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POLYNUCLEAR PALLADIUM AND GOLD PERHALOPHENYL DERIVATIVES WITH dppm BRIDGES. CRYSTAL AND MOLECULAR STRUCTURE OF *trans*-$C_6F_5Au(\mu\text{-dppm})Pd(C_6F_5)_2(\mu\text{-dppm})AuC_6F_5$ (dppm = $Ph_2PCH_2PPh_2$)

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Summary

Reactions of $PdRR'(\eta^1\text{-dppm})_2$ ($R = R' = C_6F_5$ or C_6Cl_5; $R = C_6F_5$, $R' = Cl$; dppm = $Ph_2PCH_2PPh_2$) with the gold derivatives ClAu(tht), $C_6F_5Au(tht)$, $(C_6F_5)_3Au(tht)$ or $O_3ClOAuPPh_3$ (tht = tetrahydrothiophen) in appropriate ratios yield the bi- or tri-nuclear complexes $PdRR'(dppm)_2AuCl$, $PdRR'(dppm)_2Au(C_6F_5)$; $PdRR'(dppm)_2Au(C_6F_5)_3$; $PdRR'(dppmAuCl)_2$; $PdRR'(dppmAuC_6F_5)_2$; $PdRR'\{dppmAu(C_6F_5)_3\}_2$, $[PdRR'(dppm)_2Au]X$ ($X = ClO_4$ or BPh_4); $[PPh_3Au(dppm)Pd(C_6F_5)_2(dppm)AuCl]ClO_4$ or $[PPh_3Au(dppm)Pd(C_6F_5)_2(dppm)Au(C_6F_5)_3]ClO_4$. The structure of *trans*-$Pd(C_6F_5)_2\{dppmAu(C_6F_5)\}_2$ has been determined by X-ray diffraction.

Introduction

The ligand $Ph_2PCH_2PPh_2$ (dppm) is very versatile, being able to bridge two metal atoms to give binuclear complexes by formation of (a) a metal–metal bond [1–4]; (b) A-frame compounds [1,3–6]; (c) bimetallic homo- or hetero-metallic eight-membered rings [7–9]. The ligand can also form mononuclear complexes by acting as a chelate [10] or as a monodentate ligand [10,11]. The monodentate complexes are appropriate precursors for the syntheses of binuclear homo- [4] or hetero-metallic [12,13] compounds and we now describe the synthesis of heterobimetallic (Pd, Au) derivatives (some of which contain eight-membered rings) and trinuclear complexes containing two Pd–dppm–Au bridges. These were obtained by treating $PdRR'(\eta^1\text{-dppm})_2$ derivatives ($R = R' = C_6F_5$, C_6Cl_5 or $R = C_6F_5$, $R' = Cl$) with the gold complexes ClAu(tht), $C_6F_5Au(tht)$, $(C_6F_5)_3Au(tht)$ (tht = tetrahydrothiophen) or $O_3ClOAuPPh_3$ in the appropriate molecular ratios.

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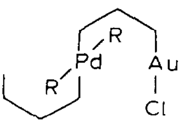
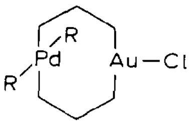
Results and discussion

Palladium(II) complexes of the type *trans*-PdRR′(η^1-dppm)$_2$ (R = R′ = C_6F_5, C_6Cl_5; R = C_6F_5, R′ = Cl), containing two unidentate dppm ligands, can act as bidentate ligands by using the two uncoordinated P-donor atoms. Thus they react with gold complexes containing easily replaceable ligands to give bi- or poly-nuclear heterometallic Au–Pd complexes.

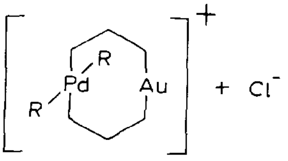
The precursors PdRR′(η^1-dppm)$_2$ show a wide range of reactions (Scheme 1). Thus, the 1 : 1 reaction with ClAu(tht) in CH_2Cl_2 gives the binuclear complexes I or II (Scheme 1, (a)) for R = R′ = C_6F_5 or R = C_6F_5, R′ = Cl (respectively) by displacement of the tht group (but when R = R′ = C_6Cl_5 a different reaction occurs (Scheme 1, (f); see below)). The molecular weights of complexes I and II (in $CHCl_3$ solution) are in agreement with the formula weights (Table 1). Both compounds are conducting in acetone solution, though the conductivity of I is lower than that expected for a 1 : 1 electrolyte [14] (see Table 1). The IR spectrum of complex II shows an absorption at 305m cm^{-1}, assignable to ν(Pd–Cl). Moreover, since the IR spectra of I and II do not exhibit the expected band arising from the stretching vibration ν(Au–Cl) (observed at ca. 330 cm^{-1} for other gold(I) complexes [15]), structure **A**



(A)



(B)



(C)

