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Tris(pentafluorophenyl)[2-(diphenylphosphino)-thiophenol-κ*P*]gold(III) dichloromethane solvate

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The title compound, $[Au(C_6F_5)_3(PPh_2C_6H_4SH)]\cdot CH_2Cl_2$, presents a square-planar geometry. The long Au—P bond, 2.3884 (16) Å, is consistent with an appreciable *trans* influence of the pentafluorophenyl group. The intramolecular Au···S contact is 3.594 (2) Å.

Key indicators

Single-crystal X-ray study
T = 143 K
Mean σ(C–C) = 0.008 Å
Disorder in solvent or counterion
R factor = 0.032
wR factor = 0.072
Data-to-parameter ratio = 12.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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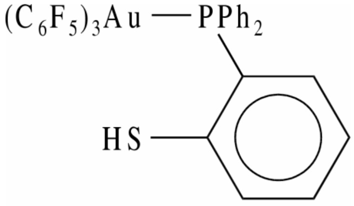
Comment

In recent years, there has been considerable interest in thiolate–gold chemistry; most of the complexes studied have also contained phosphine ligands (Terroba *et al.*, 1998; Cerrada *et al.*, 1995; Gimeno *et al.*, 1994; Yip *et al.*, 1994; Davila *et al.*, 1993; Nakamoto *et al.*, 1993). Another way of combining the aspects of both thiolate and phosphine chemistry is to work with bidentate ligands containing both S and P functions, as are found in phosphinethiols. The selective coordination of either phosphorus or sulfur to different metal centres can, in principle, allow the combination of disparate metals in the same molecule. Such heteropolynuclear compounds are of interest because of their possible application in catalysis (Simpson & Cole-Hamilton, 1996; Stephan, 1989).



(I)

The reaction of the ligand 2-(diphenylphosphino)thiophenol (Block *et al.*, 1989) with $[Au(C_6F_5)_3(tht)]$ (Usón *et al.*, 1982) proceeds with substitution of tetrahydrothiophene (tht), a labile ligand in gold chemistry, by the phosphine function of the ligand. The product obtained is the title compound, $[Au(C_6F_5)_3(PPh_2C_6H_4SH)]$, (I), still containing the unchanged thiol group, which is a potential site for further reactions.

The structure of (I) is shown in Fig. 1. The gold centre displays square-planar geometry, with bond angles (Table 1) close to the ideal values. The mean deviation of gold and its four immediate donors from their mean plane is 0.09 Å, whereby the atoms P and C21 lie on one side of the plane and C11 and C31 on the other. The Au—P distance, 2.3884 (16) Å, is amongst the longest so far observed in gold(III) complexes. This lengthening can reasonably be attributed to the *trans* influence of the pentafluorophenyl group. A search of the Cambridge Structural Database (Version of October 1998; Allen & Kennard, 1993) indeed revealed that the longest

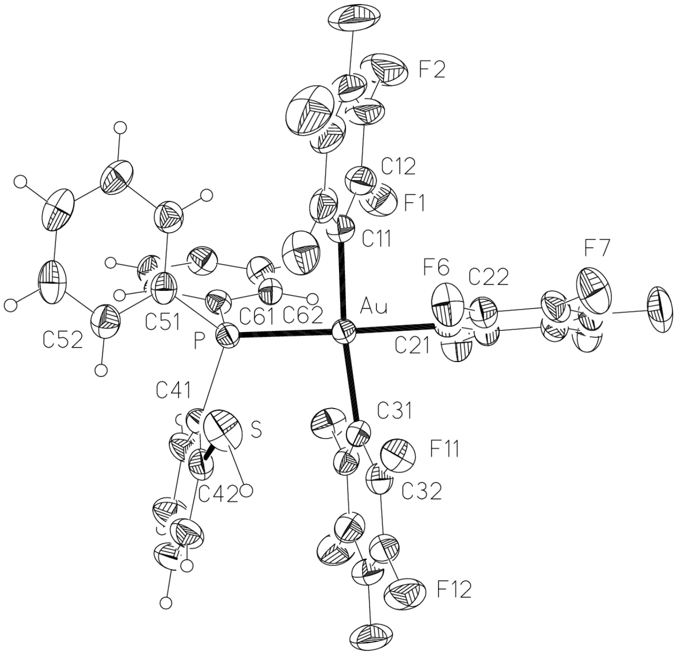


Figure 1
The molecule of the title compound in the crystal (solvent omitted). Ellipsoids represent 50% probability levels.

