Tris(diphenylphosphino)methanide Gold(III) Complexes. Crystal Structures of $[Au(C_6F_5)_2\{(Ph_2P)_2CPPh_2\}]$ and $[(F_5C_6)_2Au\{(Ph_2P)_2CPPh_2\}AuCl]$†

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The reaction of $[Au(C_6F_5)_2(acac)]$ (acac = acetylacetonate) with $(Ph_2P)_3CH$ led to $[Au(C_6F_5)_2\{(Ph_2P)_2CPPh_2\}]$ **1**, which reacts further with $[AuX(tht)]$ (X = Cl or C_6F_5, tht = tetrahydrothiophene), $[Au(tht)_2]ClO_4$ or $AgClO_4$ to give dinuclear $[(F_5C_6)_2Au\{(Ph_2P)_2CPPh_2\}AuX]$ or trinuclear complexes $[\{Au(C_6F_5)_2[(Ph_2P)_2CPPh_2]\}_2M]$ (M = Au or Ag). Complex **1** reacted with gold(III) complexes to give dinuclear $[(F_5C_6)_2Au\{(Ph_2P)_2CPPh_2\}Au(C_6F_5)_2X]$ (X = Cl or C_6F_5) or trinuclear complexes $[\{Au(C_6F_5)_2[(Ph_2P)_2CPPh_2]\}_2Au(C_6F_5)_2]$. Complex **1** is protonated by reaction with HBF_4. The structures of complex **1** and $[(F_5C_6)_2Au\{(Ph_2P)_2CPPh_2\}AuCl]$ have been established by X-ray crystallography, confirming in the latter that the gold(I) centre is co-ordinated to the free phosphorus instead of the methanide C.

Although in recent years the study of bis(diphenylphosphino)methane or -methanide gold(III) complexes has received a great deal of attention,[1–3] very few examples of complexes with tris(diphenylphosphino)methanide have been reported; these were gold(I) complexes where the triphosphine acted as a bridging ligand.[4] No gold(III) derivatives with this ligand have been described until now.

Here we describe the preparation of the mononuclear gold(III) complex $[Au(C_6F_5)_2\{(Ph_2P)_2CPPh_2\}]$, which reacts further with other gold(I), silver(I) or gold(III) derivatives to give polynuclear complexes. The structures of $[Au(C_6F_5)_2\{(Ph_2P)_2CPPh_2\}]$ and $[(F_5C_6)_2Au\{(Ph_2P)_2CPPh_2\}AuCl]$ have been established by single-crystal X-ray analysis.

Results and Discussion

The use of acetylacetonato (acac) complexes, such as $[Au(acac)(PPh_3)]$, has been previously reported in the synthesis of ylide[5] and methanide[6] gold complexes, and an analogous reaction is observed between the gold(III) derivative $[Au(C_6F_5)_2(acac)]$ and tris(diphenylphosphino)methane, leading to the methanide $[Au(C_6F_5)_2\{(Ph_2P)_2CPPh_2\}]$ **1** (see Scheme 1). This complex can also be obtained, but only in 40% yield, by equimolecular reaction of $[Au(C_6F_5)_2(OEt_2)_2]ClO_4$ with $Li[(Ph_2P)_3C]$.

The yellow complex **1** is stable at room temperature in dry air, but slowly decomposes on contact with moisture. It is non-conducting in acetone solutions. The IR spectrum shows bands at 1503s, 964vs, 793m and 780m cm^{-1}, which arise from the C_6F_5 groups, the last two confirming the *cis* disposition.[7] The methanide group gives rise to a strong absorption at 929 cm^{-1}, which is assignable to the CP_3 system.[4,8] The ^{31}P-$\{^1H\}$ NMR spectrum shows a triplet at δ −7.3 for the free phosphorus and a doublet at higher field (δ −31.7) for the phosphorus co-ordinated to gold (Table 1), as has been found for other transition-metal complexes with four-membered phosphine chelates.[9] The ^{19}F NMR spectrum confirms the presence of equivalent C_6F_5 groups (see Experimental section).

The crystal structure of complex **1** has been determined by X-ray diffraction analysis (Fig. 1), with atomic coordinates in Table 2 and selected bond lengths and angles in Table 3. The small crystal diffracted weakly and the precision is therefore only moderate. The co-ordination of the gold(III) atom is slightly distorted from square planar, whereby the restricted 'bite' of the diphosphine ligand, P(2)–Au–P(1) 70.1(2)°, represents the major deviation from ideal geometry. This bite angle lies between those found in the octahedral complexes $[Mo(CO)_4\{(Ph_2P)_2CPPh_2AuX\}]$[10] [67.72(8)–67.77(4)°] and in the square-planar derivative $[Pt\{(Ph_2P)_2CHPPh_2\}_2][BF_4]_2$[11] [72.2(1)°]. The gold atom lies 0.04 Å out of the plane formed by its four bonding neighbours. The Au–P distances of 2.330(5) and 2.346(4) Å are similar to others found in gold(III) complexes with chelated phosphines.[3] The P–C(1) distances fall in the range 1.74(2)–1.79(2) Å, shorter than those in free $(Ph_2P)_3CH$[12] [1.867(1)–1.877(1) Å] or in other phosphine derivatives. This difference may be attributed to a degree of multiple P–C bonding in the methanide ligand. The angles around the central methanide carbon C(1) are very distorted compared with the ideal value for sp^2 hybridisation [99.0(8)–135.1(11)°], but the narrowest is constrained by the four-membered ring. The carbon atom C(1) lies 0.11 Å out of the plane of the three phosphorus atoms.

