Synthesis of Polynuclear Complexes containing the Tridentate Bis(diphenylphosphino)methanide Ligand. Crystal Structures of the Compounds $[(C_6F_5)_2Au(Ph_2PCHPPh_2)Au(C_6F_5)]$ and $[(C_6F_5)_2Au(Ph_2PCHPPh_2)Au(Ph_2PCHPPh_2)Au(C_6F_5)_2]ClO_4$ *

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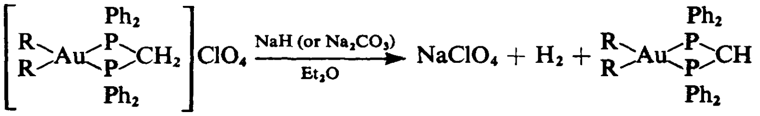
Reaction of NaH with $[Au(C_6F_5)_2(Ph_2PCH_2PPh_2)]ClO_4$ causes both deprotonation of the methylene group and elimination of the anion and leads to the neutral bis(diphenylphosphino)methanide complex $[Au(C_6F_5)_2(Ph_2PCHPPh_2)]$, which further reacts with gold(I) or silver(I) derivatives to give bi- or tri-nuclear complexes. The structures of a binuclear and a trinuclear gold derivative have been confirmed by *X*-ray crystallography. Crystals of $[(C_6F_5)_2Au(Ph_2PCHPPh_2)Au(C_6F_5)]$ are monoclinic, space group $P2_1/m$, with $a = 10.003(2)$, $b = 17.389(4)$, $c = 11.754(3)$ Å, $\beta = 103.53(2)°$, and $Z = 2$; $R = 0.034$ for 4 016 reflections. Crystals of $[(C_6F_5)_2Au(Ph_2PCHPPh_2)Au(Ph_2PCHPPh_2)Au(C_6F_5)_2]ClO_4$ ($CHCl_3$ solvate) are monoclinic, space group $P2_1/m$, with $a = 17.456(6)$, $b = 17.704(6)$, $c = 17.749(8)$ Å, $\beta = 92.86(5)°$, and $Z = 2$; $R = 0.096$ for 5 230 reflections.

We recently reported[1] a new preparation of gold(I) and gold(III) ylide complexes; the reaction of NaH with the appropriate precursor leads to the deprotonation and simultaneous abstraction of the anionic ligand [equation (i):

$$[RCH_2EPh_3][AuX(C_6F_5)] + NaH \longrightarrow NaX + H_2 + [(C_6F_5)Au{-}CHR{-}EPh_3] \quad (i)$$

E = P, R = H, Me, Et, or Ph; E = As, R = H]. This process can readily be extended to other systems; see, for example, equation (ii) (R = C_6F_5). [The preparation and structure of (1) have been described elsewhere.[2]]



$$\left[\begin{matrix}R\\R\end{matrix}{>}Au{<}\overset{Ph_2}{\underset{Ph_2}{\overset{P}{\underset{P}{}}}}{>}CH_2\right]ClO_4 \xrightarrow[Et_2O]{NaH\ (or\ Na_2CO_3)} NaClO_4 + H_2 + \begin{matrix}R\\R\end{matrix}{>}Au{<}\overset{Ph_2}{\underset{Ph_2}{\overset{P}{\underset{P}{}}}}{>}CH \quad (ii)$$

(1) (2)

Results and Discussion

Reaction (ii) renders yellow solutions, from which the bis(diphenylphosphino)methanide complex (2) can be isolated upon partial evaporation. The yellow solid is non-conducting in acetone and monomeric in chloroform (M = 966; calc. 914), m.p. 176 °C (decomp.); ^{31}P n.m.r. (^1H decoupled, C_6D_6, external standard 85% H_3PO_4), δ −60.1 p.p.m.

Complex (2) can be used as a C-donor ligand in the synthesis of bi- or tri-nuclear complexes (Scheme). To the best of our knowledge, this is the first deliberate use of the chelated bis(diphenylphosphino)methanide group as a C-donor ligand to another metal centre, although some other tridentate complexes have been structurally characterised.[3-5]

Complex (3) is a white solid, non-conducting in acetone, monomeric in $CHCl_3$ (M = 1 356; calc. 1 278), m.p. 178 °C (decomp.); ^{31}P n.m.r. (^1H decoupled, $CDCl_3$, external standard 85% H_3PO_4), δ −41.4 p.p.m. Its structure was confirmed by *X*-ray crystallography; single crystals were obtained from dichloromethane–hexane.

