Mono-, Bi-, and Tri-nuclear Bis(diphenylphosphino)methane Gold Complexes. Crystal and Molecular Structures of [Bis(diphenylphosphino)methane]bis(pentafluorophenyl)gold(III) Perchlorate and 1,2; 2,3-Di-μ-[bis(diphenylphosphino)methane]-1,3-dichlorotrigold(I) Chlorotris(pentafluorophenyl)aurate(III) †

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Reactions of gold(III) complexes of the types $[AuClR_2(dppm)]$ and $[AuR_3(dppm)]$ ($R = C_6F_5$, dppm = bis(diphenylphosphino)methane] with other gold complexes, such as $[Au(O_3ClO)(PPh_3)]$, $[Au(C_6F_5)(tht)]$, $[AuCl(tht)]$, or $[AuCl_3(tht)]$ (tht = tetrahydrothiophene) which contain a readily displaceable ligand (O_3ClO^- or tht), lead to the formation of cationic binuclear complexes of the types $[R_2ClAu(dppm)Au(PPh_3)]ClO_4$ and $[R_3Au(dppm)Au(PPh_3)]ClO_4$ or of neutral ones $[R_2ClAu(dppm)AuX]$ and $[R_3Au(dppm)AuX]$ ($R = C_6F_5$, X = Cl or C_6F_5). Reaction of $[AuClR_2(dppm)]$ with $AgClO_4$ gives $[AuR_2(dppm)]ClO_4$ which has been structurally identified by *X*-ray crystallography. The crystals are orthorhombic, space group *Pnma*, with $a = 17.204(4)$, $b = 20.053(4)$, $c = 11.348(2)$ Å, $Z = 4$, and $R = 0.065$ for 3 401 unique observed reflections. Oxidation of [XAu(dppm)AuX] (X = Cl or C_6F_5) with $[TlClR_2]$ or $TlCl_3$ leads to the cationic trinuclear complex $[ClAu(dppm)Au(dppm)AuCl][AuClR_3]$, whose crystal structure has also been determined: space group $P\bar{1}$, with $a = 12.170(6)$, $b = 14.448(8)$, $c = 23.780(10)$ Å, $\alpha = 101.29(5)$, $\beta = 90.01(4)$, $\gamma = 93.68(4)°$, $Z = 2$, and $R = 0.085$ for 4 891 unique observed reflections. The cation shows short Au · · · Au contacts (*ca.* 3.1 Å).

Although interesting inorganic gold derivatives containing the ligand bis(diphenylphosphino)methane (dppm) are known,[1,2] no systematic study of this ligand in organometallic gold chemistry has so far been carried out.[3]

Starting from gold(III) derivatives in which dppm acts as a unidentate ligand {such as the recently described[4] $[Au(C_6F_5)_3(dppm)]$ or $[AuCl(C_6F_5)_2(dppm)]$ whose preparation is reported in the present paper}, it has been possible to obtain mono-, bi-, or tri-nuclear dppm-bridged complexes by reaction with other gold complexes containing a readily displaceable ligand.

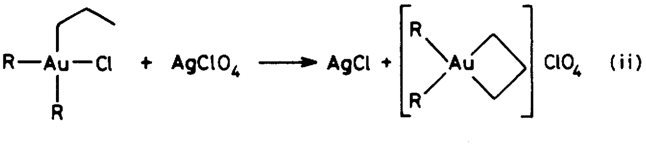
Results and Discussion

Mononuclear Complexes.—The synthesis of $[Au(C_6F_5)_3(dppm)]$ by addition of dppm to $[Au(C_6F_5)_3(tht)]$ (tht = tetrahydrothiophene) has previously been described.[4] The compound $[AuCl(C_6F_5)_2(dppm)]$ (1) is obtained by two cleavages of the binuclear derivative[5] $[\{Au(\mu-Cl)(C_6F_5)_2\}_2]$ [equation (i)]. The ^{31}P n.m.r. spectrum of compound (1)

$$[\{Au(\mu\text{-}Cl)(C_6F_5)_2\}_2] + 2\ \text{dppm} \xrightarrow{OEt_2} \underset{(1)}{2\ [AuCl(C_6F_5)_2(dppm)]} \quad (i)$$

strongly resembles that of $[Au(C_6F_5)_3(dppm)]$[4] showing two doublets at δ −23.32 and 26.49 p.p.m. [J(P–P) = 68.3 Hz]. The first of the doublets, corresponding to the phosphorus atom linked to gold, reveals coupling with the ^{19}F of the C_6F_5 groups, which indicates that one C_6F_5 group should be *trans* to the phosphorus atom and in consequence the C_6F_5 groups are mutually *cis*. Complex (1) is a white air- and moisture-stable solid, and is monomeric in chloroform (Table 1).

The abstraction of chlorine (with $AgClO_4$) from (1) gives a new mononuclear complex (2), according to equation (ii).



(2; $R = C_6F_5$)

Complex (2) is a white solid, showing two i.r. bands at 1 100s,br and 620m cm^{-1} characteristic[6] of the ClO_4^- anion. The complex is a 1 : 1 electrolyte both in acetone (Table 1) and in nitromethane; in the latter the slope B of Onsager's equation, $\Lambda_e = \Lambda_0 - B\sqrt{c}$ (where Λ_e = equivalent conductivity, Λ_0 = conductivity at infinite dilution, and c = equivalent concentration),[7] is 160.

