Synthesis of Trinuclear Gold(I) and Gold(III) Complexes containing the Tridentate Bis(diphenylphosphino)methanide Ligand. Crystal Structure of $[Cl(C_6F_5)_2Au\{Ph_2PCH(AuNC_5H_5)PPh_2\}AuCl]$†

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The reaction of $[Au(C_6F_5)_2(Ph_2PCHPPh_2)]$ with $[AuX(L)]$ [X = Cl or Br, L = tetrahydrothiophen (tht) or $AsPh_3$] leads to trinuclear complexes $[X(C_6F_5)_2Au\{Ph_2PCH(AuL)PPh_2\}AuX]$ containing the tridentate $[Ph_2PCHPPh_2]^-$ ligand. Displacement of tht with L = PPh_3, pyridine, or 4-methylpyridine leads to the corresponding derivatives. The structure of $[Cl(C_6F_5)_2Au\{Ph_2PCH(AuNC_5H_5)PPh_2\}AuCl]$ has been determined by *X*-ray diffraction: space group $P\bar{1}$, $a = 11.664(5)$, $b = 14.790(6)$, $c = 18.344(6)$ Å, $\alpha = 111.30(4)$, $\beta = 94.18(4)$, $\gamma = 107.64(4)$°, and $Z = 2$; $R = 0.075$ for 4 627 reflections.

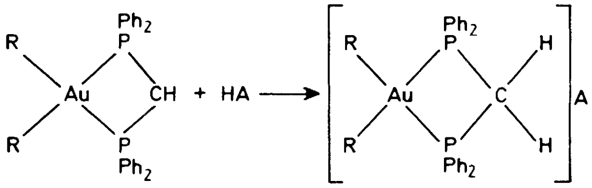
Few examples of tridentate behaviour of the bis(diphenylphosphino)methanide ligand have been reported.[1-3] In none of these examples is the ligand co-ordinated to three metal centres with different environments.

We recently reported the use of the complex $[AuR_2(Ph_2PCHPPh_2)]$ (where R = C_6F_5) as a C-donor to another metal centre, namely Au or Ag.[4] Here we report a new reaction of $[AuR_2(Ph_2PCHPPh_2)]$ (R = C_6F_5) with neutral gold(I) complexes $[AuX(L)]$ [X = Cl or Br, L = tetrahydrothiophen (tht) or $AsPh_3$], which leads to opening of the AuPCP chelate ring and formation of trinuclear derivatives $[X(C_6F_5)_2Au\{Ph_2PCH(AuL)PPh_2\}AuX]$.

Results and Discussion

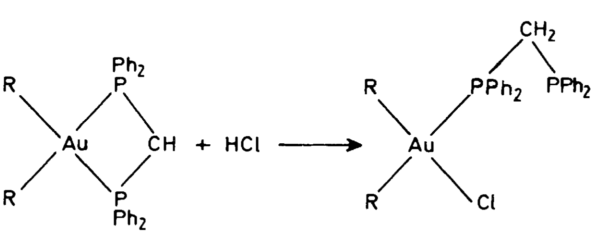
The reactions between $[AuR_2(Ph_2PCHPPh_2)]$ and $[AuR(tht)]$ (R = C_6F_5) or $[Au(tht)_2]ClO_4$ lead to bi- or tri-nuclear derivatives respectively,[4] electron density on the methanide C atom being donated to the gold(I) centres. These reactions take place without opening of the chelate ring in the gold(III) precursor. A similar reaction takes place with $[Au(C_6H_2F_3)(tht)]$ leading to $[(C_6F_5)_2Au(Ph_2PCHPPh_2)Au(C_6H_2F_3\text{-}2,4,6)]$ (**1**).

The presence of an excess of electron density on the methanide C atom can also be demonstrated by the protonation of this atom by use of acids HA, when A^- is a weak Lewis base, ClO_4 or BF_4 [equation (1)]. When A is nucleophilic, protonation and opening of the AuPCP ring can be observed [equation (2)]. The complexes with A = ClO_4 or Cl (obtained by another method) have been described elsewhere.[5] Their properties (analyses, i.r. spectra) agree well with those previously reported.[5] Complex (**2**; A = BF_4) is a white, air- and moisture-stable solid and is a 1 : 1 electrolyte in acetone solution.