The molecule (Figure 1) possesses crystallographic *m* symmetry; both gold atoms, the methanide CH, and the C_6F_5 groups at Au^1 lie in the mirror planes. The Au–P–C–P ring geometry is appreciably different from the equivalent ring in (1), which also has *m* symmetry;[2] the C atom lies 0.64 Å out of the Au^{III} ligand plane [0.28 Å in (1)] and the P–C bonds are somewhat shorter [1.815(6) Å; *cf.* 1.845(9) Å in (1)]. A related shortening of P–C bonds in gold(III) ylide complexes has been observed.[6]

The trinuclear bimetallic complex (4) is a white solid, 1 : 1 electrolyte in acetone (Λ_M = 138 ohm^{-1} cm^2 mol^{-1}), m.p. 130 °C (explodes, decomp.). Its acetone or dichloromethane solutions are yellow, due to an equilibrium [equation (iii)].

By adding Et_2O to a dichloromethane solution of (4), both it and the binuclear Au–Ag complex can be precipitated. Addition of n-hexane to the filtered CH_2Cl_2–Et_2O solution precipitates (2) [*ca.* 10% of the expected yield if equation (iii) were displaced totally to the right]. Addition of tetrahydrothiophene (tht) to dichloromethane solutions of (4) (2 : 1

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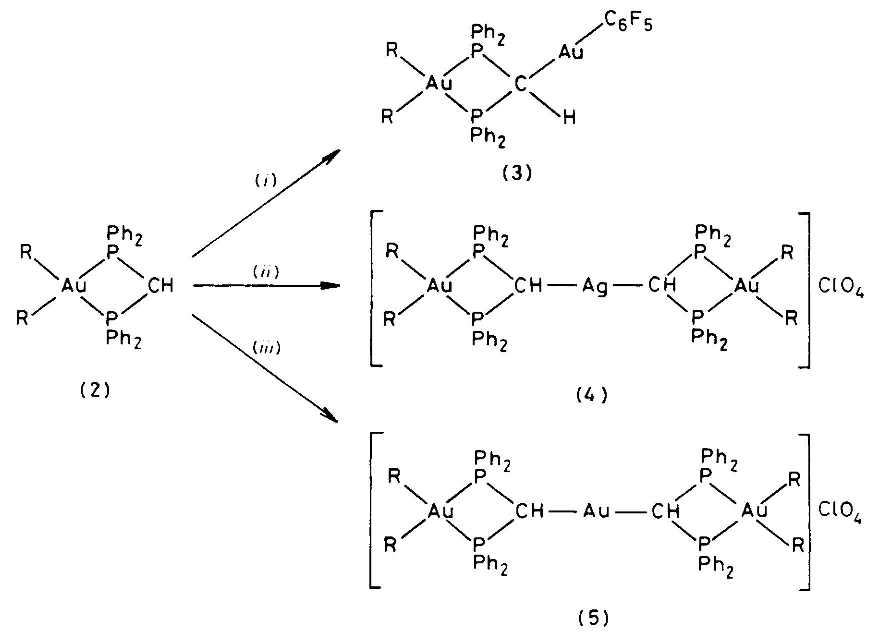
* μ-[Bis(diphenylphosphino)methanido-P^1P^2(Au^1),C(Au^2)]-1,1,2-tris(pentafluorophenyl)digold(I)/(III) and μ-[bis(diphenylphosphino)methanido-P^1P^2(Au^1),C(Au^3)]-μ-[bis(diphenylphosphino)methanido-$P^{1'}P^{2'}$(Au^2),C'(Au^3)]-1,1,2,2-tetrakis(pentafluorophenyl)trigold(I)/(III)/(III) perchlorate.

Supplementary data available (No. SUP 23857, 78 pp.): thermal parameters, H-atom co-ordinates, observed and calculated structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.