The structure of the acetone solvate of complex (2) has been determined by a single-crystal *X*-ray diffraction study. The cation possesses crystallographic *m* symmetry, the gold and methylene carbon lying in the mirror plane. The gold atom exhibits the expected planar co-ordination, lying less than 0.01 Å out of the plane of P and C(31) and their symmetry-generated equivalents (Figure 1). The acetone and perchlorate also display *m* symmetry, occupying the spaces between the phenyl rings (Figure 2).

Binuclear Complexes.—Since in $[AuR_3(dppm)]$ and $[AuClR_2(dppm)]$ ($R = C_6F_5$) the dppm ligand has one unco-ordinated phosphorus atom, the two complexes can be considered as potential ligands which are capable of displacing poorly co-ordinated neutral (tht)[8] or anionic ($OClO_3$)[9] ligands from other complexes.

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† *Supplementary data available* (No. SUP 23621, 62 pp.): thermal parameters, H-atom co-ordinates, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

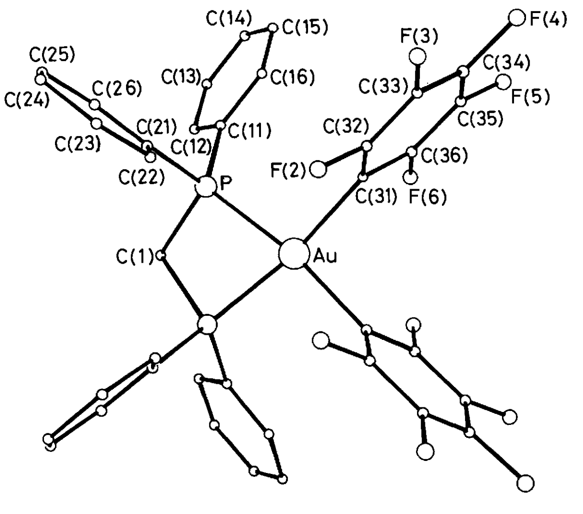


Figure 1. The $[Au(C_6F_5)_2(Ph_2PCH_2PPh_2)]^+$ cation of (2), showing the numbering scheme of the unique atoms

$$[M'(dppm)] + [Au(O_3ClO)(PPh_3)] \longrightarrow [M'(dppm)Au(PPh_3)]ClO_4 \quad \text{(iii)}$$
$$(3;\ M' = AuClR_2)$$
$$(4;\ M' = AuR_3)$$

Both $[AuClR_2(dppm)]$ and $[AuR_3(dppm)]$ react with $[Au(O_3ClO)(PPh_3)]$ [equation (iii)] to give solutions which upon evaporation yield the white complexes (3) and (4). As may be seen from their i.r. spectra (two bands[6] at 1 100s, br and 620m cm^{-1}) both contain the anion ClO_4^-. In acetone solution they behave as 1 : 1 electrolytes (Table 1).

The reaction of complexes [M'(dppm)] with gold(I) derivatives containing a neutral, readily displaceable ligand (tht) leads to the formation of binuclear complexes (5)—(7) [equation (iv)]. The resulting white solids are non-conducting

$$[M'(dppm)] + [AuX(tht)] \longrightarrow [M'(dppm)AuX] + tht \quad \text{(iv)}$$
$$M' = AuCl(C_6F_5)_2;\ X = C_6F_5\ (5)$$
$$M' = Au(C_6F_5)_3;\ X = C_6F_5\ (6)\ \text{or}\ Cl\ (7)$$

in acetone. The i.r. spectrum of complex (7) shows a band at 325m cm^{-1}, assignable to ν(Au–Cl).[10] For $M' = AuCl(C_6F_5)_2$ and X = Cl the formation of [M'(dppm)AuCl] would be expected, but the reaction is much more complex and yields a mixture of compounds which could not be resolved.

Attempts to prepare binuclear complexes with two gold(III) centres according to equation (iv) proved unsuccessful. Reaction of $M' = Au(C_6F_5)_3$ with $[AuX_3(tht)]$ (X = Cl) yielded complex (7), doubtlessly because the primary reaction product undergoes reductive elimination of chlorine, whose evolution can be observed; with $X = C_6F_5$ no reaction occurs. The oxidative addition of Cl_2 to complex (6) led to the formation of (7) and elimination of C_6ClF_5.

Trinuclear Complexes.—Two oxidative-addition reactions of gold(I) complexes of the type [XAu(dppm)AuX] (X = Cl[1] or C_6F_5[11]) have been studied. (*a*) The reaction between [ClAu(dppm)AuCl] and $[TlCl(C_6F_5)_2]$. Oxidative addition of the thallium complex leads normally[12,13] to the precipitation of TlCl and to transference of the two C_6F_5 groups to the gold atom of the gold(I) complex, so that depending upon the used molar ratio the oxidation of one or both gold(I) atoms can be expected. (*b*) The reaction between $[(C_6F_5)Au(dppm)Au(C_6F_5)]$ and $TlCl_3$. This leads normally to transference of the two Cl atoms to the gold atom and to precipitation of TlCl,[14] with the same possibilities as in (*a*), depending upon the molar ratio of the reactants.