Au^{III}—P bonds are formed *trans* to σ-carbon ligands: *e.g. cis*-[$Au(CH_3)_2(PPh_3)(OPh)$] 2.402 (4) Å (Sone *et al.*, 1991); *cis*-[$Au(CH_3)_2\{Ph_2P(O)CH_2PPh_2\}Cl$] 2.389 (2) Å (Paul & Schmidbaur, 1996); [$Au(2\text{-}PhNNC_6H_4)\{3,4,5\text{-}(CH_3O)_3\text{-}C_6H_2\text{-}COCH_2\}(PPh_3)Cl$] 2.386 and 2.390 (2) Å (Vicente *et al.*, 1993). Typical examples without such ligands are [$Au(C_6F_5)(S_2C_6H_4)PPh_3$] 2.340 (1) Å (Cerrada *et al.*, 1995); [$AuCl_3(PPh_3)$] 2.335 (4) Å (Bandoli *et al.*, 1973); [$AuMe_3(PPh_3)$] 2.350 (6) and 2.347 (6) Å (Stein *et al.*, 1981); [$Au(SC_6H_4PPh_2)_2$]BPh_4 2.325 (4) and 2.332 (4) Å (Dilworth *et al.*, 1994). The Au—C bond lengths, 2.056 (5)–2.073 (5) Å, are similar to those of other tris(pentafluorophenyl)gold(III) complexes: [$Au(C_6F_5)_3(S_2C{-}PEt_3)$] 2.037 (3) and 2.076 (4) Å (Usón *et al.*, 1987); [$(\mu\text{-}S_2C{-}PEt_3)\{Au(C_6F_5)_3\}_2$] 2.048 (16) and 2.090 (13) Å (Usón *et al.*, 1987); $NBu_4[\{Au(C_6F_5)_3PPh_2CHPh_2\}_2Au]$ 2.057 (8) and 2.080 (8) Å (Fernández *et al.*, 1995). The shortest Au—C distance (although the differences are not great) corresponds to the pentafluorophenyl group *trans* to phosphorus.

The intramolecular Au···S contact is 3.594 (2) Å, which represents, at best, a very weak interaction; such axial contacts are typical of Au^{III} complexes.

Experimental

The ligand $HSC_6H_4PPh_2$ (0.029 g, 0.1 mmol) was added to a dichloromethane solution (20 ml) of [$Au(C_6F_5)_3(tht)$] (0.079 g, 0.1 mmol). After stirring for 3 h, the solution was filtered through diatomaceous earth and concentrated *in vacuo*; addition of hexane precipitated the product as a white solid (yield: 47%). ^1H NMR: δ(SH) 3.74(*s*). $^{31P}\{^1H\}$ NMR: δ 17.7 (*s*). ^{19}F NMR: δ -118.0 (*m*, 4F, F_o), −121.6 (*m*, 2F, F_o), −157.1 (*t*, $^3JF_pF_m$ = 19.7 Hz, 1F, F_p), −157.3 (*t*, $^3JF_pF_m$ $^3JF_pF_m$ = 19.9 Hz, 2F, F_p), −161.1 (*m*, 4F, F_m), −161.3 (*m*, 2F, F_m). Crystals of the complex were obtained by slow diffusion of hexane into a dichloromethane solution.

Crystal data

[$Au(C_6F_5)_3(C_{18}H_{15}PS)$]·$CH_2Cl_2$
M_r = 1077.40
Triclinic, $P\bar{1}$
a = 10.057 (4) Å
b = 12.888 (5) Å
c = 15.236 (7) Å
α = 100.64 (3)°
β = 94.41 (3)°
γ = 106.84 (3)°
V = 1839.7 (13) $Å^3$
Z = 2
D_x = 1.945 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 52 reflections
θ = 10–11.5°
μ = 4.35 mm^{-1}
T = 143 (2) K
Tablet, colourless
0.40 × 0.40 × 0.12 mm

Data collection

Stoe Stadi-4 diffractometer
ω/θ scans
Absorption correction: ψ scan (*XEMP*; Siemens, 1994)
T_{min} = 0.527, T_{max} = 0.960
8252 measured reflections
6462 independent reflections
5909 reflections with $I > 2\sigma(I)$
R_{int} = 0.029
θ_{max} = 25.0°
$h = -11 \rightarrow 2$
$k = -15 \rightarrow 15$
$l = -18 \rightarrow 18$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.072
S = 1.05
6462 reflections
525 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0287P)^2 + 2.7433P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.022
$\Delta\rho_{max}$ = 0.87 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.70 e $Å^{-3}$

Table 1
Selected geometric parameters (Å, °).

Au—C21	2.057 (5)	P—C51	1.810 (5)
Au—C11	2.060 (5)	P—C61	1.816 (5)
Au—C31	2.074 (4)	P—C41	1.816 (5)
Au—P	2.3884 (16)	S—C42	1.740 (5)
C21—Au—C11	86.92 (18)	C51—P—C61	102.5 (2)
C21—Au—C31	86.49 (17)	C51—P—C41	106.9 (2)
C11—Au—C31	172.17 (18)	C61—P—C41	107.0 (2)
C21—Au—P	173.61 (13)	C51—P—Au	119.59 (16)
C11—Au—P	93.14 (14)	C61—P—Au	110.32 (15)
C31—Au—P	93.88 (13)	C41—P—Au	109.70 (16)

The dichloromethane molecule is disordered over two sites with occupation factors 0.727 (9) and 0.273 (9). The minor Cl component and both C components were refined isotropically. The H atom of the thiol group was tentatively identified as a peak of 0.4 e $Å^{-3}$ with acceptable geometry at sulfur, and was refined with a distance restraint (*DFIX*) of S—H = 1.33 (2) Å and fixed *U*. It makes, however, a short contact of 2.35 Å to C54 of a neighbouring molecule at $1-x, 1-y, 1-z$. Clearly this H-atom site should be interpreted with caution. We have previously failed to locate the H atom of SH groups in some gold complexes, even with apparently good data (Vicente *et al.*, 1994). Other H atoms were included using a riding model. To improve stability of refinement, an extensive system of restraints to light-atom displacement parameter components and local ring symmetry was employed. Details are given in the final instruction file, which is included in the deposited material.

Data collection: *DIF*4 (Stoe & Cie, 1992); cell refinement: *DIF*4; data reduction: *REDU*4 (Stoe & Cie, 1992); program(s) used to solve

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structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL*97.

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