

Mono- and Bi-nuclear Gold(I), Gold(II), and Gold(III) Perhalogenoaryl Complexes with the Ligand Bis(diphenylphosphino)amine. Crystal and Molecular Structure of μ -[Bis(diphenylphosphino)amine]-dichlorobis-(pentafluorophenyl)digold(II)

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Addition of bis(diphenylphosphino)amine (dppa) to neutral or cationic gold(I) and gold(III) complexes containing weakly co-ordinating neutral ligands leads to the formation of complexes of the following types: $[\text{RAu}(\text{dppa})\text{AuR}]$, $[\text{Au}_2(\text{dppa})_2][\text{ClO}_4]_2$, $[\text{AuR}_3(\text{dppa})]$, and $[\text{AuR}_2\text{Cl}(\text{dppa})]$ ($\text{R} = \text{C}_6\text{F}_5$ or C_6Cl_5). Oxidative-addition of halogens X_2 ($\text{X} = \text{Cl}$ or Br) to the gold(I) complexes leads to the gold(II) derivatives $[\text{RXAu}(\text{dppa})\text{AuXR}]$ and $[\text{XAu}(\text{dppa})_2\text{AuX}][\text{ClO}_4]_2$ which can be further arylated with $\text{Ag}(\text{C}_6\text{F}_5)$ to give $[\text{R}_2\text{Au}(\text{dppa})\text{AuR}_2]$ and $[\text{RAu}(\text{dppa})\text{AuR}][\text{ClO}_4]_2$. Mixed gold(III)-gold(I) derivatives can also be synthesized either by the spontaneous isomerization of the gold(II) complexes or from mononuclear gold(III) derivatives. The structure of the complex $[(\text{C}_6\text{F}_5)_2\text{ClAu}(\text{dppa})\text{AuCl}(\text{C}_6\text{F}_5)]$ has been determined by single-crystal X-ray diffraction: space group $\text{C}2/c$, $a = 18.009(3)$, $b = 17.033(2)$, $c = 18.420(3)$ Å, $\beta = 103.79(2)^\circ$, $Z = 4$, and $R = 0.035$ for 4 000 unique observed reflections. The molecule possesses crystallographic two-fold symmetry, with $\text{Au}-\text{Au}$ 2.576(2) Å; this is the shortest reported $\text{Au}-\text{Au}$ bond. The unit cell also contains eight di-isopropyl ether and four water molecules, which are well ordered and form a hydrogen bonding network with the amine N-H group.

In recent years the chemistry of the bis(diphenylphosphino)methane ligand (dppm) has received a great deal of attention¹ and some interesting gold derivatives have been prepared.²⁻⁴ Substitution at the methylene group has little effect and in gold complexes⁵ the mono- and di-methyl derivatives of bis(diphenylphosphino)methane behave similarly. Our knowledge of the behaviour of other diphosphines such as bis(diphenylphosphino)amine (dppa) is however very limited, $[\text{ClAu}(\text{dppa})\text{AuCl}]$ being the only known gold derivative.⁶

Binuclear gold(II) compounds have also been the subject of recent study; most contain ylide ligands⁷ and only two others have been described: $[\{\text{AuX}_2(\text{PPh}_2)\}_2(\text{CMe}_2)]$ ³ and $[\{\text{AuX}_2(\text{PPh}_2)\}_2(\text{NMe})]$ ⁶ ($\text{X} = \text{Cl}$ or Br).

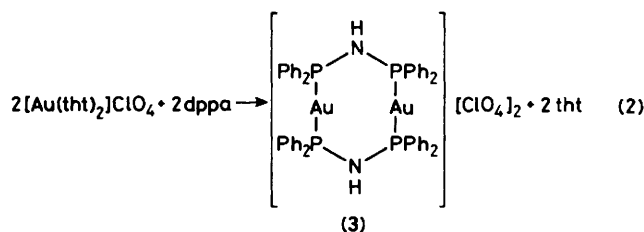
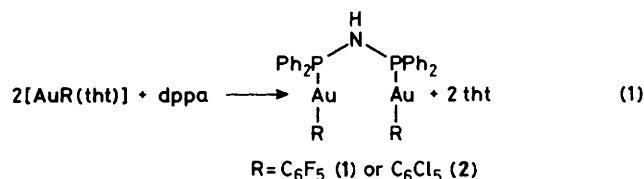
In the present paper, we describe a study of the dppa-gold system, including isolation of (a) binuclear gold(I) complexes with dppa as bridging ligand; (b) mononuclear gold(III) complexes with unidentate dppa; (c) binuclear mixed gold(III)-gold(I) complexes with bridging dppa; (d) binuclear neutral and cationic gold(II) complexes with bridging dppa. Solutions of the former readily isomerise to the corresponding gold(I)-gold(III) complexes.