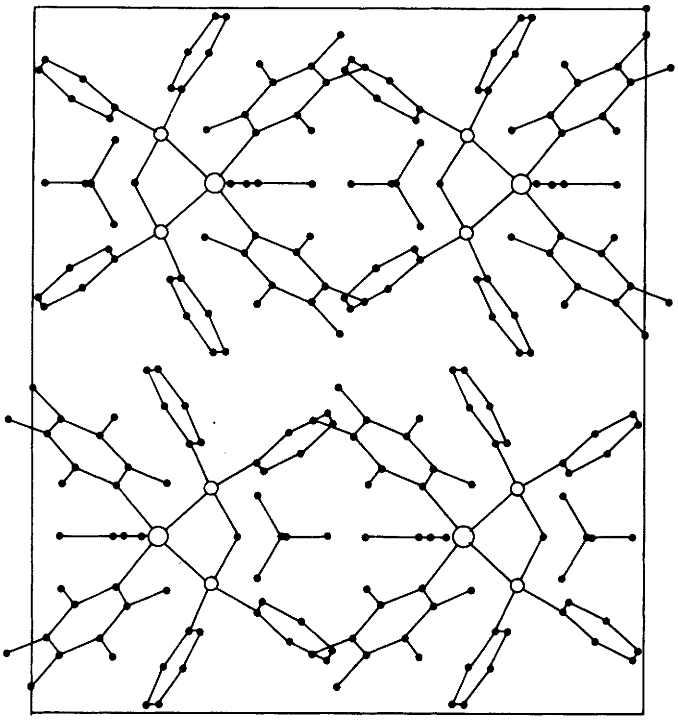
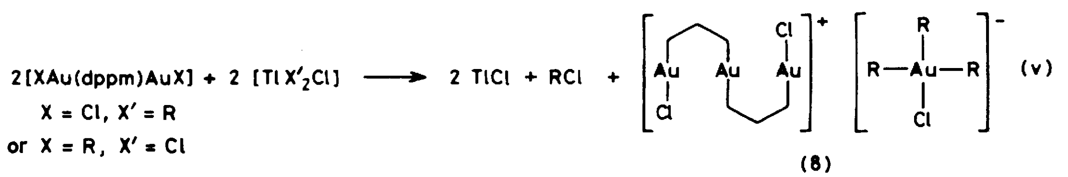


Figure 2. A packing plot of complex (2) projected down *c*. The perchlorate and acetone groups occupy spaces at *y* = 0.25

Nonetheless, a white solid of stoicheiometry $Au_4Cl_3(C_6F_5)_3(dppm)_2$ is obtained in both cases. It is conducting in acetone. Subsequent studies, including determination of its crystal structure by *X*-ray diffraction, identified it as $[ClAu(dppm)Au(dppm)AuCl][Au(C_6F_5)_3Cl]$ (8) (Figures 3 and 4). The central gold atom [Au(1)] of the cation is co-ordinated by two phosphorus atoms; there is a substantial deviation from linearity (13°), but the bond lengths [2.323(9) and 2.322(10) Å] agree well with those of $[Au(PMePh_2)_2]^+$ [2.316(4) Å, exactly linear at gold[15]]. The two P–Au–Cl 'arms,' with Au–P 2.243(10) and 2.239(10) and Au–Cl 2.288(10) and 2.301(10) Å, are very similar to those of [ClAu(dppm)AuCl] [Au–P 2.238(5), Au–Cl 2.288(7) Å[1]]. The cation conformation is such as to allow short Au ··· Au distances.[16] The anion shows the expected square-planar geometry at Au^{III}; there is a marginally significant *trans* influence in that Au(4)–C(101), *trans* to Cl(3), is the shortest Au(4)–C bond.

The overall process can in both cases be formulated according to equation (v).



(8)

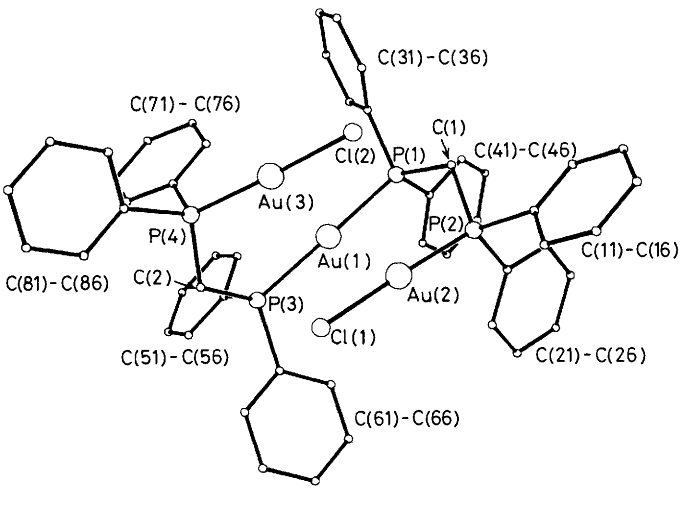


Figure 3. Perspective view of the cation of complex (8), showing the atom-numbering scheme

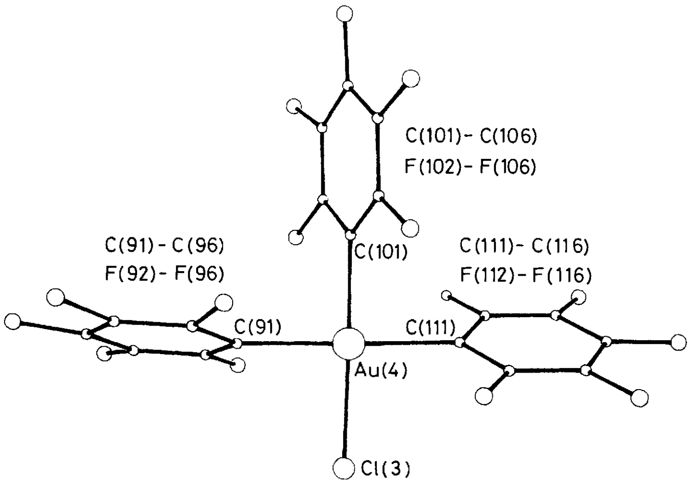
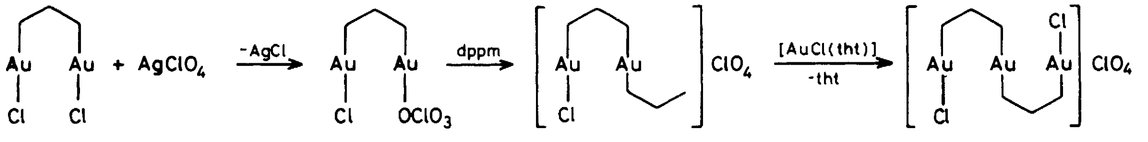