The presence of a free PPh_2 group permits the reaction with gold(I) derivatives containing one weakly co-ordinated ligand, such as tetrahydrothiophene (tht) {*e.g.* $[AuX(tht)]$ (X = Cl or C_6F_5) or $[Au(tht)_2]ClO_4$}, thus affording neutral dinuclear (**2** or **3**) or cationic trinuclear (**4**) complexes (Scheme 1). No co-

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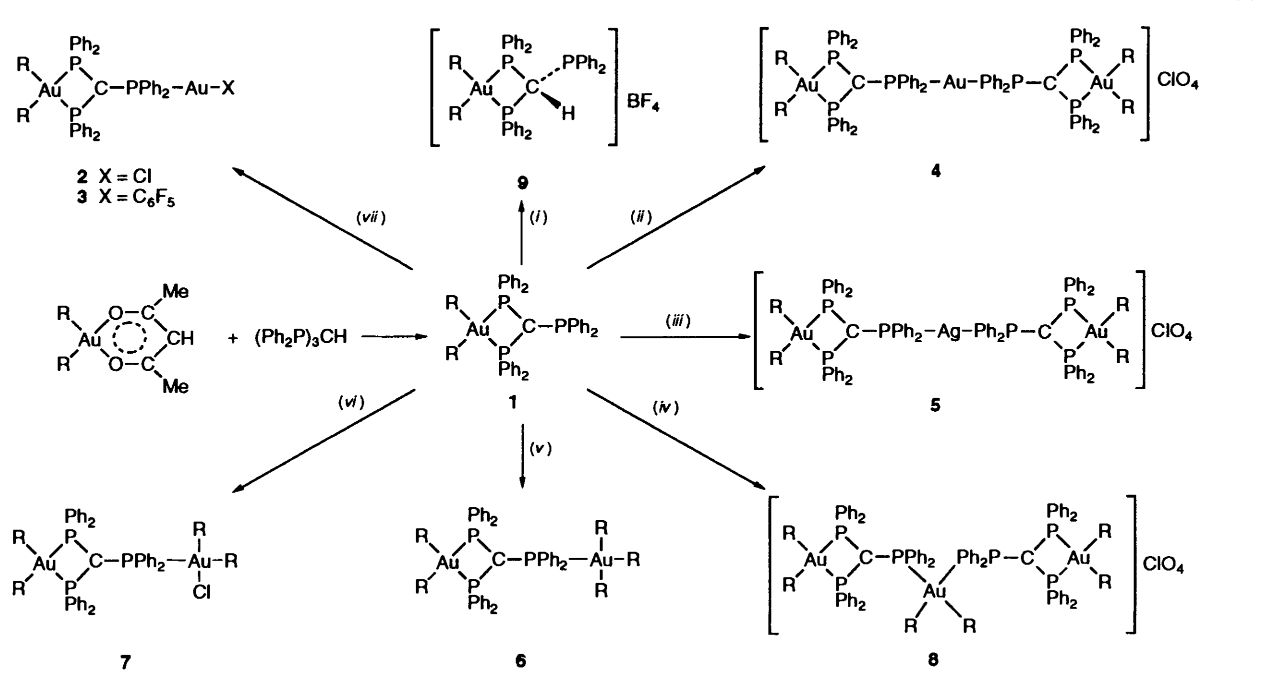
† *Supplementary data available:* Further details of the structure determination (complete bond lengths and angles, H-atom coordinates, structure factors, thermal parameters) have been deposited at the Fachsinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, 76334 Eggenstein-Leopoldshafen, Germany. Any request for this material should quote a full literature citation and the reference numbers CSD 401281 (**1**), 401282 (**2**).



Scheme 1 R = C_6F_5. (*i*) HBF_4; (*ii*) $\frac{1}{2}$ $[Au(tht)_2]ClO_4$; (*iii*) $\frac{1}{2}$ $AgClO_4$; (*iv*) $\frac{1}{2}$ $[AuR_2(OEt_2)_2]ClO_4$; (*v*) $[AuR_3(OEt_2)]$; (*vi*) $\frac{1}{2}$ $[\{Au(\mu\text{-}Cl)R_2\}_2]$; (*vii*) $[AuX(tht)]$