Some of the new gold(I) and gold(II) dppa complexes contain perhalogenoaryl groups C_6X_5 ($\text{X} = \text{F}$ or Cl) bonded to the gold atoms.

Results and Discussion

Gold(I) Complexes.—A neutral, weakly co-ordinating ligand, such as tetrahydrothiophen (tht), can be easily displaced by dppa to give binuclear gold(I) complexes [equations (1) and (2)], irrespective of the reactant ratio, *i.e.* the phosphine acts as bidentate bridging ligand even if an excess [*e.g.* a 1:1.2 ratio in equation (1)] is used.

Complexes (1), (2), and (3) are white, air- and moisture-stable solids at room temperature. Acetone solutions of (1) and (2) are non-conducting, whilst solutions of (3) behave as 2:1 electro-



lytes (Table 1). The i.r. spectrum of (3) shows two bands at 1 100s,br and 620m cm^{-1} due⁸ to the ClO_4^- anion (T_d). The spectra of (1) and (2) show bands at 1 500s, 1 070s, 955s, and 790s cm^{-1} and at 1 325m, 1 320s, 1 290s, 840w, and 670m cm^{-1} , due to the C_6F_5 ⁹ and C_6Cl_5 ¹⁰ groups, respectively. The band at 955s cm^{-1} in the spectrum of (1) has been assigned⁹ to a Fermi resonance. In the complexes described in this paper, the position of this band is affected by the oxidation state of the gold centre. The bands at 790s (1) and 670m (2) cm^{-1} have been assigned¹⁰⁻¹² to an X'-sensitive mode ($\text{X}' =$ substituent of $\text{C}_6\text{F}_5\text{X}'$ or $\text{C}_6\text{Cl}_5\text{X}'$) predominantly involving C-X' stretching. These modes have often been used for the diagnosis of the geometry and disposition of the ligands attached to the gold centre,^{13,14} but appear to be of little value in the complexes described here.

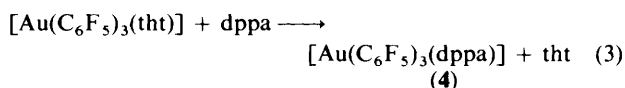
Gold(III) Complexes.—Either directly or after a suitable preliminary reaction, the action of dppa on gold(III) complexes

Table 1. Analytical and physical data for complexes (1)–(19)