Figure 4. Perspective view of the anion of complex (8), showing the atom-numbering scheme

The measured conductivity (Table 1) and the following data are in agreement with the structure of complex (8). (*a*) The i.r. spectrum shows a broad band at 330 cm^{-1}, arising from the superposition of vibrations due to $\nu(Au^{I}-Cl)$ and $\nu(Au^{III}-Cl)$. (*b*) The ^{19}F n.m.r. spectrum ($CDCl_3$) exhibits two multiplets at δ -121.0 and -162.4 p.p.m., corresponding to the *ortho* and *meta* fluorine atoms, along with two triplets at δ -158.8 and -159.7 p.p.m. [intensity ratio 2 : 1, $J(F-F) = 20$ Hz] corresponding to the *p*-F of the C_6F_5 group *trans* to Cl or, respectively, to the *p*-F of the other two C_6F_5 groups. (*c*) The ^{31}P n.m.r. spectrum ($CDCl_3$, ^1H decoupled) corresponds to a spin system $|AB|_2$: $\delta_A = -36.6$, $\delta_B = -29.0$ p.p.m.; $J(A-A) = 308.7$, $J(A-B) = 68.6$, $J(A-B') = -1.9$, and $J(B-B') = -0.2$ Hz.

The same trinuclear cation can be obtained as the perchlorate, [ClAu(dppm)Au(dppm)AuCl]ClO_4 (9), if equimolar amounts of [ClAu(dppm)AuCl] and $AgClO_4$ are allowed to react, the precipitated AgCl is removed, and a further mole of dppm along with [AuCl(tht)] are added to the filtrate. The course of the reaction is represented in equation (vi). The white solid (9) is conducting in acetone. Its i.r. spectrum shows a band due to $\nu(Au-Cl)$ at 330 cm^{-1}, and two bands at 1 100s, br and 620m cm^{-1} arising from the ClO_4^- anion.



(vi)

(9)

Experimental

Infrared spectra were recorded on a Perkin-Elmer 599 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured in *ca.* 5 × 10^{-4} mol dm^{-3} acetone solutions with a Philips 9501/01 conductimeter. Molecular weights were determined in chloroform solution

Table 1. Physical data

Complex [a]	M.p. (°C)	Λ_M [b] ohm^{-1} cm^2 mol^{-1}	M [c]
(1) [AuClR$_2$(dppm)]	165 (decomp.)	4	1 023 (950)
(2) [AuR$_2$(dppm)]ClO$_4$	208 (decomp.)	98	
(3) [R$_2$ClAu(dppm)Au(PPh$_3$)]ClO$_4$	136	146	
(4) [R$_3$Au(dppm)Au(PPh$_3$)]ClO$_4$	186 (decomp.)	156	
(5) [R$_2$ClAu(dppm)AuR]	156	6	1 239 (1 314)
(6) [R$_3$Au(dppm)AuR]	195 (decomp.)	3	1 326 (1 446)
(7) [R$_3$Au(dppm)AuCl]	198 (decomp.)	1	1 310 (1 314)
(8) [Au{(dppm)ClAu}$_2$][AuR$_3$Cl]	232	82	1 996 (2 164)
(9) [Au{(dppm)ClAu}$_2$]ClO$_4$	266 (decomp.)	131	

[a] R = C_6F_5. [b] In acetone. [c] In chloroform; calculated values in parentheses.

Table 2. Atom co-ordinates ($\times 10^4$) of complex (2)

Atom	X/a	Y/b	Z/c
Au	2 047(1)	2 500	5 812(1)
P	2 920(1)	3 188(1)	6 859(2)
C(1)	3 361(7)	2 500	7 708(10)
C(12)	2 750(4)	3 842(3)	9 025(5)
C(13)	2 484(4)	4 364(3)	9 729(5)
C(14)	2 045(4)	4 877(3)	9 231(5)
C(15)	1 873(4)	4 868(3)	8 030(5)
C(16)	2 139(4)	4 345(3)	7 326(5)
C(11)	2 578(4)	3 832(3)	7 823(5)
C(22)	3 768(3)	3 418(3)	4 794(5)
C(23)	4 391(3)	3 695(3)	4 176(5)
C(24)	4 916(3)	4 112(3)	4 753(5)
C(25)	4 819(3)	4 253(3)	5 948(5)
C(26)	4 196(3)	3 977(3)	6 566(5)
C(21)	3 671(3)	3 560(3)	5 989(5)
C(32)	1 558(6)	3 478(5)	3 892(8)
C(33)	1 102(6)	3 936(6)	3 354(9)
C(34)	456(6)	4 167(6)	3 867(9)
C(35)	238(6)	3 942(5)	4 926(9)
C(36)	701(5)	3 471(5)	5 477(8)
C(31)	1 379(5)	3 225(4)	4 996(8)
F(2)	2 192(4)	3 260(4)	3 347(6)
F(3)	1 329(4)	4 197(4)	2 275(6)
F(4)	−9(4)	4 621(3)	3 298(6)
F(5)	−415(4)	4 159(4)	5 442(6)
F(6)	481(4)	3 250(3)	6 557(6)
Cl	4 065(2)	2 500	1 354(4)
O(1)	4 814(8)	2 500	1 874(11)
O(2)	4 142(9)	2 500	125(15)
O(3)	3 673(9)	3 093(8)	1 638(14)
C(41)	8 666(9)	7 500	592(13)
C(42)	9 547(11)	7 500	876(16)
C(43)	8 475(13)	7 500	−732(18)
O(41)	8 211(8)	7 500	1 346(12)