Table 1 Analytical data and properties of the complexes

Complex	Yield (%)	Analysis[a] (%) C	H	Λ_m[b]/ S cm^2 mol^{-1}	M.p.[c] (°C)	$^{31}P\text{-}\{^1H\}$ NMR[d] P–Au–P	C–PPh$_2$
1 $[Au(C_6F_5)_2\{(Ph_2P)_2CPPh_2\}]$	92	53.0 (53.5)	2.8 (2.75)	16	164	−31.7(d) [76.8]	−7.3(t)
2 $[(F_5C_6)_2Au\{(Ph_2P)_2CPPh_2\}AuCl]$	90	44.1 (44.2)	2.1 (2.3)	10	212	−30.9(s)	30.2(s)
3 $[(F_5C_6)_2Au\{(Ph_2P)_2CPPh_2\}Au(C_6F_5)]$	75	45.4 (45.15)	2.35 (2.1)	5	206	−30.4(s)	43.6(s)
4 $[\{Au(C_6F_5)_2[(Ph_2P)_2CPPh_2]\}_2Au]ClO_4$	70	47.15 (47.2)	2.65 (2.4)	116	180	−30.7(s)	39.2(s)
5 $[\{Au(C_6F_5)_2[(Ph_2P)_2CPPh_2]\}_2Ag]ClO_4$	75	48.65 (48.95)	2.7 (2.5)	125	180	−31.9(s)	10.4(dd) [562.9, 490.0]
6 $[(F_5C_6)_2Au\{(Ph_2P)_2CPPh_2\}Au(C_6F_5)_3]$	85	44.7 (44.8)	2.05 (1.7)	12	190	−29.6(s)	21.4(s)
7 $[(F_5C_6)_2Au\{(Ph_2P)_2CPPh_2\}AuCl(C_6F_5)_2]$	90	44.05 (44.0)	1.9 (1.8)	15	185	−31.3(s)	30.3(s)
8 $[\{Au(C_6F_5)_2[(Ph_2P)_2CPPh_2]\}_2Au(C_6F_5)_2]ClO_4$	50	46.2 (46.7)	2.15 (2.15)	130	197	−38.0(s)	43.6(s)
9 $[Au(C_6F_5)_2[(Ph_2P)_2CHPPh_2]]BF_4$	80	46.6 (46.25)	2.9 (2.55)	81	206	−34.6(s)	4.0(s)

[a] Calculated values in parentheses. [b] In acetone. [c] With decomposition. [d] Recorded in $CDCl_3$. Coupling constants in Hz are given in square brackets; s = singlet, d = doublet, dd = doublet of doublets.

ordination to the methanide C, as has been observed for other methanide complexes of gold,[1] occurs, and no reaction is observed between complexes **2**–**4** and an excess of the gold(I) derivative. Similar behaviour is observed in the reaction of complex **1** with $AgClO_4$, in which the cationic trinuclear complex **5** is obtained, containing a silver atom bridging two units of **1**.

Complexes **2**–**5** are pale yellow solids, which are stable at room temperature in dry air or nitrogen, but slowly decompose in the presence of moisture. The IR spectra show a strong band at *ca.* 925 cm^{-1} due to the methanide CP_3 system and confirm the co-ordination of the gold(I) or silver centre to the free PPh_2, and not to the methanide C.[8] For the chloro complex **2** a band assignable to ν(Au–Cl) is observed at 333m cm^{-1}. For the perchlorato complexes **4** and **5** two bands at 1100s (br) and 620m cm^{-1} arise from the perchlorate ion. The complexes are conducting in acetone solutions. The $^{31}P\text{-}\{^1H\}$ NMR spectra show two resonances for the two different phosphorus atoms, $Au(PPh_2)_2$ and $M(PPh_2)$, but no coupling is observed between them. The second signal is shifted downfield after co-ordination of complex **1**, and appears as a doublet of doublets for **5** as a result of the coupling with both ^{107}Ag and ^{109}Ag [$^1J(^{107}AgP)$ = 490.0, $^1J(^{109}AgP)$ = 562.9 Hz].

Complex **4** or **5** can also be obtained by reaction of **1** and $[Au(PPh_3)(tht)]ClO_4$ or $[Ag(OClO_3)(PPh_3)]$ (molar ratio 1 : 1), but in this case a mixture of **4** or **5** and $[Au(PPh_3)_2]ClO_4$ or $[Ag(PPh_3)_2]ClO_4$, respectively, is obtained. Separation of the reaction products is difficult because of similar solubilities in organic solvents.

The structure of complex **2** (which crystallises as a dichloromethane solvate) was confirmed by X-ray diffraction analysis, (Fig. 2). Atomic coordinates are collected in Table 4