(1)

(**2**) R = C_6F_5, A = ClO_4 or BF_4



(2)

Other non-protonic Lewis acids {for instance, gold(I) complexes $[AuX(L)]$, where X = Cl or Br, L = tht or $AsPh_3$, that are partially dissociable $[AuX(L)] \rightleftharpoons [AuL]^+ + X^-$}, can also cause opening of the AuPCP ring, but the reaction is now more complicated since the free end of the diphosphine ligand easily displaces L from another $[AuX(L)]$ molecule [equation (3)] and a new trinuclear complex is formed. Some $[AuX(L)]$ complexes, *e.g.* $[AuCl(PPh_3)]$, do not react, perhaps since they do not dissociate appreciably. The above reactions are probably much more complicated than the simple representation in equation (3); with a 1 : 1 molar ratio of gold(III) to gold(I), a white solid is obtained which is a mixture of at least six different components (none of them a reactant), including the trinuclear complex. This could be connected with ambivalent dissociative behaviour of the gold(I) complexes: $[AuL]^+ + X^- \rightleftharpoons [AuX(L)] \rightleftharpoons [AuX] + L$.

The tht ligand in complex (**3**) can easily be displaced by other neutral ligands, such as $AsPh_3$ (**4**), PPh_3 (**6**), pyridine (py) (**7**), or 4-methylpyridine (4Me-py) (**8**). Complexes (**3**)—(**8**) are white, air- and moisture-stable solids, which are non-conducting in acetone solutions. Their molecular weights were in agreement with the proposed formulae. Routine spectroscopic data are given in the Experimental section. The following features are noteworthy. The i.r. spectra show a new ν(Au–C) band at 590—615 cm^{-1},[6,7] with ν(Au–halide) at 330—338 cm^{-1} [complexes (**3**), (**4**), and (**6**)—(**8**)] or 230 cm^{-1} [complex (**5**)].[8] The ^{31}P n.m.r.

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† μ_3-[Bis(diphenylphosphino)methanido-*C*(Au^3)*P*(Au^1)*P*′(Au^2)]-1,2-dichloro-1,1-bis(pentafluorophenyl)-3-pyridinetrigold.

Supplementary data available: structure factors, H-atom co-ordinates, and anisotropic thermal parameters can be ordered from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany, quoting reference number CSD/51394, the names of the authors, and the title of the paper.

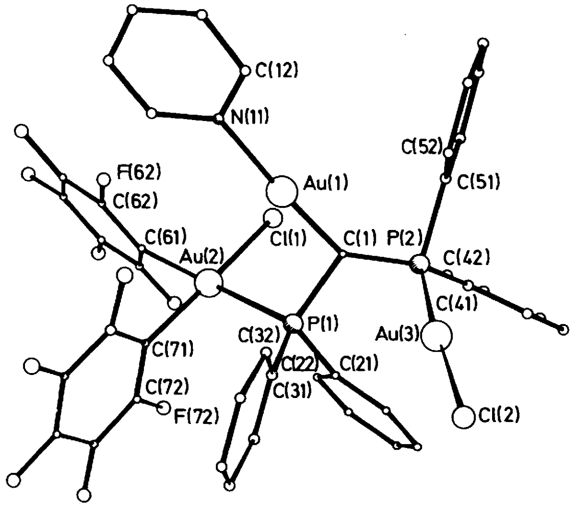
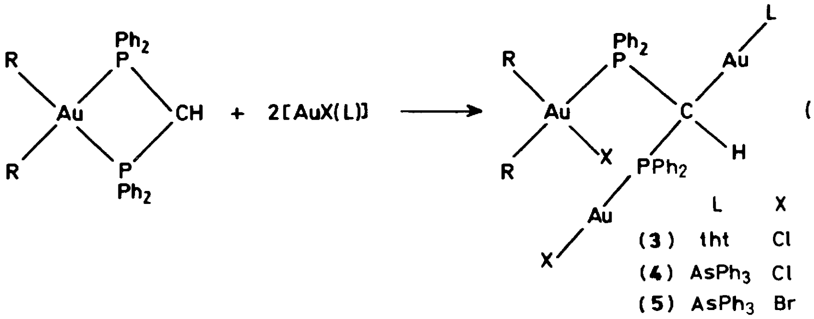