with a Hitachi–Perkin-Elmer 115 osmometer. N.m.r. spectra (^{1}H-decoupled ^{19}F and ^{31}P) were recorded on a JEOL PFT spectrometer with ^{19}F shifts relative to $CFCl_3$ (external) and ^{31}P shifts relative to H_3PO_4 (external). Carbon and hydrogen analyses were carried out with a Perkin-Elmer 240 microanalyzer, gold analyses by ashing in a crucible with aqueous hydrazine.

Preparation of the Complexes.—All the reactions were run at room temperature.

[AuCl(C_6F_5)$_2$(dppm)] (1). A solution of [{AuCl(C_6F_5)$_2$}$_2$] [5] (1.113 g, 1 mmol) and dppm (0.76 g, 2 mmol) in diethyl ether (40 cm^3) was stirred for 1 h. Concentration to *ca.* 8 cm^3 and addition of hexane (20 cm^3) led to the precipitation of white crystals of (1), yield 53% (Found: C, 47.6; H, 2.65; Au, 21.15. $C_{37}H_{22}AuClF_{10}P_2$ requires C, 46.75; H, 2.35; Au, 20.7%).

[Au(C_6F_5)$_2$(dppm)]ClO$_4$ (2). To a solution of complex (1) (0.190 g, 0.2 mmol) in a mixture of dichloromethane (15 cm^3) and diethyl ether (15 cm^3) was added AgClO$_4$ (0.041 g, 0.2 mmol) and the mixture stirred for 1 h under exclusion of daylight. The solvent was evaporated and the residue was treated with acetone (20 cm^3). Removal of the AgCl formed, concentration of the filtrate to *ca.* 5 cm^3, and subsequent slow addition of hexane led to the crystallization of complex (2). Yield 68% (Found: C, 43.0; H, 2.55; Au, 20.1. $C_{37}H_{22}AuClF_{10}O_4P_2$ requires C, 43.8; H, 2.20; Au, 19.4%). An acetone solvate was obtained on recrystallization from acetone–hexane (1 : 4).

Crystal data. $C_{37}H_{22}AuClF_{10}O_4P_2\cdot C_3H_6O$, M = 1 073.01, Orthorhombic, space group *Pnma*, a = 17.204(4), b = 20.053(4), c = 11.348(2) Å, U = 3 915 Å^3, Z = 4, D_c = 1.82 g cm^{-3}, F(000) = 2 064, λ(Mo-K_α) = 0.710 69 Å, μ(Mo-K_α) = 4.0 mm^{-1}.

Colourless prisms were obtained on recrystallization from acetone–hexane (1 : 4). A crystal of dimensions 0.4 × 0.25 × 0.15 mm was mounted in a glass capillary and used to collect 4 978 profile-fitted reflections [17] in the range $7 < 2\theta < 55°$ on a Stoe four-circle diffractometer. After Lorentz polarization and absorption corrections, averaging equivalents gave 4 615 unique reflections, 3 401 of which with $F > 4\sigma(F)$ were used for all calculations (program system SHELXTL). Cell constants were refined from 2θ values of 48 reflections in the range $20 < 2\theta < 24°$.

The structure was solved by the heavy-atom method and refined with Au, P, and Cl anisotropic to R 0.065 and R' 0.064 [weighting scheme $w^{-1} = \sigma^2(F) + 0.0004\ F^2$]. Phenyl rings of the phosphine ligand were refined as rigid groups with C–C 1.395, C–H 0.96 Å, all angles 120°, and U(H) =

Table 3. Bond lengths (Å) and angles (°) of complex (2)

Au–P	2.361(3)	C(36)–F(6)	1.357(12)	Au–C(31)	2.071(10)	C(35)–F(5)	1.340(13)
C(1)–P	1.845(9)	C(31)–C(36)	1.380(14)	C(21)–P	1.789(7)	C(31)–C(32)	1.386(14)
C(11)–P	1.792(8)	Cl–O(2)	1.402(18)	C(32)–F(2)	1.329(13)	Cl–O(1)	1.417(15)
C(32)–C(33)	1.352(16)	Cl–O(3)	1.404(17)	C(33)–F(3)	1.389(14)	C(41)–C(42)	1.550(26)
C(33)–C(34)	1.338(16)	C(41)–C(43)	1.537(27)	C(34)–F(4)	1.373(14)	C(41)–O(41)	1.160(22)
C(34)–C(35)	1.337(15)						
C(35)–C(36)	1.384(15)						