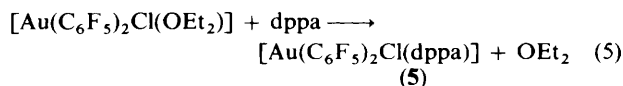
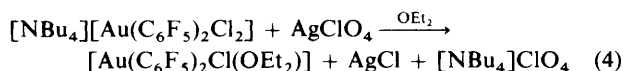
Complex	Yield (%)	Found (calc.) (%)				$\Lambda_M^a / \text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$	M^b Found (calc.)	M.p./°C
		C	H	N	Au			
(1) $[(C_6F_5)_3Au(dppa)Au(C_6F_5)]$	91	38.85 (38.85)	2.3 (1.9)	1.45 (1.25)	34.9 (35.35)	0	1 099 (1 113)	205 (decomp.)
(2) $[(C_6Cl_5)_3Au(dppa)Au(C_6Cl_5)]$	94	34.75 (33.8)	1.9 (1.65)	1.1 (1.1)	31.8 (30.8)	2	c	144 (decomp.)
(3) $[Au_2(dppa)_2][ClO_4]_2$	96	42.6 (42.3)	3.3 (3.1)	2.05 (2.05)	28.2 (28.9)	183	—	240 (decomp.)
(4) $[Au(C_6F_5)_3(dppa)]$	67	46.7 (46.55)	2.05 (1.95)	1.4 (1.3)	19.05 (18.15)	10	1 115 (1 083)	142
(5) $[Au(C_6F_5)_2Cl(dppa)]$	51	45.9 (45.4)	2.75 (2.2)	1.5 (1.45)	20.25 (20.05)	7	964 (952)	125 (decomp.)
(6) $[(C_6F_5)_3Au(dppa)AuCl]$	54	38.45 (38.3)	1.75 (1.6)	1.1 (1.05)	29.4 (29.95)	11	1 363 (1 316)	85 (decomp.)
(7) $[(C_6F_5)_3Au(dppa)Au(C_6F_5)]$	80	40.0 (39.85)	1.75 (1.45)	1.1 (0.95)	28.1 (27.2)	13	1 535 (1 447)	155
(8) $[(C_6F_5)ClAu(dppa)AuCl(C_6F_5)]$	55	35.75 (36.5)	1.7 (1.8)	0.9 (1.15)	32.95 (33.25)	2	1 152 (1 184)	145
(9) $[(C_6F_5)BrAu(dppa)AuBr(C_6F_5)]$	60	34.05 (33.95)	1.75 (1.65)	1.2 (1.1)	30.5 (30.95)	1	1 107 (1 273)	133
(10) $[(C_6Cl_5)ClAu(dppa)AuCl(C_6Cl_5)]$	70	30.95 (32.05)	1.55 (1.55)	1.2 (1.05)	27.95 (29.2)	c	c	196 (decomp.)
(11) $[(C_6Cl_5)BrAu(dppa)AuBr(C_6Cl_5)]$	64	30.95 (30.05)	1.55 (1.45)	1.3 (0.95)	27.45 (27.4)	c	c	195 (decomp.)
(12) $[(C_6F_5)Cl_2Au(dppa)Au(C_6F_5)]$	30	36.1 (36.5)	2.0 (1.8)	1.2 (1.15)	33.1 (33.25)	2	1 110 (1 184)	115 (decomp.)
(13) $[(C_6F_5)Br_2Au(dppa)Au(C_6F_5)]$	30	34.9 (33.95)	1.9 (1.65)	1.2 (1.1)	29.95 (30.95)	2	1 235 (1 273)	180 (decomp.)
(14) $[(C_6Cl_5)Cl_2Au(dppa)Au(C_6Cl_5)]$	27	32.65 (32.05)	1.5 (1.55)	0.95 (1.05)	29.4 (29.2)	10	c	125 (decomp.)
(15) $[(C_6Cl_5)Br_2Au(dppa)Au(C_6Cl_5)]$	40	30.65 (30.05)	1.65 (1.45)	1.1 (0.95)	27.2 (27.4)	4	c	182 (decomp.)
(16) $[ClAu(dppa)_2AuCl][ClO_4]_2$	75	40.1 (40.2)	2.9 (2.95)	2.1 (1.95)	27.95 (27.45)	177	—	138 (decomp.)
(17) $[BrAu(dppa)_2AuBr][ClO_4]_2$	75	37.05 (37.85)	2.45 (2.75)	1.9 (1.85)	26.0 (25.85)	148 ^d	—	87
(18) $[(C_6F_5)_2Au(dppa)_2Au(C_6F_5)][ClO_4]_2$	45	41.95 (42.45)	2.45 (2.5)	1.9 (1.65)	24.05 (23.20)	149 ^d	—	167 (decomp.)
(19) $[(C_6F_5)_2Au(dppa)Au(C_6F_5)_2]$	35	39.75 (39.85)	1.85 (1.45)	0.95 (0.95)	28.0 (27.2)	8 ^d	1 457 (1 448)	106 (decomp.)

^a In acetone. ^b In chloroform. ^c Not sufficiently soluble. ^d In nitromethane.

leads to mononuclear complexes. Thus, displacement of tht [equation (3)] gives rise to the mononuclear complex (4), whilst



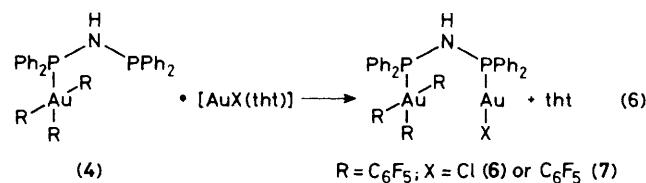
the anionic $[NBu_4][Au(C_6F_5)_2Cl_2]$ reacts (1:1) with $AgClO_4$ in diethyl ether to precipitate $AgCl$ and $[NBu_4]ClO_4$ [equation (4)], after which the solution {probably containing $[Au(C_6F_5)_2Cl(OEt_2)]$ } reacts with $dppa$ [equation (5)] to give the mononuclear complex (5).



Complexes (4) and (5) are air- and moisture-stable white solids that are non-conducting in acetone solution. The i.r. spectra of complexes (4) and (5) show a band due to the Fermi

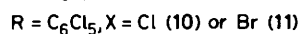
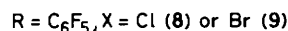
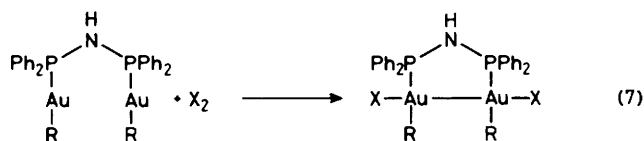
resonance of the C_6F_5 group at 965vs and 967vs cm^{-1} respectively, shifted ca. 10–12 cm^{-1} toward higher energies relative to the gold(i) complexes. Moreover, the bands at 795s,br and 790s,br cm^{-1} respectively are not well resolved, showing a broad 'shouldered' structure. A *cis* structure for complex (5) can therefore not be assigned unequivocally, though it cannot be ruled out. A band at 345m cm^{-1} can be assigned to $\nu(Au-Cl)$.¹⁵