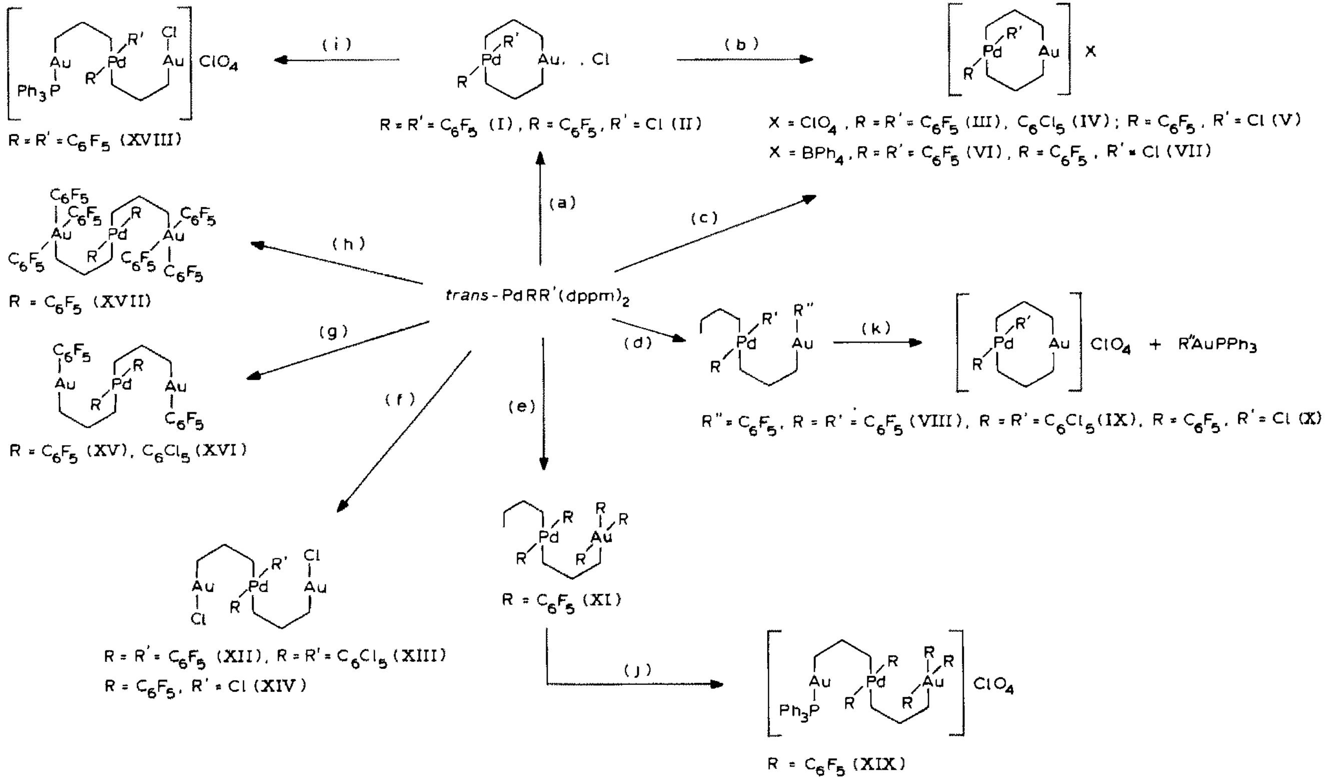
can be ruled out. Structure **B** cannot be excluded, though the measured conductivities and the absence of any ν(Au–Cl) absorption seem to favour structure **C**. The observed behaviour could arise from interactions with the solvent; tri-coordinated gold(I) complexes (with structures determined by X-ray diffraction [9,16]) behave similarly to complexes I and II, their ν(Au–Cl) absorptions appear below 200 cm^{-1} [9,17,18] (the lower limit of our instrument) and they dissociate in polar solvents to give conducting solutions [16]. Structure **C** has recently been suggested for a similar platinum/gold complex (although an analogous platinum/silver complex has structure **B** in the solid state) [8,19].

Complex I reacts (Scheme 1, (b)) with $AgClO_4$ or $NaBPh_4$ in dichloromethane or acetone to give the cationic binuclear complexes III, VI and VII. Cationic binuclear complexes can also be obtained by the 1 : 1 reaction of PdRR′(η^1-dppm)$_2$ (R = R′ = C_6F_5, C_6Cl_5; R = Cl, R′ = C_6F_5) with freshly prepared CH_2Cl_2 solutions of $O_3ClOAuPPh_3$ (Scheme 1, (c)), which results in displacement of both the O_3ClO and the PPh_3 [19] ligands and gives the complexes III, IV and V.

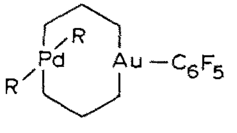
Complexes III–VII are white solids, which in acetone solution behave as 1 : 1 electrolytes [14]. Since IV is only very slightly soluble, its conductivity could not be measured (see Table 1). Complexes VI and VII show an absorption at 610s cm^{-1}, assignable [4] to the BPh_4^- anion, whilst III, IV and V exhibit absorptions at 1100s and 620m cm^{-1} due [20] to the ClO_4^- anion (T_d).