P–Au–C(31)	99.7(3)	C(36)–C(35)–F(5)	120.5(10)	C(33)–C(32)–C(31)	121.9(10)
C(31)–Au–P	171.2(3)	C(35)–C(36)–F(6)	118.1(9)	C(31)–C(32)–F(2)	118.8(10)
C(31)–Au–C(31′)	89.1(6)	Au–C(31)–C(32)	122.6(8)	C(32)–C(33)–F(3)	119.4(10)
Au–P–C(1)	95.0(4)	C(32)–C(31)–C(36)	114.4(9)	C(33)–C(34)–C(35)	120.4(11)
C(1)–P–C(11)	110.8(5)	O(1)–Cl–O(3)	109.9(8)	C(35)–C(34)–F(4)	118.9(10)
C(1)–P–C(21)	107.6(5)	O(3)–Cl–O(3′)	115.7(14)	C(34)–C(35)–F(5)	121.2(10)
P–C(1)–P′	96.8(6)	C(42)–C(41)–O(41)	120.4(16)	C(35)–C(36)–C(31)	123.5(10)
P–C(11)–C(16)	117.6(3)	P–Au–P′	71.5(2)	C(31)–C(36)–F(6)	118.4(9)
P–C(21)–C(26)	117.3(3)	Au–P–C(11)	121.3(3)	Au–C(31)–C(36)	122.9(8)
C(33)–C(32)–F(2)	119.3(10)	Au–P–C(21)	115.1(3)	O(1)–Cl–O(2)	109.2(10)
C(32)–C(33)–C(34)	121.4(11)	C(11)–P–C(21)	105.9(4)	O(2)–Cl–O(3)	105.9(8)
C(34)–C(33)–F(3)	119.1(11)	P–C(11)–C(12)	122.4(3)	C(42)–C(41)–C(43)	114.4(16)
C(33)–C(34)–F(4)	120.6(10)	P–C(21)–C(22)	122.6(3)	C(43)–C(41)–O(41)	125.2(17)
C(34)–C(35)–C(36)	118.4(10)				

Primes indicate the symmetry operator *x*, 0.5 − *y*,*z*.

1.2*U*(C). Methylene hydrogens were not included in the refinement. Final atomic co-ordinates and derived parameters are given in the Tables 2 and 3.

$[(C_6F_5)_2ClAu(dppm)Au(PPh_3)]ClO_4$ (3). To a freshly prepared solution[18] of $[Au(O_3ClO)(PPh_3)]$ (0.2 mmol) in dichloromethane (20 cm^3) was added complex (1) (0.190 g, 0.2 mmol) and the mixture stirred for 1 h. Evaporation of the solvent and recrystallization from dichloromethane–diethyl ether (1 : 4) led to the isolation of complex (3). Yield 82% (Found: C, 43.9; H, 2.55; Au, 27.45. $C_{55}H_{37}Au_2Cl_2F_{10}O_4P_3$ requires C, 43.75; H, 2.45; Au, 26.1%).

$[(C_6F_5)_3Au(dppm)Au(PPh_3)]ClO_4$ (4). To a freshly prepared[18] solution of $[Au(O_3ClO)(PPh_3)]$ (0.33 mmol) in dichloromethane (25 cm^3) was added $[Au(C_6F_5)_3(dppm)]$[4] (0.357 g, 0.33 mmol) and the mixture stirred for 1 h. Evaporation of the solvent afforded an oil which was resolved by vigorously stirring with hexane. Recrystallization from dichloromethane–hexane (1 : 4) yielded complex (4). Yield 30% (Found: C, 44.85; H, 2.65; Au, 23.75. $C_{61}H_{37}Au_2ClF_{15}O_4P_3$ requires C, 44.65; H, 2.25; Au, 24.0%).

$[(C_6F_5)_2ClAu(dppm)Au(C_6F_5)]$ (5). To a solution of $[Au(C_6F_5)(tht)]$[8] (0.136 g, 0.3 mmol) in diethyl ether (20 cm^3) was added complex (1) (0.285 g, 0.3 mmol) and the mixture stirred for 2 h. Concentration to *ca.* 5 cm^3 and addition of hexane (15 cm^3) gave a white solid (5), which was recrystallized from dichloromethane–hexane (1 : 4). Yield 78% (Found: C, 39.7; H, 1,70; Au, 31.0. $C_{43}H_{22}Au_2ClF_{15}P_2$ requires C, 39.3; H, 1.70; Au, 29.95%).

$[(C_6F_5)_3Au(dppm)Au(C_6F_5)]$ (6). To a solution of $[Au(C_6F_5)(tht)]$[8] (0.113 g, 0.25 mmol) in diethyl ether (30 cm^3) was added $[Au(C_6F_5)_3(dppm)]$[4] (0.271 g, 0.25 mmol) and the mixture stirred for 4 h. Complex (6) was isolated by evaporation to dryness and recrystallization from dichloromethane–hexane (1 : 4). Yield 74% (Found: 41.3; H, 1.95; Au, 27.4. $C_{49}H_{22}Au_2F_{20}P_2$ requires C, 40.7; H, 1.55; Au, 27.25%).

$[(C_6F_5)_3Au(dppm)AuCl]$ (7). To a solution of $[AuCl(tht)]$[8] (0.013 g, 0.04 mmol) in diethyl ether (10 cm^3) was added $[Au(C_6F_5)_3(dppm)]$[4] (0.048 g, 0.04 mmol) and the mixture stirred for 2 h. Evaporation to dryness and recrystallization of the residue from dichloromethane–hexane (1 : 4) yielded complex (7). Yield 42% (Found: C, 39.0; H, 1.85; Au, 29.3. $C_{43}H_{22}Au_2ClF_{15}P_2$ requires C, 39.25; H, 1.70; Au, 29.95%).