Figure. The molecule of complex (7) in the crystal, showing the atom numbering scheme (H atoms omitted, arbitrary radii)



spectra (^1H-decoupled) correspond to an AB system in which B appears as a multiplet (coupling to F). In the ^1H n.m.r. spectrum the CH proton is part X of an ABX system.

The ^{19}F n.m.r. spectra (^1H-decoupled) show two triplets, located at *ca.* -158.1 and -158.5 p.p.m., assigned to the *para*-fluorine (F^4) atoms of two different C_6F_5 groups, which are therefore mutually *cis*. The signals due to F^2, F^6, and F^3, F^5 are broad and complex with splittings depending on the neutral ligand L, and increasing along the series tht (**3**) < py (**7**) < 4Me-py (**8**) < PPh_3 (**6**) < $AsPh_3$ (**4**), *i.e.* with increasing volume of L. The obvious conclusion is that the pentafluorophenyl groups are not free to rotate around the Au–C bond, the obstruction presumably being the neutral L ligand. A similar situation has been observed for iridium,[9] palladium,[10] and platinum[11] complexes. In the present case, however, the features of the peaks are not well resolved; it is not possible to assign the resonance position of each F atom and hence determine the other parameters.

Despite the fact that the carbon atom in the CH group is asymmetric, the optical activity of complex (**3**) is zero. As the starting product $[AuR_2(Ph_2PCHPPh_2)]$ is symmetric, a racemic mixture of the two enantiomers of (**3**) is obtained.

Single crystals of complex (**7**) were obtained by diffusion of n-hexane into a dichloromethane solution of the complex. They decomposed by loss of solvent immediately on exposure to air or on altering the composition of the mother-liquor (*e.g.* by partial evaporation). One crystal was eventually mounted successfully with mother-liquor in a glass capillary and its structure determined by *X*-ray diffraction. The structure is shown in the Figure. High thermal motion, associated with the presence of disordered solvent, resulted in moderate precision of the molecular dimensions, which in turn precludes much useful discussion. The sum of bond angles (excluding those to hydrogen) at the methanide carbon is 341°, *cf.* 299, 343, and 313° in related$\mathrm{Au}\overline{\mathrm{PCP\ Au}}$ systems;[4] the extent of flattening at this carbon appears to be a 'soft' parameter. The metal atoms display the expected linear (Au^I) and square-planar (Au^{III}) co-ordination geometries. There are no short Au ··· Au contacts.

Experimental

The instrumentation and general experimental techniques used were as described earlier.[4] Nuclear magnetic resonance spectra were recorded on Varian FT 80A and Varian XL200 spectrometers in $CDCl_3$. Chemical shifts are quoted relative to $SiMe_4$ (^1H), 85% H_3PO_4 (external) (^{31}P), and $CFCl_3$ (external) (^{19}F). The optical activity was measured (in $CDCl_3$) with a Perkin-Elmer 241 MC polarimeter (sodium lamp).

Preparation of Complexes.—$[Au(C_6H_2F_3\text{-}2,4,6)(tht)]$. A solution of $[NBu_4][Au(C_6H_2F_3\text{-}2,4,6)_2]^{12}$ (0.351 g, 0.5 mmol) and $[Au(tht)_2]ClO_4{}^4$ (0.236 g, 0.5 mmol) in CH_2Cl_2 (30 cm^3) was stirred for 2 h at room temperature. It was then evaporated and the white residue extracted with diethyl ether (30 cm^3). After filtering off the insoluble $[NBu_4]ClO_4$, the solution was concentrated *in vacuo* to *ca.* 5 cm^3. Addition of n-hexane (20 cm^3) caused precipitation of a white solid (0.291 g, 70%) (Found: C, 28.9; H, 2.65; Au, 47.8. $C_{10}H_{10}AuF_3S$ requires C, 28.85; H, 2.4; Au, 47.35%).