The 1 : 1 reaction of the precursors *trans*-PdRR′(η^1-dppm)$_2$ with C_6F_5Au(tht) in acetone or dichloromethane results in displacement of the (tht) ligand and formation

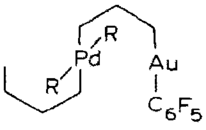
SCHEME 1. (a) ClAu(tht); (b) for III, $AgClO_4$, for VI and VII, $NaBPh_4$; (c) for III, IV and V, $O_3ClOAuPPh_3$; (d) $C_6F_5Au(tht)$; (e) $(C_6F_5)_3Au(tht)$; (f) ClAu(tht), molar ratio Pd/Au 1/2; (g) $C_6F_5Au(tht)$, molar ratio Pd/Au 1/2; (h) $(C_6F_5)_3Au(tht)$, molar ratio Pd/Au 1/2; (i) $O_3ClOAuPPh_3$, molar ratio Pd/Au 1/1; (j) O_3 $ClOAuPPh_3$, molar ratio Pd/Au 1/1; (k) $O_3ClOAuPPh_3$, molar ratio Pd/Au 1/1.



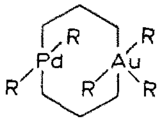
(Scheme 1, (d)) of the binuclear complexes VIII, IX and X. Use of $(C_6F_5)_3Au(tht)$ instead of $C_6F_5Au(tht)$ gives XI, a binuclear Pd^{II}–Au^{III} complex (Scheme 1, (e)). Complexes VIII–XI are white solids, which give non-conducting acetone solutions. Their molecular weights in chloroform solution are as expected for the proposed formulae (see Table 1). (The low solubility of complex IX precluded both determinations). These results are not sufficient to distinguish between structures **D** or **E**, for complexes VIII, IX and X and between structures **F** and **G**, for complex XI, but we



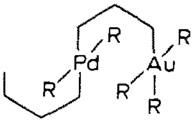
(D)



(E)



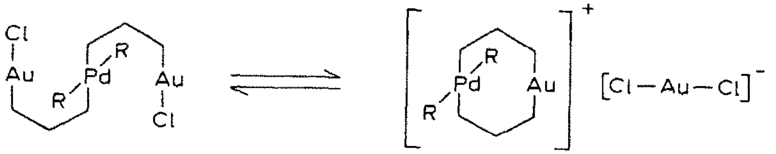
(F)



(G)

feel that structure **F** with five-coordinated gold(III) is less probable than **G**, since five-coordinated gold(III) complexes are rare [21], and even a strong chelating ligand such as *o*-phenylenebis(dimethylarsine) (diars) is unidentate in $(C_6F_5)_3Au(diars)$, which contains [22] square-planar gold(III).

In dichloromethane solution *trans*-PdRR′(η^1-dppm)$_2$ reacts with ClAu(tht) in 1/2 ratio (Scheme 1, (f)) to give the trinuclear complexes XII, XIII and XIV. Complex XIII can also be obtained if a 1/1 ratio of the reactants is used (albeit in lower yield), presumably due to its very low solubility, which also precludes reaction path (a) (see above). Despite their apparent non-ionic nature, XII and XIV are conducting in acetone solution (see Table 1), probably owing to equilibria such as that in eq. 1 of the type



(1)

observed [23] for other gold compounds. The IR spectra of complexes XII–XIV show ν(Au–Cl) at ~ 330 cm^{-1}. A weak absorption at 305 cm^{-1} in the spectrum of XIV is thought to be ν(Pd–Cl).

Similarly, 1/2 reactions of *trans*-PdRR′(η^1-dppm)$_2$ with $C_6F_5Au(tht)$ (g) or with $(C_6F_5)_3Au(tht)$ (h) lead to the trinuclear complexes XV, XVI and XVII respectively. The structure of complex XV has been resolved by a single crystal X-ray diffraction study (Fig. 1; see below).

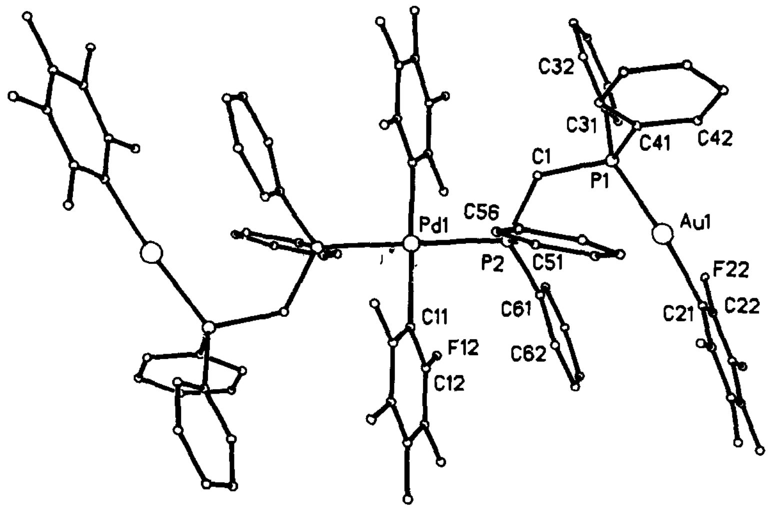
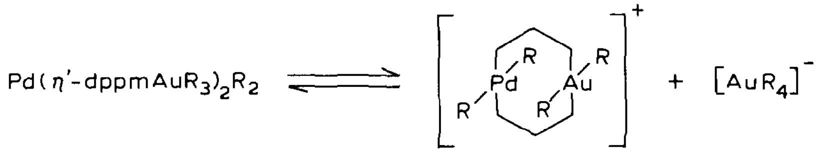