In chloroform solution both complexes are monomeric (osmometry, see Table 1). If the geometry around the gold centre is, as usual,⁴ square planar, the diphosphine is necessarily unidentate with one unco-ordinated end. Thus, complex (4) reacts with $[AuX(tht)]$ to give binuclear mixed gold(III)–gold(I) complexes [equation (6)], similar to the previously reported behaviour of $[Au(C_6F_5)_3(dppm)]$.⁴

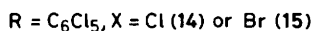
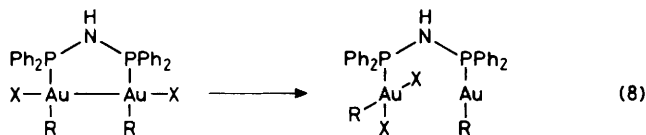


Complexes (6) and (7) are non-conducting in acetone solution and their molecular weights (Table 1) are in agreement with the binuclear formulae. In the i.r. spectrum of (6) $\nu(\text{Au}-\text{Cl})$ appears at 335m cm^{-1} along with an absorption at 965vs cm^{-1} and another asymmetric broad band at 790s,br cm^{-1} . The spectrum of (7) shows two bands at 965vs and 955vs cm^{-1} , due to the C_6F_5 groups bonded to Au^{III} or Au^{I} respectively, and again an asymmetric band at 790s,br cm^{-1} .

Gold(II) Complexes.—Complexes (1) and (2) rapidly react with halogens (Cl_2 , Br_2) at room temperature to give binuclear gold(II) derivatives [equation (7)].



Complexes (8)—(11) are air- and moisture-stable solids, although their solutions are unstable. The C_6F_5 derivatives are soluble in common organic solvents (but not in aliphatic hydrocarbons) and in polar solvents (acetone, ethanol, diethyl ether) their yellow ($\text{X} = \text{Cl}$) or orange ($\text{X} = \text{Br}$) solutions rapidly become colourless, whilst in dichloromethane at 0°C this process is very slow. In all cases this behaviour is due to the isomerisation of the gold(II) derivative into the mixed gold(III)–gold(I) isomer [equation (8)].



The C_6Cl_5 derivatives are less soluble than those of C_6F_5 but the same isomerisation is observed and is again slower in CH_2Cl_2 solution.

The mixed complexes (12)—(15) are air- and moisture-stable at room temperature and give non-conducting acetone solutions (Table 1).

Important differences between the isomers are as follows. (i) The gold(II) derivatives are yellow ($\text{X} = \text{Cl}$) or orange ($\text{X} = \text{Br}$). The mixed complexes are colourless. (ii) $\nu(\text{Au}-\text{Cl})$ appears at 270s (8) or 280s cm^{-1} (10) in the i.r. spectra of the gold(II) chloro-complexes, in accordance with observations made for other gold(II) complexes.^{3,6,16} After isomerisation, this band is shifted to higher energy and appears in both cases at 320 cm^{-1} (broad, asymmetric), which indicates a *cis* configuration.¹⁵ In the gold(II) bromo-derivatives $\nu(\text{Au}-\text{Br})$ has not been observed; it is probably located beyond the lower limit of our spectrometer (200 cm^{-1}). In the mixed isomers a band at 220m,br cm^{-1} points to a *cis* configuration.¹⁵ (iii) The only other clear modification of an i.r. absorption occurs in the spectra of the pentafluorophenyl derivatives; the bands at 961vs or 960vs cm^{-1} in the gold(II) complexes (8) and (9) change to a doublet at 967vs and 957vs (12) or 970vs and 957vs (13) cm^{-1} respectively in the mixed isomers.

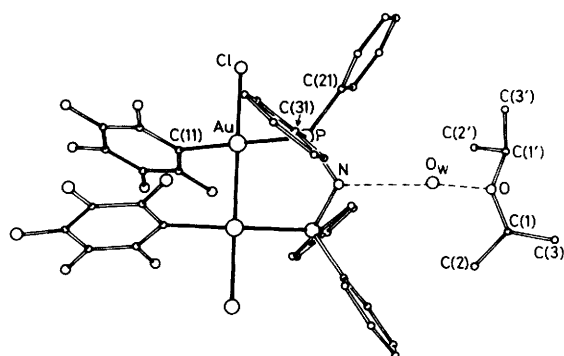


Figure. The structure of $[(\text{C}_6\text{F}_5)\text{ClAu}(\text{dppa})\text{AuCl}(\text{C}_6\text{F}_5)] \cdot 2\text{C}_6\text{H}_{14}\text{O} \cdot \text{H}_2\text{O}$ in the crystal, showing the atomic-numbering scheme of the asymmetric unit (radii arbitrary, H atoms omitted). The atoms N and O_w lie on the two-fold axis $\frac{1}{2}, y, \frac{1}{2}$. Probable hydrogen bonding contacts (\AA): $\text{N} \cdots \text{O}_w$ 2.744, $\text{O} \cdots \text{O}_w$ 2.796, and (not shown) $\text{H}(\text{N}) \cdots \text{O}_w$ 1.89