Scheme. R = C_6F_5: (*i*) [Au(C_6F_5)(tht)] (2 mol equiv.) in Et_2O; (*ii*) $AgClO_4$ (0.5 mol equiv.), Et_2O; (*iii*) [Au(tht)$_2$]ClO_4 (0.5 mol equiv.) in Et_2O

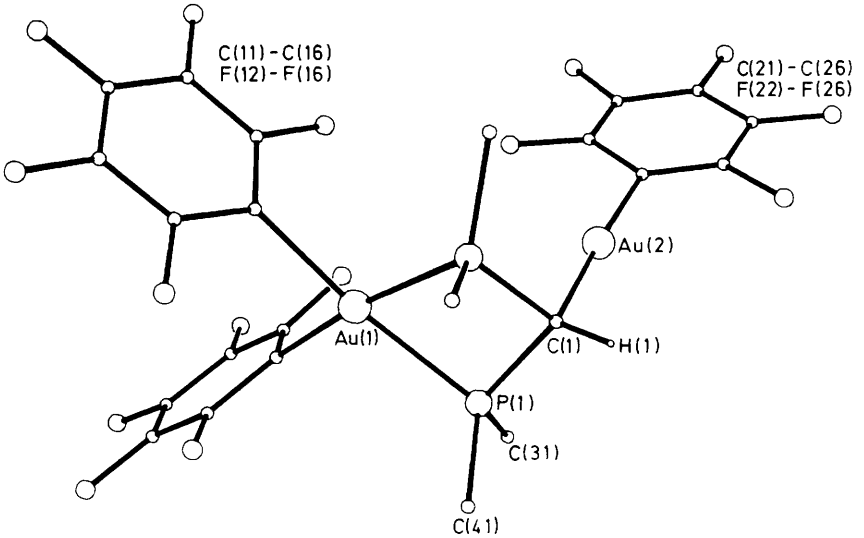
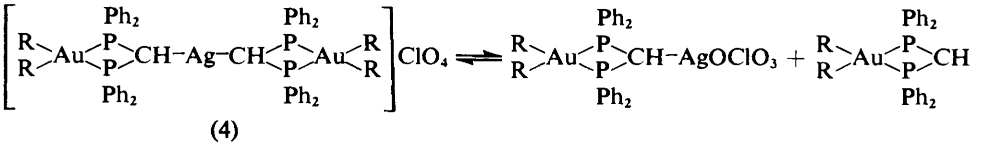


Figure 1. The molecule of (3), showing the numbering scheme of the asymmetric unit. The phenyl rings at phosphorus are represented by only the first carbon atom (for clarity)



$$\left[\mathrm{R_2Au(PPh_2)_2CH{-}Ag{-}CH(PPh_2)_2AuR_2}\right]\mathrm{ClO_4} \rightleftharpoons \mathrm{R_2Au(PPh_2)_2CH{-}AgOClO_3} + \mathrm{R_2Au(PPh_2)_2CH} \qquad \text{(iii)}$$

(4)

molar ratio) totally displaces the equilibrium, forming an equimolar mixture of (2) and [(C_6F_5)$_2$Au($Ph_2PCHPPh_2$)Ag(tht)]ClO_4 (6), which can easily be resolved, since (6) is insoluble in Et_2O. Complex (6) is conducting in acetone (Λ_M = 127 ohm^{-1} cm^2 mol^{-1}), m.p. 126 °C (decomp.).

The trinuclear complex (5) is a white solid, m.p. 155—156 °C, 1 : 1 electrolyte in acetone (Λ_M = 121 ohm^{-1} cm^2 mol^{-1}); ^{31}P n.m.r. (^1H decoupled, $CDCl_3$, external standard 85% H_3PO_4), δ −44.6 p.p.m. Its structure was confirmed by *X*-ray crystallography. Single crystals were obtained by diffusion of light petroleum (b.p. 40—60 °C) into chloroform solutions of (5). They lose solvent immediately in air and were therefore sealed in capillaries with mother-liquor. The solvent of crystallization is responsible for the low accuracy of the structure (see below), but no suitable crystals could be

Table 1. Bond lengths (Å) and angles (°) for (3)

