Crystal Structure of (Pentafluorophenyl)(triphenylphosphine)gold(I)

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The crystal structure of the title compound has been determined by single-crystal *X*-ray diffraction. Crystals are monoclinic, space group $P2_1/c$ with $Z = 4$ in a unit cell of dimensions: $a = 834{\cdot}0(3)$, $b = 1199{\cdot}1(4)$, $c = 2214{\cdot}6(7)$ pm, $\beta = 98{\cdot}33°$. Refinement of 1834 three-dimensional diffractometer data led to R 0·055. The gold atom is linearly co-ordinated, with C–Au–P 178°, Au–P 227(1) and Au–C 207(2) pm. The phenyl and pentafluorophenyl rings are planar and their bond distances and angles have the expected values. The structure is compared with other bisco-ordinated gold compounds containing Au–C or Au–P bonds.

MUCH interest has been shown in the chemistry of transition-metal complexes containing perfluoro-ligands.[1] It is known that the complex $Au^{III}(PPh_3)(C_6F_5)_2Cl$ can be reduced with hydrazine to $Au^{I}(PPh_3)(C_6F_5)$. The molecular structure of the Au^{III} complex has been reported [2] and in order to complement that work we have determined the crystal structure of $Au^{I}(PPh_3)(C_6F_5)$.

EXPERIMENTAL

Crystals are developed with the following forms: pinacoid {001} and prisms {110} and {011}, and elongated along *a*.

Crystal Data.—$C_{24}H_{15}AuF_5P$, $M = 626{\cdot}3$, Monoclinic $a = 834{\cdot}0(3)$, $b = 1199{\cdot}1(4)$, $c = 2214{\cdot}6(7)$ pm, $\beta = 98{\cdot}33°$, $U = 2191 \times 10^6$ pm^3, $D_m = 1{\cdot}91(1) \times 10^3$ kg m^{-3}, $Z = 4$, $D_c = 1{\cdot}90 \times 10^3$ kg m^{-3}. Space group $P2_1/c$ (C^5_{2h}) from systematic absences: $h0l$ for $l = 2n + 1$, $0k0$ for $k = 2n + 1$. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) = 78·3 cm^{-1}.

TABLE 1

Fractional co-ordinates and thermal motion parameters * derived from the least-squares refinement, with estimated standard deviations in parentheses

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Au(1)	314(1)	2623(1)	833(0)	680(7)	459(7)	851(0)	28(5)	78(5)	120(7)
P(2)	1765(7)	4081(4)	1283(4)	597(34)	430(29)	657(49)	35(25)	133(27)	47(27)

Atom	x	y	z	U	Atom	x	y	z	U
C(3)	339(2)	366(2)	186(1)	53(5)	C(18)	−160(3)	635(2)	221(1)	89(7)
C(4)	447(3)	281(2)	170(1)	89(7)	C(19)	−141(3)	524(2)	236(1)	99(8)
C(5)	579(3)	247(2)	215(1)	100(8)	C(20)	−43(3)	453(2)	207(1)	84(7)
C(6)	598(3)	294(2)	273(1)	100(8)	C(21)	−108(3)	132(2)	44(1)	63(6)
C(7)	492(3)	378(2)	290(1)	99(8)	C(22)	−185(3)	59(2)	76(1)	73(6)
C(8)	363(3)	415(2)	246(1)	77(6)	C(23)	−282(3)	−29(2)	50(1)	95(8)
C(9)	276(2)	495(2)	78(1)	56(5)	C(24)	−300(3)	−38(2)	−10(1)	99(8)
C(10)	226(3)	489(2)	15(1)	78(7)	C(25)	−228(3)	29(2)	−45(1)	73(6)
C(11)	296(3)	565(2)	−26(1)	89(7)	C(26)	−138(3)	115(2)	−19(1)	71(6)
C(12)	398(3)	639(2)	−4(1)	88(7)	F(27)	−166(2)	63(1)	137(1)	112(3)
C(13)	459(3)	647(2)	59(1)	81(7)	F(28)	−345(2)	−104(2)	83(1)	142(6)
C(14)	396(3)	573(2)	100(1)	73(6)	F(29)	−390(2)	−129(1)	−38(1)	132(6)
C(15)	43(2)	503(2)	167(1)	64(6)	F(30)	−239(2)	19(2)	−108(1)	129(6)
C(16)	22(3)	614(2)	149(1)	68(6)	F(31)	−61(2)	184(1)	−55(1)	116(5)
C(17)	−83(3)	681(2)	177(1)	91(8)					

* The Debye–Waller factor is defined as $T = \exp[-2\pi^2\sum_i\sum_j a_i{}^*a_j{}^*h_ih_jU_{ij}]$ for gold and phosphorus atoms and $T = \exp[-8\pi^2U \sin^2\theta/\lambda^2]$ for the carbon and fluorine atoms. The values for U are in Å^2. Fractional co-ordinates and U_{ij} for Au and P have been multiplied by 10^4 and fractional co-ordinates and U by 10^3 for C and F.