Table 2. Au–Au bond lengths in various Au^{II} complexes (R = alkyl or aryl)

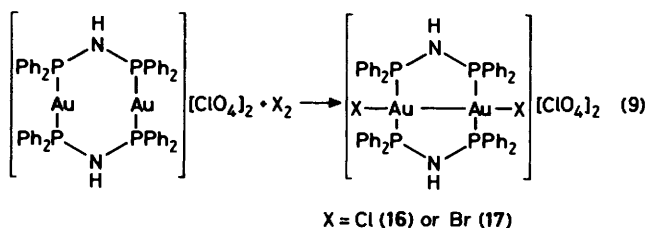
X	Y	Z	Au–Au (\AA)	Ref.
CH_2	Cl	Cl	2.597	a
CH_2	I	I	2.654	b
CH_2	I	CH_3	2.695	b
CH_2	CN	CN	2.637	c
S	I	I	2.607	d
CH_2	I	CH_2Cl	2.681	e

^a H. Schmidbaur, J. R. Mandl, A. Franck, and G. Huttner, *Chem. Ber.*, 1976, **109**, 466. ^b J. P. Fackler, jun., and J. D. Basil, *Organometallics*, 1982, **1**, 871. ^c H. H. Murray, A. M. Mazany, and J. P. Fackler, jun., *Organometallics*, 1985, **4**, 154. ^d A. M. Mazany and J. P. Fackler, jun., *J. Am. Chem. Soc.*, 1984, **106**, 801. ^e H. H. Murray, J. P. Fackler, jun., and A. M. Mazany, *Organometallics*, 1984, **3**, 1310.

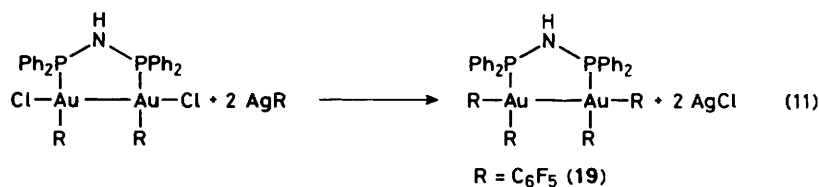
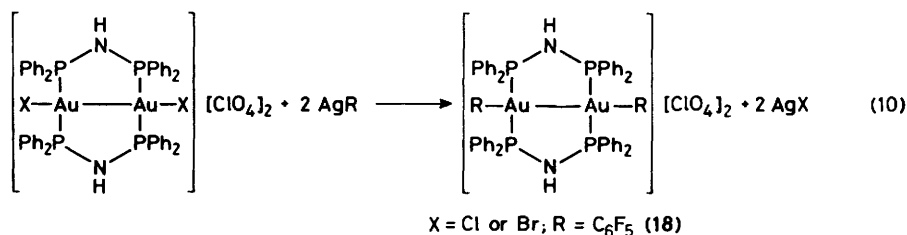
The X-ray structure determination of complex $[(\text{C}_6\text{F}_5)\text{ClAu}(\text{dppa})\text{AuCl}(\text{C}_6\text{F}_5)]$ (8), as a mixed di-isopropyl ether–water solvate, confirms the novel binuclear gold(II) structure with square-planar co-ordination at the metal atoms (see Experimental section and Figure). The Au–Au bond length of $2.576(2)\text{ \AA}$ is the shortest reported {*cf.* av. 2.584 \AA in the axial Au–Au bonds of the cluster $[\text{Au}_7(\text{PPh}_3)_7]^{+17}$ }. A fairly wide range of $\text{Au}^{\text{II}}-\text{Au}^{\text{II}}$ bond lengths (up to 2.695 \AA ; Table 2) is known; the shorter bonds are associated with chloro-ligands but there is no clear trend.

The cationic complex (3) also undergoes oxidative-addition with halogens [equation (9)] to give cationic gold(II) derivatives.