Au(1)–P	2.354(2)	C(23)–F(23)	1.388(12)	Au(2)–C(21)	2.048(8)	C(24)–C(25)	1.363(15)
Au(2)–C(1)	2.094(7)	C(24)–F(24)	1.358(10)	C(1)–H(1)	0.96(6)	C(25)–C(26)	1.405(11)
C(1)–P	1.815(6)	C(25)–F(25)	1.354(11)	C(11)–C(16)	1.377(7)	C(26)–F(26)	1.347(11)
C(11)–C(12)	1.381(8)	C(31)–P	1.809(6)	C(12)–F(12)	1.354(6)	C(31)–C(32)	1.403(8)
C(12)–C(13)	1.384(9)	C(31)–C(36)	1.391(9)	C(13)–F(13)	1.348(8)	C(32)–C(33)	1.383(9)
C(13)–C(14)	1.366(8)	C(33)–C(34)	1.371(10)	C(14)–F(14)	1.337(9)	C(34)–C(35)	1.366(11)
C(14)–C(15)	1.371(9)	C(35)–C(36)	1.394(9)	C(15)–F(15)	1.338(7)	C(41)–P	1.810(6)
C(15)–C(16)	1.382(9)	C(41)–C(42)	1.371(9)	C(21)–C(22)	1.392(12)	C(41)–C(46)	1.367(10)
C(16)–F(16)	1.350(7)	C(42)–C(43)	1.399(11)	C(22)–C(23)	1.309(11)	C(43)–C(44)	1.356(13)
C(21)–C(26)	1.339(12)	C(44)–C(45)	1.364(12)	C(23)–C(24)	1.415(15)	C(45)–C(46)	1.381(10)
C(22)–F(22)	1.316(11)	Au(1)–C(11)	2.075(6)				

P–Au(1)–C(11)	172.1(2)	C(24)–C(25)–C(26)	118.4(9)	C(15)–C(14)–F(14)	120.1(6)
C(11)–Au(1)–P^{i}	102.3(2)	C(26)–C(25)–F(25)	120.2(9)	C(14)–C(15)–F(15)	120.4(6)
C(1)–Au(2)–C(21)	177.0(4)	C(21)–C(26)–F(26)	120.7(7)	C(11)–C(16)–C(15)	123.6(6)
Au(1)–P–C(31)	117.7(3)	P–C(31)–C(32)	119.1(5)	C(15)–C(16)–F(16)	116.8(5)
Au(1)–P–C(41)	112.9(3)	C(32)–C(31)–C(36)	119.3(6)	Au(2)–C(21)–C(26)	121.1(7)
C(31)–P–C(41)	106.2(3)	C(32)–C(33)–C(34)	120.7(7)	C(21)–C(22)–C(23)	120.6(9)
Au(2)–C(1)–P	108.3(4)	C(34)–C(35)–C(36)	120.3(7)	C(23)–C(22)–F(22)	116.5(9)
Au(1)–C(11)–C(12)	122.2(4)	P–C(41)–C(42)	119.7(6)	C(22)–C(23)–F(23)	125.8(9)
C(12)–C(11)–C(16)	115.2(6)	C(42)–C(41)–C(46)	119.2(6)	C(23)–C(24)–C(25)	117.0(8)
C(11)–C(12)–F(12)	120.4(6)	C(42)–C(43)–C(44)	121.0(7)	C(25)–C(24)–F(24)	118.2(10)
C(12)–C(13)–C(14)	119.8(6)	C(44)–C(45)–C(46)	119.8(8)	C(24)–C(25)–F(25)	121.4(8)
C(14)–C(13)–F(13)	119.8(7)	P–Au(1)–P^{i}	69.9(2)	C(21)–C(26)–C(25)	123.5(9)
C(13)–C(14)–F(14)	120.3(6)	C(11)–Au(1)–C(11^{i})	85.4(4)	C(25)–C(26)–F(26)	115.8(8)
C(14)–C(15)–C(16)	119.0(6)	Au(1)–P–C(1)	92.6(3)	P–C(31)–C(36)	121.5(5)
C(16)–C(15)–F(15)	120.6(6)	C(1)–P–C(31)	115.5(3)	C(31)–C(32)–C(33)	119.4(6)
C(11)–C(16)–F(16)	119.6(6)	C(1)–P–C(41)	111.9(4)	C(33)–C(34)–C(35)	120.5(7)
Au(2)–C(21)–C(22)	121.6(6)	P–C(1)–P^{i}	96.1(4)	C(31)–C(36)–C(35)	119.8(6)
C(22)–C(21)–C(26)	117.3(7)	Au(1)–C(11)–C(16)	122.1(5)	P–C(41)–C(46)	121.0(5)
C(21)–C(22)–F(22)	122.8(7)	C(11)–C(12)–C(13)	122.7(5)	C(41)–C(42)–C(43)	119.2(7)
C(22)–C(23)–C(24)	123.2(10)	C(13)–C(12)–F(12)	116.9(6)	C(43)–C(44)–C(45)	119.6(7)
C(24)–C(23)–F(23)	111.0(7)	C(12)–C(13)–F(13)	120.3(6)	C(41)–C(46)–C(45)	121.1(7)
C(23)–C(24)–F(24)	124.8(9)	C(13)–C(14)–C(15)	119.6(7)		

Symmetry operator: i *x*, 0.5 − *y*, *z*.