Space group and preliminary cell constants were determined from Weissenberg oscillation and precession photographs. The refined cell constants and errors were determined by use of the cell refinement program described in ref. 3.

Intensity Measurements.—Three-dimensional *X*-ray diffraction data from a small single crystal (0·23 × 0·10 × 0·10 mm) were collected on a computer-controlled [3] Stoe four-circle diffractometer using Mo-K_α radiation [graphite monochromator (002)]. A coupled θ—2θ step scan with $\Delta 2\theta = 0{\cdot}04°$, a counting time of 4 s per step and a peak width of 1·4° were used. In the range $2\theta = 3$—$45°$, 3390 observations covering one quarter of reciprocal space ($+h$, $+k$, $\pm l$) were collected. The 3390 data reduced to 3020 symmetry independent observations of which 1834 were defined as observed intensities [having $I \geqslant 3\sigma(I)$], and of these 160 had been observed more than once. The data were corrected for Lorentz and polarisation effects but not for absorption or extinction.

Structure Solution and Refinement.—A three-dimensional Patterson synthesis [4] was carried out using unsharpened data. The vector distribution in the map produced was consistent with the gold atom at (i) $x = 0{\cdot}0313$, $y = 0{\cdot}2500$, $z = 0{\cdot}0844$ or (ii) $x = 0{\cdot}0313$, $y = 0{\cdot}7500$, $z = 0{\cdot}3340$ and the phosphorus atom at $x_{Au} + 0{\cdot}1407$, $y_{Au} + 0{\cdot}1350$, $z_{Au} + 0{\cdot}0436$. Two Fourier syntheses [4] obtained by use of observed data phased with the gold and phosphorus atoms corresponding to solutions (i) and (ii) respectively produced

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[1] R. S. Nyholm, *Quart. Rev.*, 1970, **24**, 1.

[2] R. W. Baker and P. Pauling, *Chem. Comm.*, 1969, 745.

[3] W. R. Busing, R. D. Ellison, H. A. Levy, S. P. King, and R. T. Roseberry, 'The Oak Ridge Computer Controlled *X*-Ray Diffractometer,' U.S.A.E.C. Publication ORNL 4143, 1968.

[4] A Fourier Program for LUNA, by J. Dollimore. University of London Institute of Computer Science Circular No. 1.2.

a satisfactory trial structure for solution (i) only. The positions of all non-hydrogen atoms were located from the Fourier map. Refinement was by full-matrix least-squares[5] with anisotropic thermal parameters for gold and phosphorus and isotropic thermal parameters for carbon and fluorine. Successive cycles of refinement were carried out until all parameter shifts were $<0{\cdot}1\sigma$. The function minimised was $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1$ for all reflection data. Atomic scattering factors for neutral gold, phosphorus, carbon, and fluorine were taken from ref. 6. The final R was 0·055. A final difference electron density synthesis confirmed that the structure was correct. All computational work was carried out on the University of London ATLAS computer and University College IBM 360 computer. Computer programs used are listed in refs. 4 and 5.

The results of this analysis are given in the Tables 1—3. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20470 (11 pp., 1 microfiche). For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

DISCUSSION

Description of the Molecular Structure.—The gold atom in this molecule is linearly co-ordinated with the angle C–Au–P 178°(1). Comparison of this structure with other compounds of gold in which the gold atom is co-ordinated to two ligands, one of which is carbon or phosphorus, suggests that two classes of compounds exist, (*a*) linear and (*b*) slightly bent. The present structure falls into the first class and another example is

TABLE 2

Interatomic distances (pm) and angles (°), with estimated standard deviations are in parentheses