$[(C_6F_5)_2Au(Ph_2PCHPPh_2)Au(C_6H_2F_3\text{-}2,4,6)]$ (**1**). To a diethyl ether solution (30 cm^3) of $[Au(C_6F_5)_2(Ph_2PCHPPh_2)]^4$ (0.183 g, 0.2 mmol) in a dry nitrogen atmosphere was added $[Au(C_6H_2F_3\text{-}2,4,6)(tht)]$ (0.083 g, 0.2 mmol) and the mixture stirred at room temperature for 1 h. The solution was concentrated *in vacuo* to 10 cm^3, and n-hexane (10 cm^3) was added. The white precipitate was filtered off and recrystallised from dichloromethane–n-hexane (0.186 g, 75% yield); m.p. 170—175 °C (Found: C, 41.7; H, 2.3; Au, 31.85. $C_{43}H_{23}Au_2F_{13}P_2$ requires C, 41.5; H, 1.85; Au, 31.7%).

$[Au(C_6F_5)_2(Ph_2PCH_2PPh_2)]BF_4$ (**2**). To a diethyl ether solution (30 cm^3) of $[Au(C_6F_5)_2(Ph_2PCHPPh_2)]^4$ (0.183 g, 0.2 mmol) was added HBF_4 (0.4 cm^3, 0.2 mmol of a 35% diethyl ether solution) in a dry nitrogen atmosphere. The yellow solution immediately turned colourless and a white precipitate formed. The mixture was stirred for 15 min at room temperature. Complex (**2**) was filtered off (0.156 g, 78% yield), m.p. 190—193 °C (Found: C, 44.7; H, 2.3; Au, 20.3. $C_{37}H_{22}AuBF_{14}P_2$ requires C, 44.35; H, 2.2; Au, 19.65%); Λ_M = 117 $ohm^{-1}\,cm^2\,mol^{-1}$ (*ca.* 5×10^{-4} mol dm^{-3} in acetone). ^1H N.m.r. spectrum: δ 7.2 (m, 20 H, Ph) and 5.73 p.p.m. [t, 2 H, CH_2, J(HP) 12.0 Hz].

$[X(C_6F_5)_2Au\{Ph_2PCH(AuL)PPh_2\}AuX]$ [L = tht, X = Cl (**3**); L = $AsPh_3$, X = Cl (**4**) *or* Br (**5**)]. To a diethyl ether solution (30 cm^3) of $[Au(C_6F_5)_2(Ph_2PCHPPh_2)]^4$ (0.183 g, 0.2 mmol) was added $[AuCl(tht)]^{13}$ (0.128 g, 0.4 mmol), $[AuCl(AsPh_3)]^{14}$ (0.215 g, 0.4 mmol), or $[AuBr(AsPh_3)]^{14}$