Complexes (16) and (17) are air- and moisture-stable, orange solids, solutions of which become colourless (after some seconds, in acetone; 10 min, in nitromethane; 30 min, in dichloromethane), giving several products, one of which is the gold(I) binuclear complex $[\text{X}\text{Au}(\text{dppa})\text{AuX}]$ ($\text{X} = \text{Cl}$ or Br). In the solid-state spectra, two bands at $1\ 100\text{s,br}$ and 620m cm^{-1} are assignable to the ClO_4^- anion (T_d). Complex (16) shows $\nu(\text{Au}-\text{Cl})$ at 287m cm^{-1} .



We have recently shown¹³ that $\text{Ag}(\text{C}_6\text{F}_5)$ is a suitable arylating agent for gold(III) chloro-complexes, since no perceptible reduction takes place. Arylation of the gold(II) complexes (8), (16), and (17) with $\text{Ag}(\text{C}_6\text{F}_5)$ leads to novel gold(II) complexes, both neutral and anionic, in which the Au centres are linked to one or two C_6F_5 groups [equations (10) and (11)].



Complexes (18) and (19) are air- and moisture-stable yellow solids, and their solutions are reasonably stable; a dichloromethane solution of (19) turns colourless after a week, giving a mixture in which complex (7) has been identified. Yellow nitromethane or dichloromethane solutions of (18) do not change within a period of two weeks.

Complex (18) behaves as a 2:1 electrolyte in nitromethane; complex (19) is non-conducting. Its molecular weight (Table 1) is as expected for the proposed formula. The i.r. spectra of both complexes show a band at 959 vs (18) or 960 vs cm^{-1} (19) due to the C_6F_5 ligands bonded to gold(II) centres. The bands in the 800 cm^{-1} region in these complexes cannot be easily assigned.

Experimental

Instrumentation and general experimental techniques were as described earlier.⁴ Yields, melting points, C, H, N, and Au analyses are listed in Table 1. All reactions were carried out at room temperature.

$[\text{RAu}(\text{dppa})\text{AuR}]$ [R = C_6F_5 (1) or C_6Cl_5 (2)].—To a dichloromethane solution (15 cm^3) of $[\text{AuR}(\text{tht})]$ (0.5 mmol) [R = C_6F_5 ¹⁸ (0.226 g) or C_6Cl_5 ¹⁹ (0.267 g)] was added dppa²⁰ (0.096 g, 0.25 mmol) and the mixture stirred for 30 min. Evaporation to 5 cm^3 and addition of n-hexane (5 cm^3) leads to (1) or (2) in over 90% yield. Recrystallization was from ethanol-hexane.

$[\text{Au}_2(\text{dppa})_2][\text{ClO}_4]_2$ (3).—To a dichloromethane solution (20 cm^3) of $[\text{Au}(\text{tht})_2][\text{ClO}_4]_2$ ²¹ was added dppa (0.096 g, 0.25

mmol) and the mixture stirred for 1 h. The solution was concentrated to 5 cm^3 , and diethyl ether (10 cm^3) was added. The white precipitate was recrystallized from acetone-hexane.

$[\text{Au}(\text{C}_6\text{F}_5)_3(\text{dppa})]$ (4).—A mixture of $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{tht})]$ ¹³ (0.079 g, 0.1 mmol) and dppa (0.039 g, 0.1 mmol) in dichloromethane (30 cm^3) was stirred for 1 h. Evaporation to 5 cm^3 and addition of hexane (15 cm^3) precipitated (4) as a white solid.

$[\text{Au}(\text{C}_6\text{F}_5)_2\text{Cl}(\text{dppa})]$ (5).—To a diethyl ether solution (20 cm^3) of *cis*- $[\text{NBu}_4][\text{Au}(\text{C}_6\text{F}_5)_2\text{Cl}_2]$ ¹⁴ (0.084 g, 0.1 mmol) was added AgClO_4 (0.021 g, 0.1 mmol) and the mixture stirred for 1 h. The precipitated AgCl and $[\text{NBu}_4]\text{ClO}_4$ were removed by filtration through a 1-cm layer of diatomaceous earth. Some dppa (0.039 g, 0.1 mmol) was added to the filtrate. After stirring for 1 h, the solution was concentrated to 5 cm^3 . Addition of

n-hexane (20 cm^3) precipitated (5) as a white solid. Recrystallization was from acetone-hexane.

$[(\text{C}_6\text{F}_5)_3\text{Au}(\text{dppa})\text{AuX}]$ [X = Cl (6) or C_6F_5 (7)].—A mixture of $[\text{AuX}(\text{tht})]$ (0.1 mmol) [X = Cl¹⁸ (0.032 g) or C_6F_5 ¹⁸ (0.045 g)] and complex (4) (0.108 g, 0.1 mmol) in diethyl ether (20 cm^3) was stirred for 3 h. Concentration to 5 cm^3 and addition of hexane (10 cm^3) precipitated complex (6) or (7). Recrystallization was from dichloromethane-hexane.