(*a*) Distances

Au(1)–P(2)	227(1)	C(15)–C(16)	139(3)
Au(1)–C(21)	207(2)	C(15)–C(20)	137(3)
P(2)–C(3)	180(2)	C(16)–C(17)	140(3)
P(2)–C(9)	181(2)	C(17)–C(18)	135(4)
P(2)–C(15)	188(2)	C(18)–C(19)	138(4)
C(3)–C(4)	144(3)	C(19)–C(20)	139(4)
C(3)–C(8)	144(3)	C(21)–C(22)	134(3)
C(4)–C(5)	142(4)	C(21)–C(26)	140(3)
C(5)–C(6)	139(4)	C(22)–C(23)	140(4)
C(6)–C(7)	143(4)	C(22)–F(27)	134(3)
C(7)–C(8)	141(4)	C(23)–C(24)	132(4)
C(9)–C(10)	142(3)	C(23)–F(28)	133(3)
C(9)–C(14)	139(3)	C(24)–C(25)	131(4)
C(10)–C(11)	146(3)	C(24)–F(29)	141(3)
C(11)–C(12)	128(4)	C(25)–C(26)	135(3)
C(12)–C(13)	142(4)	C(25)–F(30)	139(3)
C(13)–C(14)	143(3)	C(26)–F(31)	137(3)

(*b*) Angles

P(2)–Au(1)–C(21)	178(1)	C(16)–C(15)–C(20)	123(2)
Au(1)–P(2)–C(3)	113(1)	C(15)–C(16)–C(17)	119(2)
Au(1)–P(2)–C(9)	116(1)	C(16)–C(17)–C(18)	119(2)
Au(1)–P(2)–C(15)	111(1)	C(17)–C(18)–C(19)	122(2)
C(3)–P(2)–C(9)	103(1)	C(18)–C(19)–C(20)	122(2)
C(3)–P(2)–C(15)	106(1)	C(19)–C(20)–C(15)	116(2)
C(9)–P(2)–C(15)	106(1)	Au(1)–C(21)–C(26)	122(2)
P(2)–C(3)–C(4)	117(2)	Au(1)–C(21)–C(22)	124(2)
P(2)–C(3)–C(8)	122(2)	C(22)–C(21)–C(26)	114(2)
C(4)–C(3)–C(8)	121(2)	C(21)–C(22)–C(23)	124(2)
C(3)–C(4)–C(5)	118(2)	C(21)–C(22)–F(27)	120(2)
C(4)–C(5)–C(6)	120(2)	C(23)–C(22)–F(27)	115(2)
C(5)–C(6)–C(7)	122(2)	C(22)–C(23)–C(24)	117(3)
C(6)–C(7)–C(8)	119(2)	C(22)–C(23)–F(28)	122(2)
C(7)–C(8)–C(3)	120(2)	C(24)–C(23)–F(28)	121(3)
P(2)–C(9)–C(14)	123(2)	C(23)–C(24)–C(25)	123(3)
P(2)–C(9)–C(10)	119(2)	C(23)–C(24)–F(29)	118(2)
C(14)–C(9)–C(10)	118(2)	C(25)–C(24)–F(29)	119(2)
C(9)–C(10)–C(11)	120(2)	C(24)–C(25)–C(26)	120(2)
C(10)–C(11)–C(12)	120(2)	C(24)–C(25)–F(30)	124(2)
C(11)–C(12)–C(13)	124(2)	C(26)–C(25)–F(30)	117(2)
C(12)–C(13)–C(14)	118(2)	C(25)–C(26)–C(21)	123(2)
C(13)–C(14)–C(9)	121(2)	C(25)–C(26)–F(31)	120(2)
P(2)–C(15)–C(16)	121(2)	C(21)–C(26)–F(31)	118(2)
P(2)–C(15)–C(20)	116(2)		

TABLE 2(*a*)