Table 2 Atomic coordinates (× 10^4) for complex **1**

Atom	*x*	*y*	*z*
Au	5446.6(6)	5083.4(3)	5479.6(4)
P(1)	3797(4)	5106(3)	6093(2)
P(2)	3997(4)	5336(2)	4740(2)
P(3)	1520(5)	5406(2)	5421(3)
C(1)	2981(13)	5358(7)	5401(10)
C(11)	6661(11)	5176(6)	4743(7)
C(12)	7009(11)	4586(8)	4344(8)
C(13)	7744(13)	4692(9)	3810(8)
C(14)	8115(17)	5391(6)	3681(11)
C(15)	7815(15)	5986(9)	4064(9)
C(16)	7062(14)	5887(7)	4565(10)
F(1)	6692(9)	3859(5)	4458(7)
F(2)	8110(10)	4087(6)	3449(6)
F(3)	8819(10)	5508(6)	3122(6)
F(4)	8165(10)	6706(6)	3912(6)
F(5)	6791(8)	6503(5)	4946(5)
C(21)	6649(12)	4882(6)	6224(7)
C(22)	7133(12)	4182(8)	6307(7)
C(23)	8042(15)	4087(10)	6703(9)
C(24)	8494(18)	4699(6)	7049(9)
C(25)	8037(15)	5401(9)	6953(10)
C(26)	7085(14)	5486(8)	6561(9)
F(6)	6743(9)	3560(5)	5956(5)
F(7)	8521(10)	3395(5)	6779(6)
F(8)	9415(11)	4614(5)	7412(5)
F(9)	8427(10)	5992(5)	7313(6)
F(10)	6664(10)	6199(5)	6536(6)
C(31)	3381(14)	4209(9)	6482(9)
C(32)	2367(15)	4194(9)	6768(8)
C(33)	1964(15)	3489(10)	6986(9)
C(34)	2544(15)	2846(9)	6950(11)
C(35)	3557(16)	2868(9)	6653(9)
C(36)	3993(14)	3572(8)	6442(9)
C(41)	3792(14)	5797(8)	6754(8)
C(42)	3374(13)	6527(8)	6677(8)
C(43)	3346(15)	7062(9)	7209(8)
C(44)	3768(14)	6855(9)	7844(9)
C(45)	4212(15)	6111(8)	7953(8)
C(46)	4223(14)	5612(8)	7414(8)
C(51)	4174(13)	6216(8)	4286(8)
C(52)	3599(12)	6866(7)	4485(9)
C(53)	3769(14)	7550(8)	4132(8)
C(54)	4507(15)	7585(8)	3598(8)
C(55)	5126(14)	6941(7)	3397(8)
C(56)	4932(12)	6275(8)	3766(7)
C(61)	3902(13)	4582(8)	4102(8)
C(62)	4258(14)	3865(8)	4290(9)
C(63)	4298(14)	3284(8)	3801(8)
C(64)	4019(14)	3429(9)	3133(9)
C(65)	3664(16)	4135(9)	2950(8)
C(66)	3661(12)	4740(8)	3428(7)
C(71)	977(14)	4464(9)	5155(8)
C(72)	1666(15)	3859(8)	5044(8)
C(73)	1216(15)	3131(9)	4903(8)
C(74)	131(14)	3050(10)	4802(9)
C(75)	−552(19)	3636(9)	4933(9)
C(76)	−137(17)	4342(8)	5121(8)
C(81)	1197(13)	5983(8)	4679(8)
C(82)	1333(13)	5744(8)	3996(9)
C(83)	1125(15)	6230(10)	3459(9)
C(84)	824(15)	6986(9)	3570(9)
C(85)	631(17)	7201(8)	4234(8)
C(86)	875(15)	6744(9)	4794(8)

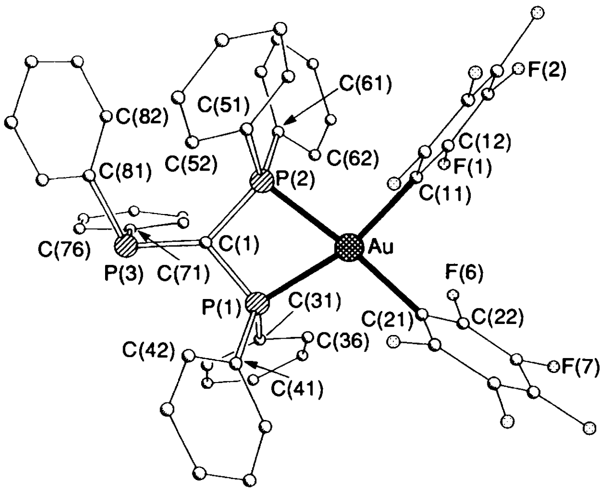


Fig. 1 The molecule of complex **1** in the crystal, showing the atomic numbering scheme. Hydrogen atoms are omitted for clarity

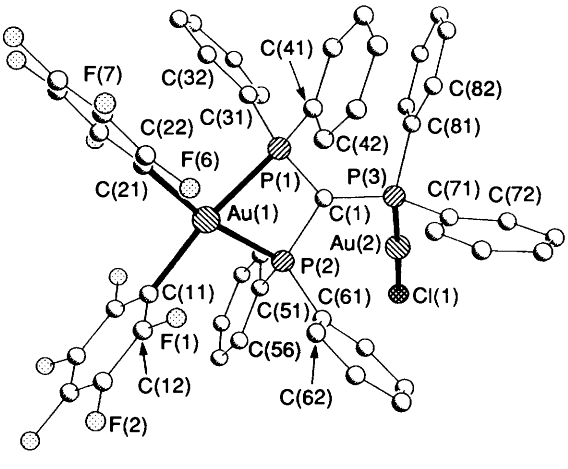


Fig. 2 The molecule of complex **2** in the crystal. Details as in Fig. 1

and selected bond lengths and angles in Table 5. The overall distances and angles of this molecule are very similar to those in complex **1**, although the precision is improved. The gold fragment co-ordinates to the phosphorus atom and not to the carbon, and C(1) thus retains sp^2 hybridisation. The gold(I) atom exhibits a linear geometry, Cl(1)–Au(2)–P(3) 178.7(1)°, and the Au–Cl and Au–P distances are normal.

The reaction of complex **1** with the gold(III) complexes $[Au(C_6F_5)_3(OEt_2)]$ or $[\{Au(\mu\text{-}Cl)(C_6F_5)_2\}_2]$ leads to the displacement of ether or bridging chloro ligands, respectively, and formation of the dinuclear complex **6** or **7**. The reaction with a freshly prepared solution of $[Au(C_6F_5)_2(OEt_2)_2]ClO_4$ gives the trinuclear complex **8**. The white complexes **6**–**8** are stable at room temperature under dry air or nitrogen. The IR spectra show a band at *ca.* 890s cm^{-1} which confirms the co-ordination of the gold(III) centre to the free P and not to the C atom. The ν(Au–Cl) appears at 350m cm^{-1} for **7**. Complexes **6** and **7** are non-conducting, but **8** behaves as a 1 : 1 electrolyte. Only two singlets are observed in the $^{31}P\text{-}\{^1H\}$ NMR spectra and no coupling is observed between the two different phosphorus atoms. The ^{19}F NMR spectrum of **8** shows a multiplet in the region for the *p*-fluorine and it is not possible to distinguish *cis* and *trans* dispositions of the two C_6F_5 groups bonded to the central gold(III) atom.