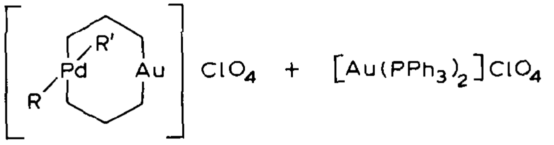
Fig. 1. The structure of XV in the crystal, showing the atom numbering scheme.

Complex XVII is also conducting in acetone solution, and again we postulate an equilibrium (eq. 2).



(2)

Complexes XV and XVII can also be prepared by 1/2 reaction of $C_6F_5Au(\eta^1$-dppm) or $(C_6F_5)_3Au(\eta^1$-dppm) [10] with *trans*-$Pd(C_6F_5)_2(tht)_2$. The 1/2 reaction between *trans*-$PdRR'(\eta^1$-dppm$)_2$ and $O_3ClOAuPPh_3$ in CH_2Cl_2 solution gives dinuclear (rather than trinuclear) derivatives and $[Au(PPh_3)_2]ClO_4$ (eq. 3).

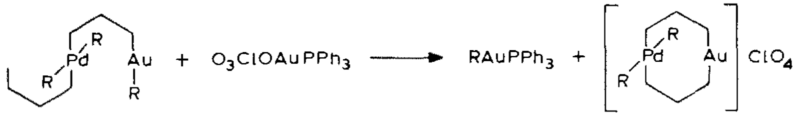


(3)

R = R' = C_6F_5 (III), C_6Cl_5 (IV) ; R' = C_6F_5, R = Cl (V)

The 1/1 reaction of I with $O_3ClOAuPPh_3$ (in CH_2Cl_2 solution) gives the trinuclear complex XVIII (Scheme 1, (i)), whose IR absorption at 330 cm^{-1} suggests a terminal (Au–Cl) bond. Its spectrum shows also absorptions at 1100s, br and 625m cm^{-1}, assignable to the ClO_4^- anion. Addition of stoicheiometric amounts of $O_3ClOAuPPh_3$ (in CH_2Cl_2) to the binuclear complex XI (Scheme 1, (j)) leads to formation of the ionic trinuclear complex XIX, which also shows the two bands due to ClO_4^- at 1100s, br and 625m cm^{-1}.

Addition of a dichloromethane solution of $O_3ClOAuPPh_3$ to complex VIII does not give a trinuclear species but results in migration of a C_6F_5 group from one Au atom to the other (eq. 4).



(4)

The IR spectra of complexes I–XIX show absorption due to the dppm ligand e.g. in the 540–520 cm^{-1} region. Absorptions arising from the C_6F_5 group [24–26] are observed in the 1645–1630, 1510–1495, 1080–1030, 970–950 and 815–780 cm^{-1} regions. The absorption at ~ 950 cm^{-1} [27], whose position changes with change in the oxidation state or the nature of the central atom, appears as a narrow band in all the complexes containing C_6F_5 groups attached to only one metal atom (Pd or Au) (I, II, III, V, VI, VII, IX, XII, XIV, XV, XVIII) and as a broad band (VIII, X, XV, XVII) or a double band (XI, XIX) when the C_6F_5 groups are linked to both Pd and Au. The band due to the X-sensitive mode of C_6F_5 (at 815–785 cm^{-1}) [28] is masked by absorptions due to dppm in this region.

The C_6Cl_5 derivatives show absorptions [29] at 1325, 1295, 1230 and 610 cm^{-1}.

Experimental

Infrared spectra were recorded on a Perkin–Elmer 599 spectrophotometer using Nujol mulls between polyethylene plates. C, H and N analyses were carried out with a Perkin–Elmer 240 microanalyser. Conductivities were measured in ca. 5×10^{-4} mol dm^{-3} acetone solutions with a Philips PW 9501/01 conductimeter.

The C, H and N analyses, yields, melting points and conductivities of the novel complexes are presented in Table 1. *trans*-$Pd(C_6F_5)_2(\eta^1\text{-dppm})_2$ and *trans*-$PdCl(C_6F_5)(\eta^1\text{-dppm})_2$ were prepared by treating *trans*-$Pd(C_6F_5)_2(tht)_2$ or $[Pd(\mu\text{-}Cl)(C_6F_5)(tht)]_2$ with dppm, as previously described [4]. *trans*-$Pd(C_6Cl_5)_2(\eta^1\text{-dppm})_2$ was prepared as described for the pentafluorophenyl derivative.