(0.233 g, 0.4 mmol) in a dry nitrogen atmosphere. The mixtures were stirred for 1 h at room temperature. Vacuum concentration of the solutions to *ca.* 10 cm^3 and addition of n-hexane (10 cm^3) gave white solids which were filtered off. Complex (**3**) (0.258 g, 88%): m.p. (decomp.) 170—172 °C [Found: C, 33.55; H, 2.0; Au, 39.5%; *M* (in CHCl$_3$) 1 550. $C_{41}H_{29}Au_3Cl_2F_{10}P_2S$ requires C, 33.55; H, 2.0; Au, 40.25%; *M* 1 467]. N.m.r. spectra: ^{1}H, δ 8.05—7 (m, 20 H, Ph), 5.2 [part X of a XAB system, 1 H, CH, *J*(HP$_A$) + *J*(HP$_B$) 21.2 Hz], 3.2 (m, 4 H, CH$_2$), and 2.05 p.p.m. (m, 4 H, SCH$_2$); ^{31}P, δ 26.0 [d of an AB system, P–Au^I, *J*(AB) 27.9 Hz] and 31.1 p.p.m. (m, P–Au^{III}); ^{19}F, δ −123.2 to −122.3 (m, F^{2,6}), −157.8 [t, F^4, *J*(F^{4}F^3) 20.2], −158.1 [t, F^4, *J*(F^{4}F^3) 20.2 Hz], and −161.2 to −162.7 p.p.m. (m, F^{3,5}). I.r. spectrum: 603m [ν(Au–C)], 335m, and 322m cm^{-1} [ν(Au–Cl)]. Complex (**4**) (0.276 g, 82%): m.p. 125—130 °C (decomp.) [Found: C, 39.0; H, 2.15; Au, 34.3%; *M* (in CHCl$_3$) 1 680. $C_{55}H_{36}AsAu_3Cl_2F_{10}P_2$ requires C, 39.2; H, 2.15; Au, 35.05%; *M* 1 686]. N.m.r. spectra: ^{1}H, δ 8.0—6.9 (m, 35 H, Ph) and 5.5 p.p.m. [part X of a XAB system, 1 H, CH, *J*(HP$_A$) + *J*(HP$_B$) 21.9 Hz]; ^{31}P, δ 25.9 [d of an AB system, P–Au^I, *J*(AB) 27.7 Hz] and 28.8 p.p.m. (m, P–Au^{III}); ^{19}F, δ −120.2, −121.9, −122.9, −124 (m, F^{2,6}), −158.1 [t, F^4, *J*(F^{4}F^3) 19.9], −158.5 [t, F^4, *J*(F^{4}F^3) 19.9 Hz] and −160.4 to −162.8 p.p.m. (m, F^{3,5}). I.r. spectrum: 590m [ν(Au–C)] and 330m, br cm^{-1} [ν(Au–Cl)]. Complex (**5**) (0.259 g, 73%): m.p. 140—145 °C (decomp.) [Found: C, 37.85; H, 2.1; Au, 32.95%; *M* (in CHCl$_3$) 1 688. $C_{55}H_{36}AsAu_3Br_2F_{10}P_2$ requires C, 37.25; H, 2.05; Au, 33.5%; *M* 1 774]. I.r. spectrum: 603m [ν(Au–C)] and 230w, br cm^{-1} [ν(Au–Br)].