The methanide complex **1** can be protonated by reaction with HBF_4. Addition of the acid to a diethyl ether solution of **1** causes decolouration of the solution and the precipitation of $[Au(C_6F_5)_2\{(Ph_2P)_3CH\}]BF_4$ **9**. Complex **9** is an air- and moisture-stable white solid. It behaves as a 1 : 1 electrolyte in acetone solution and the IR spectrum shows a band at 1062vs cm^{-1}, which is characteristic of the BF_4^- anion. The band of complexes **1**–**8** at 928–880 cm^{-1} disappears on protonation of the methanide to give **9**. The NMR spectra are consistent with the proposed structure in Scheme 1. The $^{31}P-\{^1H\}$ spectrum shows two singlets for the two different phosphorus atoms and the ^{19}F spectrum shows the resonances due to the equivalent C_6F_5 groups and a singlet from the BF_4^- anion at δ −151.3. The ^1H NMR signal of the CH group appears as a multiplet at δ 8.0, indicating an acid behaviour for this proton. Accordingly, complex **9** can be easily deprotonated, and the reaction with [AuX(tht)] (X = Cl or C_6F_5) gives **2** or **3** (Scheme 2).

Table 3 Selected bond lengths (Å) and angles (°) for complex **1**

Au–C(11)	2.074(14)	Au–C(21)	2.10(2)
Au–P(2)	2.330(5)	Au–P(1)	2.346(4)
P(1)–C(1)	1.74(2)	P(1)–C(41)	1.77(2)
P(1)–C(31)	1.82(2)	P(2)–C(1)	1.79(2)
P(2)–C(51)	1.79(2)	P(2)–C(61)	1.82(2)
P(3)–C(1)	1.79(2)	P(3)–C(81)	1.81(2)
P(3)–C(71)	1.85(2)		
C(11)–Au–C(21)	89.5(5)	C(11)–Au–P(2)	95.7(4)
C(21)–Au–P(2)	174.4(4)	C(11)–Au–P(1)	165.6(4)
C(21)–Au–P(1)	104.6(4)	P(2)–Au–P(1)	70.1(2)
C(1)–P(1)–C(41)	113.0(7)	C(1)–P(1)–C(31)	112.6(7)
C(41)–P(1)–C(31)	106.6(7)	C(1)–P(1)–Au	95.8(6)
C(41)–P(1)–Au	112.8(6)	C(31)–P(1)–Au	116.1(5)
C(1)–P(2)–C(51)	114.9(7)	C(1)–P(2)–C(61)	117.7(7)
C(51)–P(2)–C(61)	107.1(6)	C(1)–P(2)–Au	94.8(6)
C(51)–P(2)–Au	112.2(6)	C(61)–P(2)–Au	109.6(5)
C(1)–P(3)–C(81)	103.1(8)	C(1)–P(3)–C(71)	108.0(7)
C(81)–P(3)–C(71)	101.3(7)	P(1)–C(1)–P(3)	124.7(11)
P(1)–C(1)–P(2)	99.0(8)	P(3)–C(1)–P(2)	135.1(11)

Experimental

The instrumentation and general experimental techniques were as described earlier.[4] The yields, melting points, elemental analyses, conductivities and the ^{31}P NMR are listed in Table 1. All reactions were carried out at room temperature under a nitrogen atmosphere.

Syntheses.—$[Au(C_6F_5)_2\{(Ph_2P)_2CPPh_2\}]$ **1**. To a solution of $[Au(C_6F_5)_2(acac)]$[13] (0.126 g, 0.2 mmol) in diethyl ether (30 cm^3) was added $(Ph_2P)_3CH$ (0.110 g, 0.2 mmol) and the mixture was stirred for 1 h. Concentration of the solution to *ca.* 5 cm^3 and addition of hexane (20 cm^3) gave complex **1** as a yellow solid. ^{19}F NMR ($CDCl_3$, external reference $CFCl_3$): δ −121.5 (m, *o*-F), −158.1 [t, *p*-F, ^3J(FF) 19.3 Hz] and −162.0 (m, *m*-F).

$[(F_5C_6)_2Au\{(Ph_2P)_2CPPh_2\}AuX]$ (X = Cl **2** *or* C_6F_5 **3**). To a dichloromethane solution (30 cm^3) of complex **1** (0.110 g, 0.1 mmol) was added [AuX(tht)][14] (0.1 mmol; X = Cl, 0.032 g; C_6F_5, 0.045 g). The resulting clear solution was stirred for 30 min and then concentrated to *ca.* 5 cm^3. Addition of hexane (20 cm^3) gave **2** or **3** as pale yellow solids. ^{19}F NMR: **2**, δ −121.9 (m, *o*-F), −157.1 [t, *p*-F, ^3J(FF) 19.3] and −161.4 (m, *m*-F); **3**, δ −116.3 [m, *o*-F, $Au^I(C_6F_5)$], −121.8 [m, *o*-F, $Au(C_6F_5)_2$], −157.3 [t, *p*-F, ^3J(FF) 19.3, $Au(C_6F_5)_2$], −159.4 [t, *p*-F, ^3J(FF) 19.3 Hz, $Au(C_6F_5)$], −161.5 [m, *m*-F, $Au(C_6F_5)_2$] and −163.2 [m, *m*-F, $Au(C_6F_5)$].