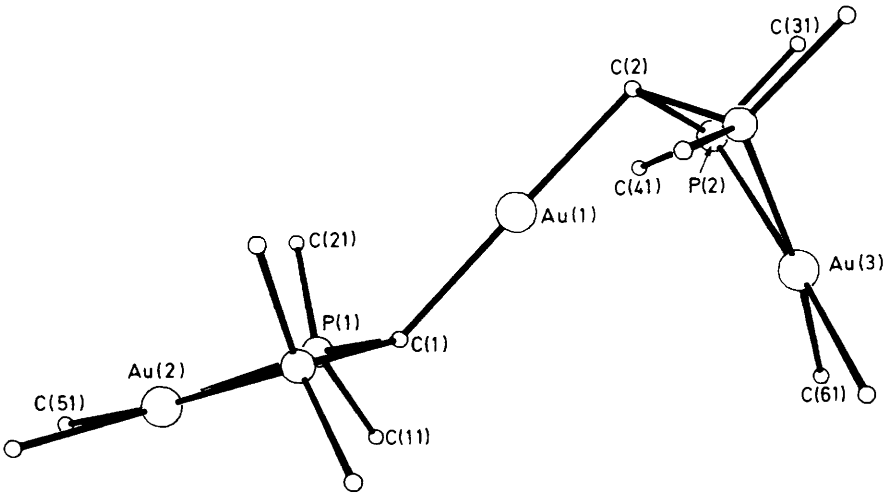


Figure 2. The cation of (5), showing the numbering scheme of the asymmetric unit. All aromatic rings are represented by only the first carbon atom (for clarity)

obtained from other solvents. The cation (Figure 2) possesses crystallographic *m* symmetry; all three gold atoms and the methanide C atom lie in the mirror plane. The two chemically equivalent halves of the cation display strikingly different geometries; the four-membered ring Au(2)–P(1)–C(1)–P(1^{i}) is almost planar [C(1) < 0.1 Å out of the Au(2) ligand plane], but Au(3)–P(2)–C(2)–P(2^{i}) is not [C(2) is 0.8 Å out of the Au(3) ligand plane]. Associated with this is an appreciably greater ' bending ' of the cation at C(2) than at C(1) [Au(1)–C(2)–P(2) 102.5, Au(1)–C(1)–P(1) 121.7°].

Experimental

Infrared spectra were recorded with a Perkin-Elmer 599 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured for *ca.* 5×10^{-4} mol dm^{-3} solutions in acetone with a Philips PW 9509 conductimeter. Molecular weights were determined for *ca.* 10^{-3} mol dm^{-3} solutions in $CHCl_3$ using the isopiestic method on a Hitachi-Perkin-Elmer 115 apparatus. ^{1}H-Decoupled ^{31}P n.m.r. spectra were recorded on a Varian FT80A spectrometer with 85% H_3PO_4 as external standard. Analyses (C,H) were carried out with a Perkin-Elmer 240 microanalyzer. Gold was determined by ashing the sample with an aqueous solution of hydrazine. For (4), Au and Ag were jointly determined in the same way.

All solvents were distilled from drying agents under nitrogen, and all operations were conducted in oxygen-free anhydrous nitrogen.

$[Au(C_6F_5)_2(Ph_2PCHPPh_2)]$ (2).—To a suspension of NaH (0.4 g, 16.6 mmol) in diethyl ether (50 cm^3) was added $[Au(C_6F_5)_2(Ph_2PCH_2PPh_2)]ClO_4$ [2] (0.710 g, 0.7 mmol). After 1 h stirring at room temperature, the excess of NaH was removed by filtration. Evaporation of the yellow filtrate gave (2) (0.499 g, 78%) (Found: C, 49.05; H, 2.5; Au, 22.35. $C_{37}H_{21}AuF_{10}P_2$ requires C, 48.6; H, 2.3; Au, 21.55%).