[Cl(C$_6$F$_5$)$_2$Au{Ph$_2$PCH(AuL)PPh$_2$}AuCl] [L = AsPh$_3$ (**4**), PPh$_3$ (**6**), py (**7**), *or* 4Me-py (**8**)]. To a dichloromethane solution (30 cm^3) of complex (**3**) (0.294 g, 0.2 mmol) was added AsPh$_3$ (0.061 g, 0.2 mmol), PPh$_3$ (0.052 g, 0.2 mmol), py or 4Me-py (8 cm^3, 0.8 mmol, in the form of a 0.1 mol dm^{-3} solution in hexane), and the mixtures were stirred at room temperature for 1 h. Vacuum concentration of the solutions to *ca.* 8 cm^3 and subsequent addition of n-hexane (*ca.* 10 cm^3) gave white solids which were filtered off. Complex (**4**) (0.286 g, 85%). Complex (**6**) (0.273 g, 83%): m.p. 145—150 °C (decomp.) [Found: C, 40.65; H, 2.35; Au, 35.2%; *M* (in CHCl$_3$) 1 654. $C_{55}H_{36}Au_3Cl_2F_{10}P_3$ requires C, 40.25; H, 2.2; Au, 36.0%; *M* 1 642]. N.m.r. spectra: ^{1}H, δ 8.2—7.0 (m, 35 H, Ph) and 5.4 p.p.m. (m, 1 H, CH); ^{31}P, δ 26.1 [part A of an ABX system, Ph$_2$P–Au^I, *J*(AB) 27.7, *J*(AX) 9.5 Hz], 28.4 (m, P–Au^{III}), and 40.5 p.p.m. [m, PPh$_3$, *J*(AX) ≈ *J*(BX)]; ^{19}F, δ −120.3, −122.3, −122.8, −124.2 (m, F^{2,6}), −158.1 [t, F^4, *J*(F^{4}F^3) 20.0], −158.5 [t, F^4, *J*(F^{4}F^3) 20.0 Hz], and −160.5 to −162.9 p.p.m. (m, F^{3,5}). I.r. spectrum: 592m [ν(Au–C)] and 332m, br cm^{-1} [ν(Au–Cl)]. Complex (**7**) (0.251 g, 86%): m.p. 160—162 °C (decomp.) [Found: C, 34.15; H, 2.3; Au, 39.4; N, 0.85%; *M* (in CHCl$_3$) 1509. $C_{42}H_{26}Au_3Cl_2F_{10}NP_2$ requires C, 34.6; H, 1.8; Au, 40.5; N, 0.95%; *M* 1 458]. N.m.r. spectra: ^{1}H, δ 8.3—7.0 (m, 25 H, Ph and NC$_5$H$_5$) and 5.2 p.p.m. [part X of a XAB system, 1 H, CH, *J*(HP$_A$) + *J*(HP$_B$) 23.7 Hz]; ^{31}P, δ 27.4 [d of an AB system, P–Au^I, *J*(AB) 27.4 Hz] and 31.5 p.p.m. (m, P–Au^{III}); ^{19}F, δ −122.5 to −124.2 (m, F^{2,6}), −158.0 [t, F^4, *J*(F^{4}F^3) 20.0], and −161.0 to −162.4 p.p.m. (m, F^{3,5}). I.r. spectrum: 615m [ν(Au–C)], 338m, and 330m cm^{-1} [ν(Au–Cl)]. Complex (**8**) (0.283 g, 96%): m.p. 165—170 °C (decomp.) [Found: C, 35.3; H, 2.05; Au, 39.95; N, 1.0%; *M* (in CHCl$_3$) 1 328. $C_{43}H_{28}Au_3Cl_2F_{10}NP_2$ requires C, 35.05; H, 1.9; Au, 40.15; N, 0.95%; *M* 1 472]. N.m.r. spectra: ^{1}H, δ 8.2—7.0 (m, 24 H, Ph and NC$_5$H$_4$), 5.4 [part X of a XAB system, 1 H, CH,