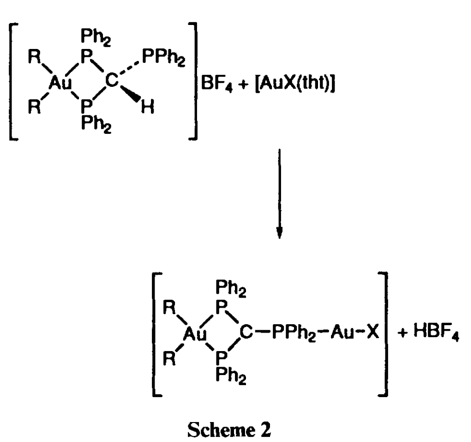
$[\{Au(C_6F_5)_2[(Ph_2P)_2CPPh_2]\}_2M]ClO_4$ (M = Au **4** *or* Ag **5**). To a solution of complex **1** (0.220 g, 0.2 mmol) in dichloromethane (**4**) or diethyl ether (**5**) (30 cm^3) was added $[Au(tht)_2]ClO_4$[15] (0.047 g, 0.1 mmol) or $AgClO_4$ (0.027 g, 0.1 mmol). After stirring for 30 min a pale yellow precipitate of **5** was filtered off. Concentration of the dichloromethane solution to *ca.* 5 cm^3 and addition of diethyl ether (20 cm^3) led to complex **4** as a pale yellow solid. ^{19}F NMR: **4**, δ −121.8 (m, *o*-F), −156.9 [t, *p*-F, ^3J(FF) 19.3] and −161.2 (m, *m*-F); **5**,

Table 4 Atomic coordinates (× 10^4) for complex **2**

Atom	*x*	*y*	*z*
Au(1)	2969.5(2)	4286.3(2)	1615.6(1)
Au(2)	2498.4(3)	4429.2(3)	4315.6(1)
P(1)	2758(2)	6073(2)	2291.7(9)
P(2)	2465(2)	3680(2)	2532.8(9)
P(3)	1750(2)	5567(2)	3547.9(9)
Cl(1)	3312(3)	3257(2)	5097.3(11)
C(1)	2363(6)	5222(6)	2867(4)
C(11)	3111(6)	2512(7)	1145(3)
C(12)	2150(8)	1845(7)	644(4)
C(13)	2257(9)	684(8)	335(4)
C(14)	3386(8)	188(8)	533(5)
C(15)	4371(9)	832(8)	1037(5)
C(16)	4206(8)	1980(7)	1330(4)
F(1)	1030(5)	2315(5)	413(2)
F(2)	1301(6)	44(5)	−166(3)
F(3)	3533(7)	−934(6)	237(4)
F(4)	5486(6)	359(6)	1223(4)
F(5)	5221(4)	2599(4)	1820(2)
C(21)	3398(6)	5170(6)	878(3)
C(22)	2416(7)	5364(6)	361(4)
C(23)	2658(8)	6004(7)	−120(4)
C(24)	3906(7)	6478(8)	−94(4)
C(25)	4909(7)	6331(7)	414(4)
C(26)	4633(6)	5655(7)	883(4)
F(6)	1183(4)	4909(5)	316(2)
F(7)	1676(5)	6160(5)	−614(3)
F(8)	4150(6)	7094(5)	−561(3)
F(9)	6123(5)	6790(5)	437(3)
F(10)	5653(4)	5491(5)	1369(3)
C(31)	4264(7)	7128(7)	2571(4)
C(32)	4724(8)	7772(7)	2137(4)
C(33)	5948(9)	8464(8)	2315(5)
C(34)	6708(9)	8542(9)	2936(5)
C(35)	6259(8)	7976(9)	3389(5)
C(36)	5032(8)	7240(7)	3201(4)
C(41)	1557(7)	6995(7)	1911(3)
C(42)	439(8)	6371(7)	1461(4)
C(43)	−533(9)	7026(9)	1194(4)
C(44)	−399(10)	8303(8)	1366(5)
C(45)	715(11)	8933(9)	1801(6)
C(46)	1686(9)	8289(8)	2074(5)
C(51)	3668(6)	2914(6)	3020(4)
C(52)	4668(7)	3614(7)	3520(4)
C(53)	5627(8)	3003(9)	3864(4)
C(54)	5604(8)	1736(8)	3705(5)
C(55)	4609(8)	1030(8)	3208(5)
C(56)	3638(8)	1632(8)	2871(4)
C(61)	958(7)	2646(6)	2369(3)
C(62)	72(7)	2447(7)	1755(4)
C(63)	−1164(7)	1816(8)	1649(4)
C(64)	−1535(8)	1387(8)	2167(4)
C(65)	−691(8)	1551(8)	2767(4)
C(66)	560(7)	2181(7)	2868(4)
C(71)	−19(7)	5345(7)	3276(4)
C(72)	−701(8)	5508(8)	3741(4)
C(73)	−2080(8)	5360(10)	3536(5)
C(74)	−2703(9)	5019(10)	2903(5)
C(75)	−2034(7)	4809(9)	2442(5)
C(76)	−677(7)	4996(7)	2633(4)
C(81)	2181(7)	7243(7)	3841(4)
C(82)	1449(8)	8098(7)	3543(5)
C(83)	1771(11)	9351(8)	3769(5)
C(84)	2808(11)	9797(9)	4299(5)
C(85)	3503(12)	8952(9)	4598(5)
C(86)	3207(9)	7683(8)	4380(4)
C(99)	313(12)	8206(11)	5161(6)
Cl(2)	786(3)	6908(3)	5525(2)
Cl(3)	1131(3)	9617(3)	5660(2)