$[\text{RXAu}(\text{dppa})\text{AuXR}]$ [R = C_6F_5 , X = Cl (8) or Br (9); R = C_6Cl_5 , X = Cl (10) or Br (11)].—1 cm^3 of a halogen solution in chloroform (0.1 mmol cm^{-3}) was added to a dichloromethane solution (10 cm^3) of (1) (0.111 g, 0.1 mmol) or (2) (0.129 g, 0.1 mmol). The solution instantaneously turned yellow (X = Cl) or orange (X = Br). Thereafter the solutions were vacuum evaporated to ca. 5 cm^3 , and hexane (5 cm^3) was added. The yellow [(8) and (10)] or orange [(9) and (11)] solids were filtered off and vacuum dried.

$[\text{RX}_2\text{Au}(\text{dppa})\text{AuR}]$ [R = C_6F_5 , X = Cl (12) or Br (13); R = C_6Cl_5 , X = Cl (14) or Br (15)].—Dichloromethane solutions [R = C_6F_5 (20 cm^3) or C_6Cl_5 (100 cm^3) containing 0.1 mmol] of (8), (9), (10), or (11) were stirred for 10–24 h and thereafter concentrated to 5 cm^3 . Addition of n-hexane (20 cm^3) precipitated (12)–(15) as white solids.

$[\text{XAu}(\text{dppa})_2\text{AuX}][\text{ClO}_4]_2$ [X = Cl (16) or Br (17)].—To a suspension of (3) (0.136 g, 0.1 mmol) in dichloromethane (5 cm^3) was added 1 cm^3 of a solution containing 0.1 mmol X_2

Table 3. Atom co-ordinates ($\times 10^4$) for $[(C_6F_5)ClAu(dppa)AuCl(C_6F_5)] \cdot 2C_6H_{14}O \cdot H_2O$

Atom	X/a	Y/b	Z/c
Au	5 401(1)	6 205(1)	2 007(1)
P	5 763(1)	4 932(1)	2 383(1)
Cl	6 125(1)	6 195(1)	1 107(1)
N	5 000	4 448(3)	2 500
C(11)	5 088(3)	7 346(3)	1 703(3)
C(12)	4 386(4)	7 551(4)	1 264(3)
C(13)	4 216(4)	8 290(4)	990(4)
C(14)	4 752(5)	8 875(4)	1 167(5)
C(15)	5 457(5)	8 699(4)	1 620(5)
C(16)	5 618(4)	7 941(4)	1 867(3)
F(12)	3 836(2)	7 005(2)	1 084(2)
F(13)	3 528(3)	8 452(3)	543(3)
F(14)	4 590(4)	9 594(3)	894(3)
F(15)	6 009(3)	9 253(3)	1 802(3)
F(16)	6 321(2)	7 788(2)	2 313(2)
C(21)	6 140(3)	4 346(3)	1 746(3)
C(22)	6 848(3)	4 013(4)	1 929(3)
C(23)	7 110(4)	3 572(5)	1 422(4)
C(24)	6 656(4)	3 463(5)	709(4)
C(25)	5 958(4)	3 802(4)	510(4)
C(26)	5 682(3)	4 248(4)	1 014(3)
C(31)	6 463(3)	4 946(3)	3 259(3)
C(32)	7 044(3)	5 505(4)	3 355(4)
C(33)	7 587(5)	5 542(5)	4 038(4)
C(34)	7 555(4)	5 022(5)	4 585(4)
C(35)	6 984(4)	4 491(5)	4 498(4)
C(36)	6 441(4)	4 439(4)	3 832(3)
O	4 064(3)	1 874(3)	1 433(3)
C(1)	3 344(4)	1 586(5)	1 548(5)
C(2)	3 075(6)	2 201(6)	2 049(7)
C(3)	3 433(7)	775(6)	1 881(7)
C(1')	4 285(6)	1 641(6)	767(5)
C(2')	3 871(10)	2 178(8)	132(7)
C(3')	5 180(7)	1 622(8)	954(8)
O _w	5 000	2 837(3)	2 500

(X = Cl or Br) in chloroform (1 cm³). An orange colour immediately appeared and after a few seconds (16) or (17) precipitated as an orange solid. By evaporating the solution to 5 cm³ a second crop was obtained.

$[(C_6F_5)Au(dppa)_2Au(C_6F_5)] [ClO_4]_2$ (18).—To a freshly prepared diethyl ether solution (10 cm³) of $Ag(C_6F_5)_2^{22}$ (0.2 mmol) was added a dichloromethane solution (40 cm³) of (17) (0.152 g, 0.1 mmol) and the mixture stirred for 10 min. After filtering off the AgBr the solution was concentrated to 5 cm³. Addition of di-isopropyl ether (10 cm³) precipitated (18), which was recrystallized from dichloromethane–diethyl ether.