The gold complexes were obtained as previously described: ClAu(tht) [30], $C_6F_5Au(tht)$ [30], $(C_6F_5)_3Au(tht)$ [22], $O_3ClOAuPPh_3$ [31], $(C_6F_5)_3Au(\eta^1\text{-dppm})$ [22].

All the reactions were carried out at room temperature.

Reaction of $PdRR'(\eta^1\text{-dppm})_2$ *with ClAu(tht)* ($R = R' = C_6F_5$ *(I)*; $R = C_6F_5$, $R' = Cl$ *(II)*)

(i) 1/1 molar ratio. ClAu(tht) (0.09 g, 0.28 mmol) was added to a solution of *trans*-$Pd(C_6F_5)_2(\eta^1\text{-dppm})_2$ (0.339 g, 0.28 mmol) in 50 ml of CH_2Cl_2 and the mixture was stirred for 30 min. (The free tht could be detected by its unpleasant smell.) Concentration to ca. 10 ml and addition of n-hexane led to the crystallization of I, which was recrystallized from CH_2Cl_2/n-hexane and dried at 70 °C for 2 h.

Similar reaction of $PdCl(C_6F_5)(\eta^1\text{-dppm})_2$ and ClAu(tht) gave complex II.

trans-$Pd(C_6Cl_5)_2(\eta^1\text{-dppm})_2$ reacted with ClAu(tht) to give the trinuclear complex XIII, which separated after partial evaporation of the solvent (40% yield); addition of n-hexane to the mother liquors yielded some $Pd(C_6Cl_5)_2(\eta^1\text{-dppm})_2$.

(ii) 1/2 molar ratio. Use of a 1/2 ratio of the above reactants gave complex XII, *trans*-$Pd(C_6F_5)_2(\eta^1\text{-dppm})_2$ (0.302 g, 0.25 mmol) with ClAu(tht) (0.160 g, 0.50

TABLE 1

ANALYTICAL RESULTS[a], MELTING POINTS, YIELDS, CONDUCTIVITIES AND MOLECULAR WEIGHTS FOR THE NOVEL COMPLEXES[b]

Complex	C (%)	H (%)	M.p. (°C)	Yield (%)	Λ_M (Ω^{-1} cm^2 mol^{-1})	M.W.
trans-$(C_6F_5)_2$Pd(dppm)$_2$AuCl (I)	51.54	3.09	140(d)	83	64	1355
	(51.60)	(3.05)				(1441)
trans-(C_6F_5)ClPd(dppm)$_2$AuCl (II)	51.06	3.62	187(d)	87	111	1321
	(51.34)	(3.36)				(1310)
trans-[$(C_6F_5)_2$Pd(dppm)$_2$Au]ClO$_4$ (III)	48.88	3.11	160(d)	63	128	
	(49.43)	(2.92)				
[*trans*-$(C_6Cl_5)_2$Pd(dppm)$_2$Au]ClO$_4$ (IV)	44.30	3.08	219(d)	54	[c]	
	(44.54)	(2.63)				
[*trans*-(C_6F_5)ClPd(dppm)$_2$Au]ClO$_4$(V)	49.21	3.35	175(d)	85	134	
	(48.95)	(3.20)				
trans-[$(C_6F_5)_2$Pd(dppm)$_2$Au]BPh$_4$ (VI)	60.72	4.17	129(d)	73	80	
	(59.80)	(3.70)				
trans-[(C_6F_5)ClPd(dppm)$_2$Au]BPh$_4$ (VII)	60.37	4.19	146(d)	90	90	
	(60.28)	(4.01)				
trans-$(C_6F_5)_2$Pd(dppm)$_2$AuC$_6$F$_5$ (VIII)	52.08	3.08	191(d)	68	10	1406
	(51.86)	(2.79)				(1583)
trans-$(C_6Cl_5)_2$Pd(dppm)$_2$AuC$_6$F$_5$ (IX)	47.15	2.70	203(d)	78	[c]	
	(46.92)	(2.53)				
trans-(C_6F_5)ClPd(dppm)$_2$AuC$_6$F$_5$ (X)	50.99	2.77	150(d)	72	2	1328
	(51.65)	(3.05)				(1441)
trans-$(C_6F_5)_2$Pd(dppm)$_2$Au$(C_6F_5)_3$ (XI)	49.65	2.53	143(d)	84	2	1769
	(50.33)	(2.30)				(1907)
trans-$(C_6F_5)_2$Pd(dppmAuCl)$_2$ (XII)	44.17	2.95	132(d)	87	15	1583
	(44.48)	(2.62)				(1674)
trans-$(C_6Cl_5)_2$Pd(dppmAuCl)$_2$ (XIII)	39.60	2.47	215(d)	89	[c]	[d]
	(40.46)	(2.39)				
trans-(C_6F_5)ClPd(dppmAuCl)$_2$ (XIV)	44.12	2.99	157(d)	82	20	1516
	(43.60)	(2.85)				(1542)
trans-$(C_6F_5)_2$Pd(dppmAuC$_6$F$_5$)$_2$ (XV)	45.48	2.56	198(d)	76	3	1989
	(45.83)	(2.29)				(1937)
trans-$(C_6Cl_5)_2$Pd(dppmAuC$_6$F$_5$)$_2$ (XVI)	42.65	2.19	193(d)	66	[c]	[d]
	(42.28)	(2.08)				
trans-$(C_6F_5)_2$Pd[dppmAu$(C_6F_5)_3$]$_2$ (XVII)	44.29	2.16	167(d)	71	24	[d]
	(45.17)	(1.68)				
[*trans*-PPh$_3$Au(dppm)Pd$(C_6F_5)_2$-(dppm)AuCl]ClO$_4$ (XVIII)	47.14	3.13	153(d)	72	102	
	(48.03)	(2.94)				
[*trans*-PPh$_3$AudppmPd$(C_6F_5)_2$-dppmAu$(C_6F_5)_3$]ClO$_4$ (XIX)	47.31	2.83	128(d)	71	95	
	(47.68)	(2.39)				