$[Au\{(dppm)ClAu\}_2][AuCl(C_6F_5)_3]$ (8). A suspension of $[ClAu(dppm)AuCl]$[1] (0.425 g, 0.5 mmol) and $[TlCl(C_6F_5)_2]$[19] (0.287 g, 0.5 mmol) in benzene (30 cm^3) was stirred for 2 d and then evaporated to dryness. The residue was treated with dichloromethane (30 cm^3) and the insoluble TlCl was filtered off. The filtrate was concentrated to *ca.* 8 cm^3 and hexane was slowly added to crystallize complex (8). Yield 79% (Found: C, 37.85; H, 2.25; Au, 35.85. $C_{68}H_{44}Au_4Cl_3F_{15}P_4$ requires C, 37.75; H, 2.05; Au, 36.4%).

The complex could also be obtained by adding $TlCl_3$ (0.142 g, 0.45 mmol) to a suspension of the complex $[(C_6F_5)Au(dppm)Au(C_6F_5)]$[11] (0.509 g, 0.45 mmol) in benzene (30 cm^3). The suspension was stirred for 1 d and subsequently evaporated to dryness. The residue was treated with dichloromethane (30 cm^3), the insoluble TlCl was filtered off, and the filtrate was concentrated to *ca.* 8 cm^3. Addition of hexane led to the isolation of complex (8). Yield 63% (Found: C, 37.9; H, 2.15; Au, 36.85%).

Crystal data. $C_{68}H_{44}Au_4Cl_3F_{15}P_4$, $M = 2\,164.20$, Triclinic, space group $P\bar{1}$, $a = 12.170(6)$, $b = 14.448(8)$, $c = 23.780(10)$ Å, $\alpha = 101.29(5)$, $\beta = 90.01(4)$, $\gamma = 93.68(4)°$, $U = 4\,092$ Å^3, $Z = 2$, $D_c = 1.76$ g cm^{-3}, $F(000) = 2\,298$, μ(Mo-K_α) = 7.1 mm^{-1}.

After many unsuccessful attempts to grow single crystals suitable for *X*-ray work, one colourless, needle-shaped (0.7 × 0.1 × 0.1 mm) crystal of moderate quality was obtained from acetone–di-isopropyl ether–light petroleum (b.p. 40–60 °C) (1 : 1 : 5) and sealed in a glass capillary. 8 976 Profile-fitted[17] intensities were recorded in the range $7 < 2\theta < 40°$ on a Stoe four-circle diffractometer using monochromated Mo-K_α radiation. After application of Lorentz polarization and absorption corrections, averaging equivalents gave 7 585 unique reflections of which 4 891 with $F > 4\sigma(F)$ were used for all calculations. Accurate cell constants were obtained by least-squares analysis of the 2θ values of 30 strong reflections. A lattice geometry program (written locally by Dr. W. Clegg) indicated no higher symmetry cell.

The structure was solved by direct methods (to locate Au) and successive difference syntheses, and refined to *R* 0.085 and *R′* 0.080 [weighting scheme $w^{-1} = \sigma^2(F) + 0.00075\ F^2$]. The Au, P, and Cl atoms were refined anisotropically, all other atoms isotropically. Phenyl rings were refined as rigid

Table 4. Atomic co-ordinates * (× 10^4) of complex (8)