Table 1. Atom co-ordinates (× 10^4) of complex (**7**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Au(1)	5 195(1)	3 411(1)	5 914(1)
Au(2)	6 986(1)	5 215(1)	7 955(1)
Au(3)	4 162(1)	413(1)	6 095(1)
Cl(1)	5 110(5)	5 470(5)	8 044(3)
Cl(2)	4 732(11)	−999(9)	5 708(5)
P(1)	6 019(5)	3 422(6)	7 584(3)
P(2)	3 503(6)	1 747(5)	6 490(3)
C(1)	4 640(16)	3 030(16)	6 815(10)
N(11)	5 691(16)	3 907(16)	5 013(10)
C(12)	4 968(23)	3 301(22)	4 251(14)
C(13)	5 291(24)	3 741(23)	3 677(16)
C(14)	6 221(23)	4 619(22)	3 871(15)
C(15)	6 906(28)	5 178(27)	4 610(18)
C(16)	6 609(24)	4 725(23)	5 171(16)
C(22)	5 876(13)	4 060(10)	9 200(9)
C(23)	5 543(13)	3 888(10)	9 867(9)
C(24)	5 025(13)	2 877(10)	9 811(9)
C(25)	4 841(13)	2 037(10)	9 089(9)
C(26)	5 175(13)	2 208(10)	8 422(9)
C(21)	5 692(13)	3 220(10)	8 477(9)
C(32)	6 976(14)	2 192(14)	6 401(8)
C(33)	7 829(14)	1 713(14)	6 166(8)
C(34)	8 649(14)	1 679(14)	6 740(8)
C(35)	8 616(14)	2 124(14)	7 549(8)
C(36)	7 763(14)	2 603(14)	7 783(8)
C(31)	6 943(14)	2 637(14)	7 209(8)
C(42)	2 660(12)	2 671(10)	7 873(8)
C(43)	1 973(12)	2 616(10)	8 457(8)
C(44)	1 291(12)	1 652(10)	8 442(8)
C(45)	1 297(12)	744(10)	7 842(8)
C(46)	1 985(12)	799(10)	7 258(8)
C(41)	2 666(12)	1 763(10)	7 274(8)
C(52)	2 465(15)	1 162(14)	4 907(10)
C(53)	1 657(15)	1 138(14)	4 295(10)
C(54)	803(15)	1 630(14)	4 480(10)
C(55)	757(15)	2 146(14)	5 277(10)
C(56)	1 565(15)	2 170(14)	5 889(10)
C(51)	2 419(15)	1 678(14)	5 704(10)
C(61)	7 800(15)	6 772(13)	8 286(11)
C(62)	8 029(15)	7 162(12)	7 702(11)
C(63)	8 427(15)	8 230(12)	7 912(11)
C(64)	8 595(15)	8 908(12)	8 707(11)
C(65)	8 366(15)	8 519(12)	9 291(11)
C(66)	7 968(15)	7 451(12)	9 080(11)
F(62)	7 899(15)	6 599(13)	6 978(8)
F(63)	8 723(23)	8 652(19)	7 371(13)
F(64)	9 068(25)	9 943(16)	8 938(14)
F(65)	8 523(24)	9 195(19)	10 050(12)
F(66)	7 654(16)	7 128(14)	9 622(8)
C(71)	8 647(13)	5 007(16)	7 928(11)
C(72)	9 357(13)	5 221(16)	8 658(11)
C(73)	10 533(13)	5 170(16)	8 691(11)
C(74)	10 999(13)	4 905(16)	7 994(11)
C(75)	10 289(13)	4 690(16)	7 265(11)
C(76)	9 113(13)	4 742(16)	7 232(11)
F(72)	8 949(15)	5 440(22)	9 315(11)
F(73)	11 133(17)	5 270(29)	9 359(19)
F(74)	12 057(16)	4 794(21)	7 962(17)
F(75)	10 717(18)	4 446(20)	6 638(14)
F(76)	8 437(14)	4 608(16)	6 563(9)
Cl(11)	8 614(31)	3 301(29)	4 580(19)
Cl(12)	8 853(36)	2 584(36)	3 262(23)
C(100)	9 314(48)	3 522(35)	4 005(27)
Cl(21)	3 580(48)	260(42)	2 131(29)
Cl(22)	4 741(46)	1 398(47)	1 601(34)
C(200)	4 758(54)	667(77)	1 954(69)

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

Au(1)–C(1)	2.019(23)	Au(1)–N(11)	2.088(24)
Au(2)–Cl(1)	2.337(8)	Au(2)–P(1)	2.352(8)
Au(2)–C(61)	2.037(18)	Au(2)–C(71)	2.052(20)
Au(1)–Cl(2)	2.269(15)	Au(3)–P(2)	2.229(9)
C(1)–P(1)	1.85(2)	C(1)–P(2)	1.80(2)
C(12)–N(11)	1.39(3)	C(12)–C(13)	1.44(5)
C(13)–C(14)	1.32(4)	C(14)–C(15)	1.34(4)
C(15)–C(16)	1.43(5)	C(16)–N(11)	1.27(3)
C(21)–P(1)	1.81(2)	C(31)–P(1)	1.81(2)
C(41)–P(2)	1.79(2)	C(51)–P(2)	1.80(2)
C(62)–F(62)	1.25(2)	C(63)–F(63)	1.37(4)
C(64)–F(64)	1.35(3)	C(65)–F(65)	1.35(3)
C(66)–F(66)	1.28(3)	C(72)–F(72)	1.30(3)
C(73)–F(73)	1.30(4)	C(74)–F(74)	1.30(3)
C(75)–F(75)	1.26(3)	C(76)–F(76)	1.32(2)