$[(C_6F_5)_2Au(dppa)Au(C_6F_5)_2]$ (19).—To a freshly prepared diethyl ether solution (10 cm³) of $Ag(C_6F_5)_2^{22}$ (0.2 mmol) was added a dichloromethane solution (40 cm³) of (8) (0.118 g, 0.1 mmol). After stirring for 5 min the AgCl was filtered off and the filtrate concentrated to 5 cm³. By adding diethyl ether (20 cm³) yellow (19) precipitated and was recrystallized from dichloromethane–hexane.

Crystal-structure Determination of (8)·2C₆H₁₄O·H₂O.—Attempts to obtain single crystals of (8) by liquid diffusion of

* Additional crystallographic material (complete bond lengths and angles, structure factors, H atom co-ordinates, thermal parameters) can be ordered from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany. Please quote reference number CSD/51430, the names of the authors, and the title of the paper.

Table 4. Selected bond lengths (Å) and angles (°) for $[(C_6F_5)ClAu(dppa)AuCl(C_6F_5)] \cdot 2C_6H_{14}O \cdot H_2O$ *

Au–P	2.322(2)
Au–C(11)	2.064(6)
N–P	1.659(4)
Au–Cl	2.341(3)
Au–Au [†]	2.576(2)
C(21)–P	1.794(7)
C(31)–P	1.795(6)
P–Au–Cl	92.3(2)
Cl–Au–C(11)	88.6(3)
C(11)–Au–Au [†]	91.7(3)
P–Au–Au [†]	87.4(2)
P–Au–C(11)	178.4(2)
Cl–Au–Au [†]	179.5(2)
Au–P–N	108.7(3)
P–N–P [†]	120.5(5)
Au–P–C(21)	116.5(3)
Au–P–C(31)	110.0(3)
C(21)–P–C(31)	107.5(3)
N–P–C(21)	105.2(3)
N–P–C(31)	108.5(3)

* Symmetry operator (I): 1 – x, y, 0.5 – z.

light petroleum (b.p. 60–80 °C) into dichloromethane solutions at –21 °C afforded irregular yellow plates, which were mounted in glass capillaries with the mother-liquor to prevent the immediate loss of solvent of crystallization. The cell constants and space group could be determined [$P2_1/n$, $a = 12.492(5)$, $b = 27.858(10)$, $c = 14.364(4)$ Å, $\beta = 113.64(2)^\circ$] but the crystals decomposed rapidly on irradiation. A different, air-stable, modification in the form of yellow prisms was then obtained by using di-isopropyl ether instead of light petroleum as precipitant. The crystallization solvents were not dried prior to use.

Crystal data. $C_{36}H_{21}Au_2Cl_2F_{10}NP_2 \cdot 2C_6H_{14}O \cdot H_2O$, $M = 1228.7$, monoclinic, space group $C2/c$, $a = 18.009(3)$, $b = 17.033(2)$, $c = 18.420(3)$ Å, $\beta = 103.79(2)^\circ$, $U = 5487$ Å³, $Mo-K_\alpha$ radiation ($\lambda = 0.71069$ Å), $Z = 4$, $D_c = 1.68$ g cm⁻³, crystal dimensions $0.55 \times 0.3 \times 0.15$ mm, $\mu = 5.6$ mm⁻¹, $F(000) = 2688$.

Data collection and processing. Stoe-Siemens four-circle diffractometer, graphite-monochromated $Mo-K_\alpha$ radiation, 5672 profile-fitted²³ reflections ($2\theta_{max} = 50^\circ$, $+h+k \pm l$ and some $-h$ equivalents), 4930 unique, 4000 with $F > 4\sigma(F)$ used for all calculations. Absorption correction based on ψ -scans; transmissions 0.66–0.97. Crystal decay ca. 6% based on 3 check reflections; intensities corrected accordingly. Cell constants refined from 20 values of 54 reflections in the range 20–23°.

Structure solution and refinement. Heavy-atom method; least-squares refinement on F to R 0.035, R' 0.038 [all non-H atoms isotropic; isotropic H, most located in difference syntheses, included in refinement using a riding model with C–H 0.96 Å, $U(H) = 1.2 U_{eq}(C)$ except for water and methyl H (not located), N–H (fixed at position from difference Fourier); weighting scheme $w^{-1} = \sigma^2(F) + 0.00025 F^2$; 308 parameters]. Program system SHELXTL (written by G. M. S.). Final atomic co-ordinates and derived parameters are given in Tables 3 and 4.*

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