6(16)	−0.085 2(12)	1.157 2(28)
O(4)	0.024 1(14)	−0.109 6(9)	1.214 2(20)
C(5)	0.012 4(13)	−0.096 7(9)	0.974 6(21)
O(5)	0.012 7(11)	−0.131 9(8)	0.977 0(18)
C(6)	0.118 4(15)	−0.043 7(11)	0.905 9(24)
O(6)	0.157 1(12)	−0.065 2(8)	0.888 6(18)
C(7)	0.0000	0.0000	0.167 2(64)
O(7)	0.0000	0.0000	1.250 4(37)
C(8)	0.106 4(12)	0.056 2(8)	0.563 9(18)
C(9)	0.156 3(13)	0.058 3(9)	0.500 1(19)
C(10)	0.142 7(18)	0.061 6(12)	0.407 7(27)
C(11)	0.081 2(18)	0.058 8(12)	0.391 2(29)
C(12)	0.032 7(21)	0.051 5(14)	0.442 3(32)
C(13)	0.049 8(15)	0.054 2(10)	0.538 7(23)
C(14)	0.203 8(10)	0.043 9(7)	0.695 2(16)
C(15)	0.220 9(12)	0.002 8(8)	0.707 8(18)
C(16)	0.280 7(12)	−0.007 4(9)	0.709 8(19)
C(17)	0.321 6(15)	0.023 4(11)	0.699 8(25)
C(18)	0.306 1(16)	0.063 1(12)	0.689 7(25)
C(19)	0.248 8(14)	0.073 8(10)	0.683 1(21)
C(20)	0.117 7(12)	0.107 9(8)	0.716 6(18)
C(21)	0.112 5(13)	0.141 8(9)	0.655 4(21)
C(22)	0.109 5(17)	0.184 8(13)	0.685 9(28)
C(23)	0.108 4(13)	0.191 0(10)	0.774 1(24)
C(24)	0.113 1(15)	0.160 7(11)	0.834 0(25)
C(25)	0.123 1(13)	0.116 6(9)	0.804 2(19)

recrystallization problems} was filtered and the brick-red product recovered was washed with propan-2-ol (4 × 5 cm^3) and vacuum dried. Yield: 650 mg, 63% (Found: C, 29.75; H, 1.40. Calc. for $C_{50}H_{30}Au_2O_{13}P_2Rh_6$: C, 31.40; H, 1.60%). The product obtained in this way is generally of satisfactory purity. Should ^{31}P n.m.r. spectroscopy indicate the presence of impurities, recrystallization can be performed from thf–propan-2-ol.

Dark red crystals of a size suitable for *X*-ray diffraction studies were obtained by the slow diffusion of n-hexane cautiously layered on a thf solution of the complex; however, due to the long time required for the process to be completed, partial decomposition occurred yielding also relevant amounts of yellow-orange crystals of $[Rh_6C(CO)_{15}\{Au(PPh_3)\}_2]$ and a black amorphous material.

Crystallography.—Crystal data and details of measurements are reported in Table 2. The diffraction experiments were carried out on an Enraf–Nonius CAD4 diffractometer equipped with Mo-K_α radiation, at room temperature. The unit-cell parameters were determined by least-squares refinement of the setting angles of 25 well centred high-θ reflections. Diffraction intensities were corrected for Lorentz and polarization factors. The space group choice was based on systematic absences and confirmed by successful refinement. The structure was solved by direct methods and refined by full-matrix least squares. An absorption correction was applied by the Walker and Stuart method[20] once a complete structural model was available and all atoms refined isotropically (correction range 0.69—1.00). The Rh, Au, and P atoms were treated anisotropically, C and O atoms isotropically. The limited number of observations and an incompletely satisfactory correction for absorption prevented extension of the anisotropic treatment to these latter atoms. A rigid-body model was applied to the phenyl groups (C–C–C 120°, C–C 1.395 Å) whose H atoms were added in calculated positions (C–H 1.08 Å) and refined 'riding' on their corresponding C atoms. A single isotropic thermal parameter (0.101 Å^2) was also refined for the H atoms. For all calculations the SHELX 76[21] package of crystallographic programs was used. Residual peaks of about 2 e Å^{-3} were found in the proximity of the heavy atoms. The co-ordinates of all non-hydrogen atoms are reported in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

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