[a] Calculated values in parentheses. [b] dppm = Ph$_2$PCH$_2$PPh$_2$. [c] Low solubility precludes conductivity determination. [d] Low solubility precludes molecular weight determination.

mmol); complex XIII, *trans*-Pd$(C_6Cl_5)_2(\eta^1$-dppm$)_2$ (0.1373 g, 0.1 mmol) with ClAu(tht) (0.064 g, 0.2 mmol); and complex XIV, *trans*-PdCl$(C_6F_5)(\eta^1$-dppm$)_2$ (0.215 g, 0.2 mmol) with ClAu(tht) (0.128 g, 0.4 mmol).

All the isolated complexes were dried at 70 °C for 24 h.

Reaction of PdRR'(η^1-dppm)$_2$ with $C_6F_5Au(tht)$

(i) 1/1 molar ratio. *trans*-Pd(C_6F_5)$_2$(η^1-dppm)$_2$ (0.241 g, 0.2 mmol) was added to a solution of C_6F_5Au(tht) (0.09 g, 0.2 mmol) in 60 ml of acetone and the mixture was stirred for 2 h. Concentration to ~ 10 ml and addition of 15 ml of n-hexane led to precipitation of VIII, which was washed with n-hexane.

A similar reaction of PdCl(C_6F_5)(η^1-dppm)$_2$ with C_6F_5Au(tht) in CH_2Cl_2 led to complex X.

The reaction of *trans*-Pd(C_6Cl_5)$_2$(η^1-dppm)$_2$ (0.274 g, 0.2 mmol) in 60 ml of CH_2Cl_2 with C_6F_5Au(tht) (0.0904 g, 0.2 mmol) followed by 2 h stirring led to partial precipitation of IX. To complete the precipitation the filtrate was concentrated to ~ 10 ml and 10 ml of n-hexane was added.

(ii) 1/2 molar ratio. The reaction of *trans*-Pd(C_6F_5)$_2$(η^1-dppm)$_2$ or *trans*-Pd(C_6Cl_5)$_2$(η^1-dppm)$_2$ with C_6F_5Au(tht) in dichloromethane and work-up as above gave complexes XV and XVI, respectively.

Reaction of trans-Pd(C_6F_5)$_2$(η^1-dppm)$_2$ with (C_6F_5)$_3$Au(tht)

(i) 1/1 molar ratio. *trans*-Pd(C_6F_5)$_2$(η^1-dppm)$_2$ in 50 ml of CH_2Cl_2 was stirred for 30 min with (C_6F_5)$_3$Au(tht) (0.078 g, 0.1 mmol). Partial concentration to ~ 10 ml and addition of n-hexane led to precipitation of XI.

(ii) 1/2 molar ratio. Using 1/2 molar ratio of the same reagents and work-up as above led to XII which was dried at 74 °C for 24 h.

Reaction of trans-PdRR'(η^1-dppm)$_2$ with $O_3ClOAuPPh_3$

(i) 1/1 molar ratio. To a solution of *trans*-Pd(C_6F_5)$_2$(η^1-dppm)$_2$ (0.2 g, 0.165 mmol) in 30 ml of CH_2Cl_2 was added $O_3ClOAuPPh_3$ (0.165 mmol) in 40 ml of CH_2Cl_2. The solution was stirred for 30 min then evaporated to ca. 10 ml. Addition of n-hexane led to precipitation of III, which was recrystallized from CH_2Cl_2/hexane and dried at 70 °C for 10 h.

Treatment of *trans*-Pd(C_6Cl_5)$_2$(η^1-dppm)$_2$ or *trans*-PdCl(C_6F_5)(η^1-dppm)$_2$ with $O_3ClOAuPPh_3$ (1/1 molar ratio) as above gave complexes IV and V respectively.