Atom	*X/a*	*Y/b*	*Z/c*
Au(1)	2 894(1)	4 752(1)	8 112(1)
Au(2)	3 096(1)	6 649(1)	8 962(1)
Au(3)	1 549(1)	4 501(1)	9 217(1)
P(1)	1 559(7)	5 322(6)	7 595(3)
P(2)	2 197(8)	7 272(6)	8 316(4)
P(3)	4 319(7)	3 978(6)	8 426(3)
P(4)	2 561(7)	3 248(7)	9 166(4)
Cl(1)	4 038(8)	6 083(7)	9 642(3)
Cl(2)	461(7)	5 768(7)	9 328(4)
C(12)	1 984(17)	8 880(18)	9 146(10)
C(13)	1 511	9 713	9 398
C(14)	596	10 002	9 142
C(15)	154	9 457	8 633
C(16)	627	8 624	8 381
C(11)	1 542	8 335	8 637
C(22)	4 178(19)	7 591(15)	7 822(9)
C(23)	4 846	7 865	7 399
C(24)	4 375	8 175	6 940
C(25)	3 235	8 211	6 904
C(26)	2 566	7 938	7 327
C(21)	3 038	7 628	7 786
C(32)	−529(22)	4 571(16)	7 850(8)
C(33)	−1 427	3 909	7 742
C(34)	−1 447	3 191	7 254
C(35)	−568	3 136	6 875
C(36)	330	3 798	6 983
C(31)	350	4 516	7 471
C(42)	1 285(14)	5 674(14)	6 510(9)
C(43)	1 631	5 806	5 971
C(44)	2 740	5 759	5 828
C(45)	3 504	5 579	6 224
C(46)	3 158	5 447	6 764
C(41)	2 049	5 494	6 907
C(52)	3 906(17)	2 618(17)	7 425(11)
C(53)	4 148	1 839	7 007
C(54)	5 090	1 361	7 063
C(55)	5 790	1 662	7 537
C(56)	5 548	2 442	7 955
C(51)	4 606	2 919	7 899
C(62)	5 849(17)	5 338(15)	8 202(7)
C(63)	6 850	5 877	8 280
C(64)	7 591	5 758	8 704
C(65)	7 332	5 100	9 049
C(66)	6 331	4 561	8 971
C(61)	5 589	4 680	8 548
C(72)	2 751(18)	1 460(19)	8 518(10)
C(73)	2 480	716	8 060
C(74)	1 667	808	7 665
C(75)	1 126	1 644	7 727
C(76)	1 397	2 388	8 185
C(71)	2 210	2 296	8 581
C(82)	1 378(15)	2 507(15)	9 975(9)
C(83)	1 230	2 036	10 431
C(84)	2 143	1 787	10 710
C(85)	3 203	2 010	10 533
C(86)	3 351	2 482	10 076
C(81)	2 438	2 730	9 797
C(1)	1 094(23)	6 472(19)	7 970(11)
C(2)	3 988(26)	3 527(23)	9 064(12)
Au(4)	1 883(1)	3 053(1)	3 642(1)
Cl(3)	1 334(9)	2 934(9)	2 700(4)
C(91)	2 442(21)	4 452(14)	3 723(11)
C(92)	3 318	4 737	3 404
C(93)	3 644	5 695	3 464
C(94)	3 095	6 368	3 843
C(95)	2 220	6 084	4 162
C(96)	1 893	5 126	4 102
F(92)	3 832(19)	4 105(15)	3 079(9)
F(93)	4 536(20)	5 940(16)	3 160(9)
F(94)	3 446(22)	7 304(18)	3 886(10)
F(95)	1 643(22)	6 792(18)	4 493(11)
F(96)	998(21)	4 939(17)	4 397(10)
C(101)	2 395(26)	3 111(17)	4 460(9)
C(102)	3 524	3 193	4 577
C(103)	3 907	3 189	5 130
C(104)	3 161	3 105	5 565
C(105)	2 032	3 024	5 448
C(106)	1 649	3 027	4 895
F(102)	4 272(22)	3 278(18)	4 187(10)
F(103)	4 933(30)	3 330(24)	5 229(13)
F(104)	3 503(28)	3 080(23)	6 097(14)
F(105)	1 203(30)	2 903(24)	5 813(14)
F(106)	530(21)	2 886(17)	4 751(10)
C(111)	1 261(28)	1 668(17)	3 583(10)
C(112)	129	1 484	3 630
C(113)	−298	565	3 632
C(114)	407	−170	3 586
C(115)	1 539	15	3 539
C(116)	1 966	934	3 537
F(112)	−523(24)	2 089(20)	3 694(11)
F(113)	−1 334(27)	327(21)	3 725(12)
F(114)	20(30)	−1 070(25)	3 647(14)
F(115)	2 292(33)	−790(28)	3 515(16)
F(116)	3 080(25)	1 112(20)	3 565(11)

* Estimated standard deviations are given for the first atom of each rigid group.

Table 5. Bond lengths (Å) and angles (°) at gold in complex (8)

Au(1)–P(1)	2.323(9)	Au(1)–P(3)	2.322(10)
Au(2)–P(2)	2.243(10)	Au(2)–Cl(1)	2.288(10)
Au(3)–P(4)	2.239(10)	Au(3)–Cl(2)	2.301(10)
Au(4)–Cl(3)	2.307(10)	Au(4)–C(91)	2.064(20)
Au(4)–C(101)	2.028(24)	Au(4)–C(111)	2.071(25)
P(3)–Au(1)–P(1)	166.9(3)	Cl(1)–Au(2)–P(2)	177.4(3)
Cl(2)–Au(3)–P(4)	176.0(3)	C(101)–Au(4)–Cl(3)	177.9(8)
C(91)–Au(4)–Cl(3)	93.0(8)	C(111)–Au(4)–Cl(3)	87.8(7)
C(101)–Au(4)–C(91)	88.5(10)	C(111)–Au(4)–C(101)	90.9(10)
C(111)–Au(4)–C(91)	177.4(11)		

Short non-bonded distances

Au(1) · · · Au(2)	3.067(5)	Au(1) · · · Au(3)	3.164(5)

groups with C–C 1.395, C–H 1.08 Å, and all angles 120°; C_6F_5 rings with C–C 1.395 Å, C–C–C 120°, but F atoms refining freely; CH_2 groups with a riding model (C–H 1.08 Å, H–C–H 109.5°). Hydrogen atom thermal parameters were fixed at 0.1 Å^2. Final atomic co-ordinates and derived parameters are given in the Tables 4 and 5.

[Au{(dppm)ClAu}$_2$]ClO$_4$ (9). To a suspension of AgClO$_4$ (0.111 g, 0.54 mmol) in a mixture of dichloromethane (30 cm^3) and diethyl ether (20 cm^3) was added [ClAu(dppm)-AuCl][1] (0.456 g, 0.54 mmol). After stirring for 2 h under exclusion of daylight, AgCl was filtered off. To the filtrate was added dppm (0.208 g, 0.54 mmol), and after 5 min, [AuCl(tht)][8] (0.173 g, 0.54 mmol), and the mixture was stirred for another 60 min. Complex (9) precipitated and was recrystallized from dichloromethane–hexane (1 : 4). Yield 65% (Found: C, 40.0; H, 3.25; Au, 38.8. $C_{50}H_{44}Au_3Cl_3O_4P_4$ requires C, 39.25; H, 2.90; Au, 38.6%).

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