Intramolecular contacts <350 pm

Au(1) ··· C(3)	341	C(11) ··· C(13)	238
Au(1) ··· C(9)	347	C(11) ··· C(14)	280
Au(1) ··· C(15)	342	C(12) ··· C(14)	244
Au(1) ··· C(22)	303	C(14) ··· C(16)	347
Au(1) ··· C(26)	305	C(15) ··· C(17)	241
Au(1) ··· F(27)	322	C(15) ··· C(18)	272
Au(1) ··· F(31)	318	C(15) ··· C(19)	234
P(2) ··· C(4)	277	C(16) ··· C(18)	236
P(2) ··· C(8)	284	C(16) ··· C(19)	274
P(2) ··· C(10)	279	C(16) ··· C(20)	243
P(2) ··· C(14)	282	C(17) ··· C(19)	238
P(2) ··· C(16)	285	C(17) ··· C(20)	282
P(2) ··· C(20)	277	C(18) ··· C(20)	242
C(3) ··· C(5)	246	C(21) ··· C(23)	242
C(3) ··· C(6)	281	C(21) ··· C(24)	275
C(3) ··· C(7)	247	C(21) ··· C(25)	241
C(3) ··· C(9)	283	C(21) ··· F(27)	233
C(3) ··· C(14)	321	C(21) ··· F(31)	237
C(3) ··· C(15)	295	C(22) ··· C(24)	231
C(3) ··· C(20)	345	C(22) ··· C(25)	266
C(4) ··· C(6)	244	C(22) ··· C(26)	229
C(4) ··· C(7)	287	C(22) ··· F(28)	239
C(4) ··· C(8)	250	C(23) ··· C(25)	231
C(4) ··· C(9)	346	C(23) ··· C(26)	269
C(5) ··· C(7)	247	C(23) ··· F(27)	231
C(5) ··· C(8)	285	C(23) ··· F(29)	234
C(6) ··· C(8)	244	C(24) ··· C(26)	230
C(8) ··· C(15)	316	C(24) ··· F(28)	230
C(8) ··· C(20)	340	C(24) ··· F(30)	238
C(9) ··· C(11)	249	C(25) ··· F(29)	235
C(9) ··· C(12)	280	C(25) ··· F(31)	235
C(9) ··· C(13)	245	C(26) ··· F(30)	233
C(9) ··· C(15)	295	F(27) ··· F(28)	268
C(9) ··· C(16)	315	F(28) ··· F(29)	266
C(10) ··· C(12)	237	F(29) ··· F(30)	277
C(10) ··· C(13)	279	F(30) ··· F(31)	265
C(10) ··· C(14)	241		

σ(Au ··· C) 2, σ(Au ··· F) 2, σ(P ··· C) 2, σ(C ··· C) 3—4, σ(C ··· F) 3, and σ (F ··· F) 2—3 pm.

TABLE 2(*b*)

Intermolecular contacts <360 pm

Au(1) ··· C(11$^{\mathrm{I}}$)	351	C(17) ··· F(31$^{\mathrm{I}}$)	351
C(4) ··· F(29$^{\mathrm{II}}$)	343	C(19) ··· F(27$^{\mathrm{IV}}$)	355
C(6) ··· F(30$^{\mathrm{III}}$)	358	C(21) ··· C(25$^{\mathrm{II}}$)	340
C(7) ··· F(28$^{\mathrm{IV}}$)	324	C(21) ··· F(30$^{\mathrm{II}}$)	353
C(7) ··· F(30$^{\mathrm{III}}$)	319	C(23) ··· C(24$^{\mathrm{VII}}$)	356
C(10) ··· C(12$^{\mathrm{V}}$)	353	C(23) ··· F(29$^{\mathrm{VII}}$)	331
C(12) ··· C(11$^{\mathrm{V}}$)	353	C(23) ··· F(31$^{\mathrm{II}}$)	340
C(12) ··· F(29$^{\mathrm{VI}}$)	344	C(24) ··· C(24$^{\mathrm{VII}}$)	356
C(13) ··· C(11$^{\mathrm{V}}$)	341	C(24) ··· F(28$^{\mathrm{VII}}$)	359
C(13) ··· F(28$^{\mathrm{VI}}$)	340	C(24) ··· F(29$^{\mathrm{VII}}$)	355
C(16) ··· F(31$^{\mathrm{I}}$)	324	C(24) ··· F(31$^{\mathrm{II}}$)	360

σ(Au ··· C) 3, σ(C ··· C) 3—4, and σ(C ··· F) 2—3 pm.

Roman numerals as superscripts denote the following transformations relative to the reference molecule at x, y, z:

I $-x, 1 - y, -z$
II $-x, -y, -z$
III $1 + x, \frac{1}{2} - y, \frac{1}{2} + z$
IV $-x, \frac{1}{2} + y, \frac{1}{2} - z$
V $1 - x, 1 - y, -z$
VI $1 + x, 1 + y, z$
VII $-1 - x, -y, -z$

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[5] A Crystallographic SFLS Program in AA by G. Shearing, University of Manchester, 1965.

[6] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 105.