(ii) 1/2 molar ratio. The above reactions in 1/2 molar ratio gave precipitates of III, IV or V. Evaporation of the mother liquors gave [Au(PPh_3)$_2$]ClO_4.

Reaction of PdRR'(η^1-dppm)$_2$AuCl with $AgClO_4$ or $NaBPh_4$

(i) $AgClO_4$ (0.0308 g, 0.15 mmol) was added in the absence of light to a solution of I (0.216 g, 0.15 mmol) in 50 ml of CH_2Cl_2 and the solution was stirred for 1 h then filtered and concentrated to ~ 10 ml. n-Hexane (15 ml) was added to precipitate a white solid (III), which was recrystallized from CH_2Cl_2/n-hexane and dried at 70 °C for 3 h (61% yield).

(ii) Complex I (0.216 g, 0.15 mmol) in 150 ml of acetone was treated with $NaBPh_4$ (0.051 g, 0.15 mmol) and stirred for 30 min. After filtration, the solution was evaporated to dryness and the residue was extracted with CH_2Cl_2. Partial evaporation (~ 10 ml) and addition of n-hexane afforded VI (76% yield).

Analogous treatment of II with $NaBPh_4$ yielded VIII (90% yield).

Reaction of trans-Pd(C_6F_5)$_2$(dppm)$_2$AuCl (I) with $O_3ClOAuPPh_3$

To complex I (0.18 g, 0.125 mmol) in 40 ml of CH_2Cl_2 was added freshly

TABLE 2

ATOMIC COORDINATES ($\times 10^4$) AND ISOTROPIC TEMPERATURE FACTORS ($Å^2 \times 10^3$) FOR XV

Atom	x/a	y/b	z/c	U^a
Au(1)	1458(1)	5434(1)	5774(1)	46(1)*
Pd(1)	5000	5000	5000	29(1)*
P(1)	2143(2)	4545(1)	6569(3)	39(1)*
P(2)	3790(1)	5261(1)	5863(2)	32(1)*
C(12)	5001(4)	6418(3)	3922(6)	46(3)
C(13)	5188(4)	7099(3)	3850(6)	60(3)
C(14)	5653(4)	7394(3)	4823(6)	66(4)
C(15)	5930(4)	7007(3)	5866(6)	60(3)
C(16)	5743(4)	6326(3)	5938(6)	48(3)
C(11)	5278(4)	6031(3)	4965(6)	36(2)
F(12)	4609(4)	6151(3)	2948(6)	66(3)*
F(13)	4890(5)	7487(4)	2920(8)	107(4)*
F(14)	5816(5)	8049(3)	4774(10)	124(5)*
F(15)	6403(4)	7277(4)	6759(8)	99(4)*
F(16)	6037(4)	5973(3)	6890(6)	62(2)*
C(22)	465(4)	6262(3)	3891(7)	51(3)
C(23)	203(4)	6853(3)	3300(7)	68(4)
C(24)	407(4)	7475(3)	3835(7)	77(4)
C(25)	874(4)	7505(3)	4961(7)	68(4)
C(26)	1137(4)	6913(3)	5552(7)	61(3)
C(21)	932(4)	6292(3)	5017(7)	49(3)
F(22)	274(4)	5691(4)	3350(7)	83(3)*
F(23)	−260(4)	6825(4)	2248(8)	104(4)*
F(24)	150(5)	8052(4)	3296(8)	105(4)*
F(25)	1088(5)	8100(3)	5389(9)	98(3)*
F(26)	1582(4)	6962(3)	6596(7)	79(3)*
C(32)	2153(4)	3139(4)	6547(6)	57(3)
C(33)	1992(4)	2515(4)	5982(6)	75(4)
C(34)	1534(4)	2477(4)	4847(6)	79(4)
C(35)	1236(4)	3062(4)	4279(6)	70(4)
C(36)	1397(4)	3686(4)	4844(6)	55(3)
C(31)	1855(4)	3724(4)	5979(6)	39(2)
C(42)	1436(4)	4622(4)	8943(8)	78(4)
C(43)	1379(4)	4572(4)	10295(8)	107(5)
C(44)	2031(4)	4385(4)	11044(8)	78(4)
C(45)	2740(4)	4247(4)	10441(8)	75(4)
C(46)	2796(4)	4297(4)	9089(8)	56(3)
C(41)	2145(4)	4484(4)	8340(8)	44(3)
C(52)	3129(3)	5938(3)	7965(6)	46(3)
C(53)	3124(3)	6165(3)	9253(6)	57(3)
C(54)	3786(3)	6082(3)	10049(6)	61(3)
C(55)	4453(3)	5774(3)	9559(6)	51(3)
C(56)	4458(3)	5547(3)	8271(6)	50(3)
C(51)	3796(3)	5629(3)	7475(6)	34(2)
C(62)	3285(4)	6524(3)	5023(6)	50(3)
C(63)	2934(4)	6963(3)	4129(6)	68(4)
C(64)	2561(4)	6710(3)	3014(6)	67(4)
C(65)	2537(4)	6018(3)	2793(6)	69(4)
C(66)	2888(4)	5579(3)	3687(6)	47(3)
C(61)	3262(4)	5832(3)	4802(6)	37(2)
C(1)	3159(5)	4518(4)	6023(10)	37(2)

[a] * means equivalent isotropic U calculated from anisotropic U.

prepared $O_3ClOAuPPh_3$ (0.125 mmol) in CH_2Cl_2. After 30 min stirring the solution was concentrated to ~ 10 ml and n-hexane was added to precipitate XVIII.