Table 5 Selected bond lengths (Å) and angles (°) for complex **2**

Au(1)–C(21)	2.077(7)	Au(1)–C(11)	2.097(8)
Au(1)–P(2)	2.330(2)	Au(1)–P(1)	2.342(2)
Au(2)–P(3)	2.229(2)	Au(2)–Cl(1)	2.294(2)
P(1)–C(1)	1.742(7)	P(1)–C(31)	1.799(8)
P(1)–C(41)	1.814(7)	P(2)–C(1)	1.760(7)
P(2)–C(61)	1.797(7)	P(2)–C(51)	1.800(7)
P(3)–C(1)	1.770(7)	P(3)–C(81)	1.816(8)
P(3)–C(71)	1.825(8)		
C(21)–Au(1)–C(11)	92.0(3)	C(21)–Au(1)–P(2)	169.1(2)
C(11)–Au(1)–P(2)	98.9(2)	C(21)–Au(1)–P(1)	98.3(2)
C(11)–Au(1)–P(1)	169.7(2)	P(2)–Au(1)–P(1)	70.78(7)
P(3)–Au(2)–Cl(1)	178.7(1)	C(1)–P(1)–C(31)	114.9(3)
C(1)–P(1)–C(41)	116.5(3)	C(31)–P(1)–C(41)	105.9(3)
C(1)–P(1)–Au(1)	94.0(2)	C(31)–P(1)–Au(1)	111.0(2)
C(41)–P(1)–Au(1)	114.4(2)	C(1)–P(2)–C(61)	112.6(3)
C(1)–P(2)–C(51)	115.3(3)	C(61)–P(2)–C(51)	105.8(3)
C(1)–P(2)–Au(1)	94.0(2)	C(61)–P(2)–Au(1)	114.3(2)
C(51)–P(2)–Au(1)	114.9(2)	C(1)–P(3)–C(81)	107.9(3)
C(1)–P(3)–C(71)	108.5(3)	C(81)–P(3)–C(71)	103.8(3)
C(1)–P(3)–Au(2)	111.6(2)	C(81)–P(3)–Au(2)	111.8(3)
C(71)–P(3)–Au(2)	112.9(3)	P(1)–C(1)–P(2)	101.2(4)
P(1)–C(1)–P(3)	135.1(4)	P(2)–C(1)–P(3)	123.1(4)



Scheme 2

δ −121.7 (m, *o*-F), −157.2 [t, *p*-F, ^3J(FF) 19.2 Hz] and −161.4 (m, *m*-F).

$[(F_5C_6)_2Au\{(Ph_2P)_2CPPh_2\}Au(C_6F_5)_2X]$ (X = C_6F_5 **6** *or* Cl **7**) *and* $[\{Au(C_6F_5)_2[(Ph_2P)_2CPPh_2]\}_2Au(C_6F_5)_2]ClO_4$ **8**. To a solution of complex **1** (0.110 g, 0.1 mmol) in diethyl ether (30 cm^3) (**6** or **8**) or dichloromethane (**7**) was added $[Au(C_6F_5)_3(OEt_2)]$[16] (0.077 g, 0.1 mmol), $[\{AuCl(C_6F_5)_2\}_2]$[13] (0.056 g, 0.05 mmol) or a freshly prepared diethyl ether solution (20 cm^3) of $[Au(C_6F_5)_2(OEt_2)_2]ClO_4$[17] (0.1 mmol) and the mixture was stirred for 30 min. Concentration of the solution to *ca.* 5 cm^3 and addition of hexane gave complexes **6**–**8**. ^{19}F NMR: **6**, δ −118.2, −121.7 and −122.1 (m, *o*-F), −156.8, −157.2 −157.4 [t, *p*-F, ^3J(FF) 19.3] and −160.6, −161.3 and −162.7 (m, *m*-F); **7**, δ −121.7 and −122.4 (m, *o*-F) −156.9, −157.2 and −157.3 [t, *p*-F, ^3J(FF) 19.2 Hz] and −160.7 and −161.1 (m, *m*-F); **8**, δ −121.7 (m, *o*-F), −156.9 (m, *p*-F) and −161.3 (m, *m*-F).

$[Au(C_6F_5)_2\{(Ph_2P)_2CHPPh_2\}]BF_4$ **9**. To a solution of complex **1** (0.110 g, 0.1 mmol) in diethyl ether (30 cm^3) was added a diethyl ether solution of HBF_4 (0.02 cm^3, 0.15 mmol) and the mixture was stirred for 2 h. The white precipitate of **9** was filtered off and washed with diethyl ether. ^{19}F NMR: δ −121.7 (m, *o*-F), −156.0 [t, *p*-F, ^3J(FF) 19.3 Hz] and −160.8 (m, *m*-F).