$Pr^iNH_2AuC⋮CPh$ in which the N–Au–C angle is 177°.[7] Examples of compounds falling into the second class contain metal–gold bonds M–Au, with the M–Au–P angles differing significantly from 180°. In $(\pi\text{-}C_5H_5)W(CO)_3Au(PPh_3)$,[8] W–Au–P is 173·8°, in $(Ph_3P)Au\text{–}Mn(CO)_4P(OPh)_3$,[9] P–Au–Mn is 165·5°, and in $(Ph_3P)Au\text{–}Mn(CO)_5$ [10] the angle P–Au–Mn is 168°. The departure from 180° may be due to the metal–metal bonding in these compounds.

The Au–P bond length [227(1)pm] is similar to Au–P bond lengths found in other bis-co-ordinated gold compounds [225(1),[8] 221 pm [10]] but somewhat shorter than the other reported values [233(1) [9] and 232(3) pm [2]]. The Au–C bond length [207(2) pm] may be compared with the reported values in Au^I–C [212(14) pm [11]] and Au^{III}–C compounds [212(9),[2] 218(10),[2] and 205(8) pm [12]].

TABLE 3

Equations of best mean planes in the form $lX + mY + nZ = P$ where X, Y, and Z refer to an orthonormalised co-ordinate system with X parallel to crystallographic a axis, Y in the plane ab and perpendicular to X, and Z perpendicular to the plane ab and completes a right-handed set of axes XYZ. Deviations (pm) of atoms from the plane are given in square brackets

Plane (1):
C(3)—(8) $0{\cdot}636X + 0{\cdot}706Y - 0{\cdot}311Z = 7{\cdot}156$
[C(3) 0, C(4) −1, C(5) 1, C(6) 0, C(7) −1, C(8) 1]

Plane (2):
C(9)—(14) $0{\cdot}747X - 0{\cdot}657Y - 0{\cdot}096Z = 7{\cdot}384$
[C(9) −2, C(10) 0, C(11) 2, C(12) −3, C(13) 1, C(14) 2]

Plane (3):
C(15)—(20) $0{\cdot}662X + 0{\cdot}237Y + 0{\cdot}711Z = 8{\cdot}095$
C(15) 3, C(16) −1, C(17) −2, C(18) 2, C(19) 1, C(20) −3

Plane (4):
C(21)—(26), F(27)—(31) $0{\cdot}805X - 0{\cdot}587Y + 0{\cdot}082Z = 1{\cdot}926$
[C(21) 0, C(22) −3, C(23) −4, C(24) −5, C(25) −1, C(26) −3, F(27) 3, F(28) 5, F(29) 1, F(30) 4, F(31) 3]

The angles between the normals to the phenyl rings on the phosphorus atom are: ring[C(3)]–ring[C(9)] 87, ring[C(9)]–ring[C(15)] 74, and ring[C(15)]–ring[C(3)] 68°. All other distances and angles found in the molecule have the expected values within experimental error. The temperature factors for the fluorine atoms are similar to those previously reported.[13,14]

The atomic numbering is shown in Figure 1 and the molecular packing in Figure 2.

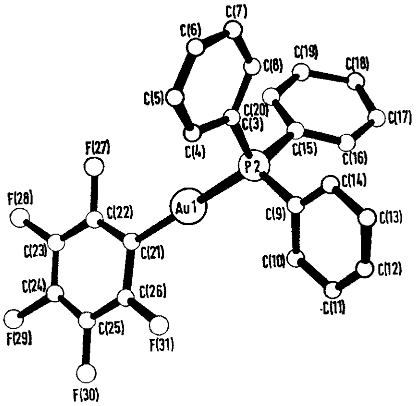

FIGURE 1 Perspective drawing and atomic numbering

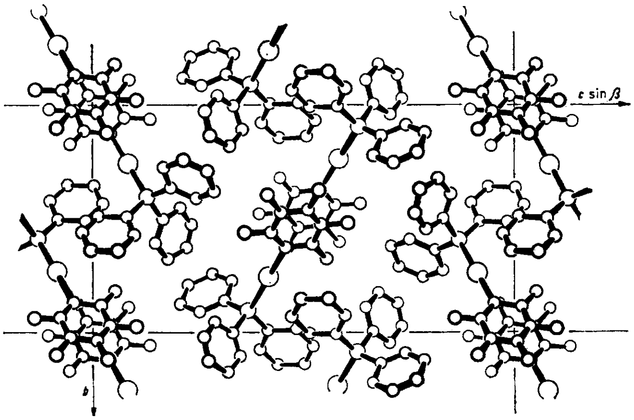

FIGURE 2 Molecular packing projected on (100)

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