Reaction of trans-$Pd(C_6F_5)_2(dppm)_2Au(C_6F_5)_3$ (XI) with $O_3ClOAuPPh_3$

To a solution of XI (0.1 g, 0.052 mmol) in 60 ml of CH_2Cl_2 was added freshly prepared $O_3ClOAuPPh_3$ (0.052 mmol) in 20 ml of CH_2Cl_2. The mixture was stirred for 30 min then evaporated to ~ 10 ml, and addition of n-hexane gave XIX.

X-Ray structure determination of trans-$Pd(C_6F_5)_2\{dppmAu(C_6F_5)\}_2$ (XV)

Colourless tabular crystals were obtained from dichloromethane/petroleum ether and mounted in glass capillaries. A crystal 0.6 × 0.2 × 0.05 mm was used to collect 9794 profile-fitted intensities [32] on a Stoe-Siemens four-circle diffractometer (monochromated Mo-K_α radiation, $2\theta_{max}$ 50°). After Lp and empirical absorption corrections (transmission 0.36–0.53), averaging equivalents gave 6120 unique reflections, 4324 of which with $F > 4\sigma(F)$ were used for all calculations (program system SHELXTL). Cell constants were refined from 2θ values of 32 reflections in the range 20–24°.

Crystal data

Monoclinic, $P2_1/c$, a 17.091(4), b 19.892(4), c 10.254(2) Å, β 90.85(2)°, U 3485.7 Å^3, $Z = 2$, D_x 1.85 g cm^{-3}, $F(000)$ 1864, μ(Mo-K_α) 4.6 mm^{-1}.

The structure was solved by the heavy-atom method and refined to R 0.059, R_w 0.056 [Au, Pd and F anisotropic; all aromatic rings as rigid groups with C–C 1.395, C–H 0.96 Å, all C–C–C and H–C–C angles 120°; methylene CH_2 with C–H 0.96 Å, H–C–H 109.5°; all U(H) fixed at 1.2 U(C); weighting scheme $w^{-1} = \sigma^2(F) + 0.0004\ F^2$]. A final difference map showed no peaks > 1.1 eÅ^{-3}. Final atomic

TABLE 3

SELECTED BOND LENGTHS (Å) AND ANGLES (deg.) FOR XV

Au(1)–P(1)	2.266(4)	Au(1)–C(21)	2.074(7)
P(2)–Pd(1)	2.321(4)	C(12)–F(12)	1.306(10)
C(13)–F(13)	1.322(11)	C(14)–F(14)	1.333(10)
C(15)–F(15)	1.325(11)	C(16)–F(16)	1.299(10)
C(11)–Pd(1)	2.106(8)	C(22)–F(22)	1.304(11)
C(23)–F(23)	1.330(12)	C(24)–F(24)	1.345(11)
C(25)–F(25)	1.313(10)	C(26)–F(26)	1.308(11)
C(31)–P(1)	1.807(9)	C(41)–P(1)	1.819(10)
C(51)–P(2)	1.808(8)	C(61)–P(2)	1.805(8)
C(1)–P(1)	1.833(11)	C(1)–P(2)	1.838(10)
P(1)–Au(1)–C(21)	174.6(3)	P(2)–Pd(1)–C(11)	89.5(3)
C(11)–Pd(1)–P(2)	90.5(3)	P(2)–Pd(1)–P(2a)	180.0
C(11)–Pd(1)–C(11a)	180.0	Au(1)–P(1)–C(31)	116.6(3)
Au(1)–P(1)–C(41)	113.8(4)	C(31)–P(1)–C(41)	105.7(4)
Au(1)–P(1)–C(1)	113.5(4)	C(31)–P(1)–C(1)	97.3(5)
C(41)–P(1)–C(1)	108.4(5)	Pd(1)–P(2)–C(51)	116.5(3)
Pd(1)–P(2)–C(61)	110.6(3)	C(51)–P(2)–C(61)	107.0(4)
Pd(1)–P(2)–C(1)	112.4(4)	C(51)–P(2)–C(1)	103.8(5)
C(61)–P(2)–C(1)	105.7(5)		

Symmetry operator: (a) $1 - x, 1 - y, 1 - z$

coordinates and derived parameters are given in Tables 2 and 3.

The palladium atom lies on a crystallographic symmetry centre. Coordination geometries, bond lengths and angles at the metal atoms are as expected. There are no unusually short Au ··· Au contacts [33].

Further crystallographic details (hydrogen atomic coordinates, anisotropic temperature factors, structure factors) can be obtained from P.G.J.

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