$[(C_6F_5)_2Au(Ph_2PCHPPh_2)Au(C_6F_5)]$ (3).—To a solution of (2) (0.183 g, 0.2 mmol) in diethyl ether (30 cm^3) was added $[Au(C_6F_5)(tht)]$ [7] (0.181 g, 0.4 mmol) and the mixture was stirred for 1 h at room temperature. The solution was concentrated to 12 cm^3 and the white precipitate of (3) was filtered off and recrystallized from dichloromethane–hexane (0.158 g, 62%) (Found: C, 40.55; H, 1.65; Au, 30.95. $C_{43}H_{21}Au_2F_{15}P_2$ requires C, 40.4; H, 1.65; Au, 30.8%).

$[(C_6F_5)_2Au(Ph_2PCHPPh_2)Ag(Ph_2PCHPPh_2)Au(C_6F_5)_2]ClO_4$ (4).—To a solution of (2) (0.183 g, 0.2 mmol) in diethyl ether (30 cm^3) was added $AgClO_4$ (0.021 g, 0.1 mmol) and the mixture was stirred for 1 h at room temperature. The white precipitate of (4) was filtered off (0.189 g, 93%) (Found: C, 43.35; H, 2.25; Au + Ag, 25.3. $C_{74}H_{42}AgAu_2ClF_{20}O_4P_4$ requires C, 43.65; H, 2.05; Au + Ag, 24.65%).

$[(C_6F_5)_2Au(Ph_2PCHPPh_2)Au(Ph_2PCHPPh_2)Au(C_6F_5)_2]ClO_4$ (5).—To a solution of (2) (0.183 g, 0.2 mmol) in diethyl ether (30 cm^3) was added $[Au(tht)_2]ClO_4$ (0.047 g, 0.1 mmol) {obtained from [AuCl(tht)] with $AgClO_4$ and tetrahydrothiophen}. After 1 h stirring at room temperature, the white complex (5) was filtered off and recrystallized from dichloromethane–diethyl ether (0.166 g, 78%) (Found: C, 41.85; H, 1.95; Au, 27.7. $C_{74}H_{42}Au_3ClF_{20}O_4P_4$ requires C, 41.8; H, 2.0; Au, 27.8%).

$[(C_6F_5)_2Au(Ph_2PCHPPh_2)Ag(tht)]ClO_4$ (6).—To a solution of (4) (0.204 g, 0.1 mmol) in dichloromethane (20 cm^3) was added tht [0.2 mmol, 2 cm^3 of a hexane solution (10%)]. After 0.5 h stirring at room temperature, evaporation to dryness and treatment of the residue with diethyl ether gave a white solid (6) which was filtered off (0.079 g, 65%) (Found: C, 40.5; H, 2.6; Au + Ag, 25.05. $C_{41}H_{29}AgAuClF_{10}O_4P_2S$ requires C, 40.7; H, 2.4; Au + Ag, 25.2%).

Crystal Data for (3).—$C_{43}H_{21}Au_2F_{15}P_2$, M = 1 278, monoclinic, space group $P2_1/m$, a = 10.003(2), b = 17.389(4),

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

Au(1)–C(1)	2.127(29)	Au(1)–C(2)	2.098(28)
Au(2)–P(1)	2.347(7)	Au(2)–C(51)	2.108(10)
Au(3)–P(2)	2.356(7)	Au(3)–C(61)	2.118(11)
C(1)–P(1)	1.787(20)	C(2)–P(2)	1.826(19)
C(11)–P(1)	1.765(19)	C(21)–P(1)	1.783(17)
C(31)–P(2)	1.741(17)	C(41)–P(2)	1.766(16)
Cl(1)–O(1)	1.316(37)	Cl(1)–O(2)	1.394(30)
Cl(1)–O(3)	1.352(45)	C(3)–Cl(32)	1.777(36)
C(3)–Cl(31)	1.704(61)		

C(1)–Au(1)–C(2)	179.1(11)	P(1)–Au(2)–C(51)	101.1(4)
P(1)–Au(2)–P(1^{i})	71.0(4)	C(51)–Au(2)–P(1^{i})	171.5(4)
P(2)–Au(3)–C(61)	100.8(4)	C(51)–Au(2)–C(51^{i})	86.5(6)
P(2)–Au(3)–P(2^{i})	68.9(4)	C(61)–Au(3)–P(2^{i})	168.8(4)
C(61)–Au(3)–C(61^{i})	89.0(7)	Au(3)–P(2)–C(2)	91.9(8)
Au(2)–P(1)–C(1)	94.6(8)	P(2)–C(2)–P(2^{i})	93.8(13)
P(1)–C(1)–P(1^{i})	99.5(15)	Au(1)–C(2)–P(2)	102.5(11)
Au(1)–C(1)–P(1)	121.7(10)		

Symmetry operator: i x, 0.5 − y, z.