C(1)–Au(1)–N(11)	174.7(10)	Cl(1)–Au(2)–P(1)	91.2(3)
Cl(1)–Au(2)–C(61)	87.9(7)	P(1)–Au(2)–C(61)	179.0(6)
Cl(1)–Au(2)–C(71)	177.5(7)	P(1)–Au(2)–C(71)	89.0(7)
C(61)–Au(2)–C(71)	91.9(9)	Cl(2)–Au(3)–P(2)	176.6(4)
Au(2)–P(1)–C(1)	104.9(9)	Au(2)–P(1)–C(21)	108.1(6)
C(1)–P(1)–C(21)	114.5(9)	Au(2)–P(1)–C(31)	115.8(7)
C(1)–P(1)–C(31)	110.6(9)	C(21)–P(1)–C(31)	103.4(10)
Au(3)–P(2)–C(1)	117.3(9)	Au(3)–P(2)–C(41)	112.4(8)
C(1)–P(2)–C(41)	106.8(9)	Au(3)–P(2)–C(51)	112.0(7)
C(1)–P(2)–C(51)	103.4(11)	C(41)–P(2)–C(51)	103.7(9)
Au(1)–C(1)–P(1)	108.1(10)	Au(1)–C(1)–P(2)	114.2(9)
P(1)–C(1)–P(2)	118.8(15)		

$J(\mathrm{HP_A}) + J(\mathrm{HP_B})$ 21.6 Hz] and 2.5 p.p.m. (s, 3 H, CH_3); ^{31}P, δ 27.8 [d of an AB system, P–Au^{I}, J(AB) 27.6 Hz] and 31.9 p.p.m. (m, P–Au^{III}); ^{19}F, δ −122.5 to −124.0 (m, $F^{2,6}$), −158.0 [t, F^4, $J(F^4F^3)$ 20.0], −158.3 [t, F^4, $J(F^4F^3)$ 20.0 Hz], and −161.0 to −162.4 p.p.m. (m, $F^{3,5}$). I.r. spectrum: 612m [ν(Au–C)] and 330m, br cm^{-1} [ν(Au–Cl)].

Crystal Structure Determination for Complex (**7**).—*Crystal data.* $C_{42}H_{26}Au_3Cl_2F_{10}NP_2{\cdot}xCH_2Cl_2$, triclinic, space group $P\bar{1}$, $a = 11.664(5)$, $b = 14.790(6)$, $c = 18.334(6)$ Å, $\alpha = 111.30(4)$, $\beta = 94.18(4)$, $\gamma = 107.64(4)°$, $U = 2\,748$ Å^3, Mo-K_α radiation ($\lambda = 0.710\,69$ Å), $Z = 2$, colourless block *ca.* 0.5 mm in all dimensions, $\mu = 8.3$ mm^{-1}, $F(000)$ *ca.* 1 436.

Data collection and processing. Stoe-Siemens four-circle diffractometer, monochromated Mo-K_α radiation, 9 252 profile-fitted intensities[15] ($2\theta_{max.}$ 45°), 7 139 unique, 4 627 > $4\sigma(F)$ used for all calculations. Absorption correction based on ψ scans; transmission 0.26—0.59. Crystal decay (based on check reflections) *ca.* 12%; appropriate scaling.

Structure solution and refinement. Gold atoms located from Patterson function, other non-H atoms from difference syntheses. Least-squares refinement on F to R 0.075, R' 0.073 [Au, Cl, P, and F anisotropic; phenyl rings as rigid groups with C–C 1.395, C–H 0.96 Å, all angles 120°, $U(\mathrm{H}) = 1.2U(\mathrm{C})$; other H using riding model with $U(\mathrm{H}) = 1.2U(\mathrm{C})$; two isotropic CH_2Cl_2 molecules with occupancy 0.5; weighting scheme $w^{-1} = \sigma^2(F) + 0.000\,85\,F^2$]. Program system SHELXTL.[16]

Final atomic co-ordinates and derived parameters are given in Tables 1 and 2.

Acknowledgements

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