Table 6 Details of data collection and structure refinement for complexes **1** and **2**

	1	**2**·CH_2Cl_2
Chemical formula	$C_{49}H_{30}AuF_{10}P_3$	$C_{50}H_{32}Au_2Cl_3F_{10}P_3$
M	1098.61	1415.95
T/°C	−100	−130
Space group	$P2_12_12_1$	$P\bar{1}$
a/Å	12.227(3)	10.749(4)
b/Å	17.534(5)	10.826(4)
c/Å	19.528(4)	21.597(6)
α/°	—	97.12(2)
β/°	—	104.36(2)
γ/°	—	96.18(2)
U/Å^3	4187(2)	2390.7(14)
Z	4	2
D_c/Mg m^{-3}	1.743	1.967
F(000)	2152	1352
μ(Mo-Kα)/mm^{-1}	3.71	6.47
Crystal size/mm	0.35 × 0.15 × 0.06	0.70 × 0.40 × 0.12
Transmission	0.52–0.76	0.32–0.73
$2\theta_{max}$/°	45	50
Reflections measured	4583	15 462
Unique reflections	4402	8453
R_{int}	0.055	0.037
$R[F > 4\sigma(F)]$	0.052	0.043
$R'(F^2$, all reflections)	0.086	0.118
No. parameters	323	613
No. restraints	196	562
S	0.79	1.04
Maximum Δρ/e Å^{-3}	0.82	2.17

Crystal Structure Determinations.—Crystals were mounted in inert oil (type RS3000, donated by Riedel de Haën) on glass fibres. Data were collected using monochromated Mo-Kα radiation (λ = 0.710 73 Å). Diffractometer type: Siemens R3 (**1**), Stoe STADI-4 (**2**), both with Siemens LT-2 low-temperature attachment. Scan type: ω (**1**) and ω–θ (**2**). Cell constants were refined from setting angles (**1**) or ±ω angles (**2**) of *ca.* 50 reflections in the range 2θ 20–23°. Absorption corrections were applied with SHELXA[18] for complex **1** and on the basis of Ψ scans for **2**.

Structures were solved by the heavy-atom method and refined on F^2 using the program SHELXL 93.[19] Hydrogen atoms were included using a riding model. The absolute structure of complex **1** was determined using an *x* refinement.[20] Other data are collected in Table 6.

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

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References

1 A. Laguna and M. Laguna, *J. Organomet. Chem.*, 1990, **394**, 743.
2 H. Schmidbaur, A. Wholleben, U. Schubert, A. Frank and G. Huttner, *Chem. Ber.*, 1977, **110**, 2751, 2758.
3 E. J. Fernández, M. C. Gimeno, P. G. Jones, A. Laguna, M. Laguna and J. M. López de Luzuriaga, *J. Chem. Soc., Dalton Trans.*, 1992, 3365.
4 E. J. Fernández, M. C. Gimeno, P. G. Jones, A. Laguna, M. Laguna and J. M. López de Luzuriaga, *J. Chem. Soc., Dalton Trans.*, 1993, 3401; A. Stützer, P. Bissinger and H. Schmidbaur. *Chem. Ber.*, 1992, **125**, 367.
5 J. Vicente, M. T. Chicote and M. C. Lagunas, *Inorg. Chem.*, 1993, **32**, 3748 and refs therein.
6 M. C. Gimeno, A. Laguna, M. Laguna, F. Sanmartín and P. G. Jones, *Organometallics*, 1993, **12**, 3984.
7 R. Usón, A. Laguna, J. García and M. Laguna, *Inorg. Chim. Acta*, 1979, **37**, 201.

8 R. Usón, A. Laguna, M. Laguna and M. C. Gimeno, *J. Chem. Soc., Dalton Trans.*, 1989, 1883.

9 P. E. Garrou, *Chem. Rev.*, 1981, **81**, 229.

10 E. J. Fernández, M. C. Gimeno, P. G. Jones, A. Laguna, M. Laguna and E. Olmos, *J. Chem. Soc., Dalton Trans.*, 1994, 2891.

11 K. J. Beckett and S. J. Loeb, *Can. J. Chem.*, 1988, **66**, 1073.

12 H. Schmidbaur, A. Stützer and E. Herdtweck, *Chem. Ber.*, 1991, **124**, 1095.

13 R. Usón, A. Laguna, M. Laguna and M. Abad, *J. Organomet. Chem.*, 1983, **249**, 437.

14 R. Usón, A. Laguna and M. Laguna, *Inorg. Synth.*, 1990, **26**, 85.

15 R. Usón, A. Laguna, M. Laguna, J. Jiménez, M. P. Gómez, A. Sáinz and P. G. Jones, *J. Chem. Soc., Dalton Trans.*, 1990, 3457.

16 R. Usón, A. Laguna, M. Laguna, J. Jiménez and M. E. Durana, *Inorg. Chim. Acta*, 1990, **168**, 89.

17 R. Usón, A. Laguna and M. L. Arrese, *Synth. React. Inorg. Metal-Org. Chem.*, 1984, **14**, 557.

18 G. M. Sheldrick, SHELXA, unpublished work.

19 G. M. Sheldrick, SHELXL 93, a program for crystal structure refinement, University of Göttingen, 1993.

20 H. D. Flack, *Acta Crystallogr., Sect. A*, 1983, **39**, 876.

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