Table 3. Atom co-ordinates (× 10^4) for (3)

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Au(1)	4 348(1)	2 500	3 313(1)	C(25)	−2 933(9)	2 500	−1 264(7)
Au(2)	371(1)	2 500	1 843(1)	C(26)	−2 119(8)	2 500	−115(6)
P	2 660(1)	3 276(1)	3 841(1)	F(22)	1 240(6)	2 500	−646(5)
C(1)	1 413(7)	2 500	3 609(6)	F(23)	−318(6)	2 500	−2 868(4)
C(11)	5 651(5)	1 691(3)	2 851(4)	F(24)	−3 082(7)	2 500	−3 276(4)
C(12)	5 478(5)	1 428(3)	1 717(4)	F(25)	−4 321(6)	2 500	−1 458(5)
C(13)	6 426(6)	958(3)	1 370(5)	F(26)	−2 810(5)	2 500	740(4)
C(14)	7 602(6)	750(4)	2 160(5)	C(31)	2 131(5)	4 136(3)	2 990(4)
C(15)	7 812(5)	989(4)	3 300(5)	C(32)	2 038(6)	4 121(3)	1 781(5)
C(16)	6 838(5)	1 452(3)	3 618(4)	C(33)	1 668(6)	4 783(3)	1 129(5)
F(12)	4 382(3)	1 657(2)	874(3)	C(34)	1 392(6)	5 450(3)	1 653(6)
F(13)	6 222(4)	731(3)	246(3)	C(35)	1 487(6)	5 474(3)	2 831(6)
F(14)	8 546(4)	317(2)	1 823(3)	C(36)	1 855(6)	4 817(3)	3 513(5)
F(15)	8 953(4)	783(3)	4 087(3)	C(41)	3 127(5)	3 578(3)	5 355(4)
F(16)	7 082(3)	1 664(2)	4 753(3)	C(42)	4 373(6)	3 926(4)	5 788(6)
C(21)	−743(7)	2 500	143(6)	C(43)	4 720(7)	4 159(5)	6 960(6)
C(22)	−105(8)	2 500	−790(6)	C(44)	3 853(8)	4 037(5)	7 671(6)
C(23)	−836(9)	2 500	−1 871(7)	C(45)	2 596(8)	3 713(5)	7 228(5)
C(24)	−2 291(10)	2 500	−2 167(7)	C(46)	2 245(7)	3 479(4)	6 073(5)

Table 4. Atom co-ordinates ($\times 10^4$) for (5)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Au(1)	983(1)	2 500	1 580(1)
Au(2)	3 603(1)	2 500	564(1)
Au(3)	110(1)	2 500	3 340(1)
P(1)	2 700(3)	3 270(3)	1 130(3)
P(2)	−366(4)	3 253(3)	2 326(3)
C(1)	2 199(16)	2 500	1 530(15)
C(2)	−213(15)	2 500	1 647(14)
C(11)	3 013(13)	3 868(10)	1 880(9)
C(12)	2 492(13)	4 378(10)	2 166(9)
C(13)	2 738(13)	4 903(10)	2 711(9)
C(14)	3 505(13)	4 919(10)	2 971(9)
C(15)	4 027(13)	4 409(10)	2 685(9)
C(16)	3 781(13)	3 883(10)	2 140(9)
C(21)	2 173(9)	3 839(10)	457(7)
C(22)	1 552(9)	3 562(10)	14(7)
C(23)	1 217(9)	4 006(10)	−562(7)
C(24)	1 503(9)	4 727(10)	−695(7)
C(25)	2 124(9)	5 004(10)	−253(7)
C(26)	2 459(9)	4 560(10)	323(7)
C(31)	−1 336(8)	3 461(10)	2 384(11)
C(32)	−1 829(8)	3 467(10)	1 741(11)
C(33)	−2 583(8)	3 718(10)	1 787(11)
C(34)	−2 843(8)	3 962(10)	2 476(11)
C(35)	−2 350(8)	3 956(10)	3 119(11)
C(36)	−1 596(8)	3 705(10)	3 073(11)
C(41)	83(8)	4 113(7)	2 104(8)
C(42)	265(8)	4 254(7)	1 361(8)
C(43)	567(8)	4 952(7)	1 166(8)
C(44)	687(8)	5 510(7)	1 714(8)
C(45)	505(8)	5 370(7)	2 457(8)
C(46)	203(8)	4 671(7)	2 652(8)
C(52)	4 021(5)	3 607(5)	−644(5)
C(53)	4 459(5)	4 136(5)	−1 014(5)
C(54)	5 162(5)	4 374(5)	−690(5)
C(55)	5 427(5)	4 083(5)	6(5)
C(56)	4 989(5)	3 554(5)	376(5)
C(51)	4 286(5)	3 315(5)	51(5)
F(52)	3 340(5)	3 376(5)	−958(5)
F(53)	4 202(5)	4 418(5)	−1 687(5)
F(54)	5 586(5)	4 887(5)	−1 048(5)
F(55)	6 107(5)	4 313(5)	320(5)
F(56)	5 245(5)	3 272(5)	1 049(5)
C(62)	1 299(6)	3 628(6)	4 001(5)
C(63)	1 599(6)	4 168(6)	4 506(5)
C(64)	1 166(6)	4 419(6)	5 096(5)
C(65)	432(6)	4 129(6)	5 181(5)
C(66)	132(6)	3 589(6)	4 676(5)
C(61)	565(6)	3 339(6)	4 086(5)
F(62)	1 719(6)	3 386(6)	3 430(5)
F(63)	2 309(6)	4 449(6)	4 424(5)
F(64)	1 456(6)	4 941(6)	5 585(5)
F(65)	13(6)	4 371(6)	5 753(5)
F(66)	−578(6)	3 309(6)	4 759(5)
Cl(1)	704(6)	7 500	444(5)
O(1)	1 017(19)	7 500	1 134(20)
O(2)	867(15)	6 823(16)	84(14)
O(3)	−71(24)	7 500	417(22)
C(3)	2 842(34)	7 500	925(31)
Cl(31)	3 237(11)	7 500	66(10)
Cl(32)	3 075(9)	6 663(9)	1 441(8)

c = 11.754(3) Å, β = 103.53(2)°, U = 1 988 Å^3, Z = 2, D_c = 2.14 g cm^{-3}, F(000) = 1 204, Mo-K_α radiation, λ = 0.710 69 Å, μ = 7.5 mm^{-1}, crystal size 0.4 × 0.4 × 0.4 mm.

5 876 Profile-fitted [8] data to $2\theta_{\text{max.}}$ = 55° were measured on a Stoe-Siemens four-circle diffractometer. After Lorentz-polarisation and absorption corrections, merging equivalents gave 4 697 unique reflections, 4 016 of which with $F > 4\sigma(F)$ were used for all calculations (program system SHELXTL, written by G. M. S.). The structure was solved by the heavy-atom method and refined anisotropically to R = 0.034, R' = 0.034 [weighting scheme $w^{-1} = \sigma^2(F) + 0.0002\,F^2$]; H atoms were included with a riding model [C–H 0.96 Å, U(H) = 1.2U(C)] except for the methanide H, clearly identified in a difference map, which was given fixed U but otherwise refined freely. Atomic co-ordinates are in Table 3, bond lengths and angles in Table 1.

Crystal Data for (5).—$C_{74}H_{42}Au_3ClF_{20}O_4P_4 \cdot xCHCl_3$, monoclinic, space group $P2_1/m$, a = 17.456(6), b = 17.704(6), c = 17.749(8) Å, β = 92.86(5)°, U = 5 478 Å^3, Z = 2, Mo-K_α radiation, λ = 0.710 69 Å, μ = 4.2 mm^{-1}, crystal size 0.4 × 0.4 × 0.4 mm.

Data collection and reduction were as for (3), but with $2\theta_{\text{max.}}$ = 45°, 8 021 intensities, 7 414 unique, 5 230 observed [$F > 3\sigma(F)$]. The presence of much disordered chloroform, only one molecule of which could be satisfactorily refined, led to high R values: R = 0.096, R' = 0.098 with weighting scheme $w^{-1} = \sigma^2(F) + 0.001\,F^2$. Gold, P, and perchlorate Cl were refined anisotropically, phenyl and C_6F_5 rings as rigid groups with C–C 1.395, C–F 1.350 Å, all angles 120°. Hydrogen atoms were not included. Atomic co-ordinates are in Table 4, bond lengths and angles in Table 2.

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