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Key indicators

Single-crystal X-ray study

T = 173 K

Mean $\sigma(C-C)$ = 0.009 Å

R factor = 0.037

wR factor = 0.069

Data-to-parameter ratio = 18.0

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.**cis-Bis[diphenyl(phenylsulfanylmethyl)diphenylphosphine- κP]bis(pentafluorophenyl)gold(III) perchlorate chloroform solvate**

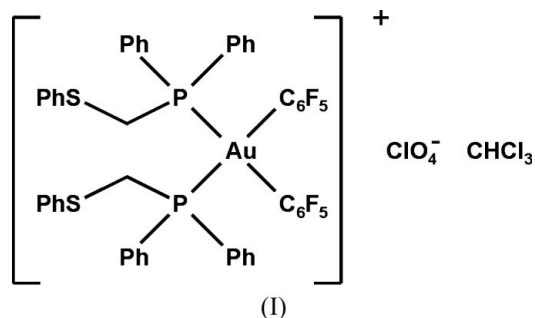
The title compound, $[\text{Au}(\text{C}_6\text{F}_5)_2(\text{C}_{19}\text{H}_{17}\text{PS})_2]\text{ClO}_4 \cdot \text{CHCl}_3$, involves a planar Au^{III} centre with $\text{Au}-\text{P} = 2.3818$ (14) and 2.3990 (15) Å, and $\text{Au}-\text{C} = 2.079$ (5) and 2.083 (5) Å. Ligand S atoms are not involved in coordination at gold. The $\text{P}-\text{C}-\text{S}-\text{C}$ torsion angles are very approximately antiperiplanar. The anion is well resolved and acts as an acceptor for $\text{C}-\text{H} \cdots \text{O}$ interactions.

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Comment

The combination of P- and S-donor functionalities at a common metal centre may promote stability or reactivity for a given substrate. The use of a bidentate ligand such as diphenyl(phenylsulfanylmethyl)phosphine, $\text{PhSCH}_2\text{PPh}_2$ (henceforth DPSP) (Paul, 1996; Garrou, 1981), thus allows, as a first step, the selective coordination of phosphorus to gold(I), leaving the S atom as a potentially coordinative heteroatom (Fernández *et al.*, 2000). We have reported the synthesis and structure of three of its gold(I) complexes, namely bis- $\{\mu_2$ -diphenyl(phenylsulfanylmethyl)diphenylphosphine-*P,S*\}digold(I) bis(trifluoromethanesulfonate), $[\mu_2$ -(DPSP) $_2\text{Au}_2](\text{CF}_3\text{SO}_3)_2$ (Fernández *et al.*, 1998), bis{diphenyl(phenylsulfanylmethyl)diphenylphosphine-*P*}gold(I) perchlorate, $[(\text{DPSP})_2\text{Au}]\text{ClO}_4$ (Fernández *et al.*, 2000), and chloro{diphenyl(phenylsulfanylmethyl)phosphine-*P*}gold(I), $(\text{DPSP})\text{AuCl}$ (Crespo *et al.*, 2000). We report here the structure of the title compound, the gold(III) derivative $[(\text{DPSP})_2\text{Au}(\text{C}_6\text{F}_5)_2]\text{ClO}_4 \cdot \text{CHCl}_3$, which can be employed as precursor for the synthesis of homo- and heteropolynuclear gold complexes by selective coordination of further metals by the thioether functions.



The structure is shown in Fig. 1. The gold(III) centre is to a good approximation square-planar coordinated, although the donor atoms alternate above and below the mean plane [P1 by 0.134 (2), P2 by 0.138 (2), C71 by 0.177 (2) and C81 by 0.178 (3) Å]. The S atoms are not coordinated to gold, with $\text{Au} \cdots \text{S1} = 4.297$ (2) Å and $\text{Au} \cdots \text{S2} = 3.320$ (2) Å, as was also observed for two of the three structures mentioned above. The

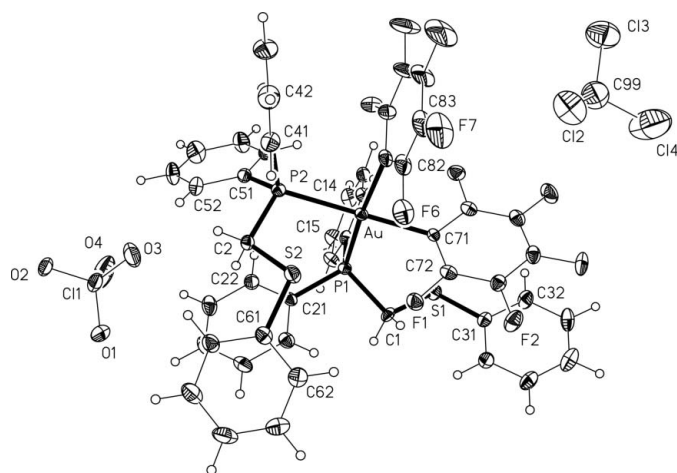


Figure 1
The asymmetric unit of the title compound. Displacement ellipsoids represent 30% probability levels. The rings C11–C16 and C41–C46 are viewed edge on.

Au–P bond lengths are rather long, whereas the Au–C bond lengths are normal; a search of the Cambridge Database (Allen, 2002; Version 5.27) revealed 17 examples of the fragment *cis*-Au(C₆F₅)₂(phosphine)₂, with Au–P = 2.322–2.394 Å (average 2.356 Å) and Au–C = 2.033–2.154 Å (average 2.081 Å). Bond lengths and angles at sulfur are closely similar to values in the structures mentioned above.

The conformations associated with the thiophenyl groups are defined by torsion angles Au–P–C–S, P–C–S–C and C–S–C–C (Table 1). The DPSP ligand appears to be very flexible in this respect; values from the gold(I) complexes cited above vary over wide ranges, *e.g.* P–C–S–C (absolute values, °) 66.9; 103.9, 103.3; 65.2 [*cf.* here 144.2 (3), –161.4 (3)].

The perchlorate anion is well resolved and displays low displacement parameters. Consistent with this are a number of C–H···O interactions (Table 2), the shortest being H52···O3 = 2.41 Å within the asymmetric unit, that could be regarded as ‘weak’ hydrogen bonds (Desiraju & Steiner, 1999).

Experimental

To a diethyl ether solution of [Au(C₆F₅)₂(OEt₂)₂]ClO₄, prepared by reaction of NBu₄[Au(C₆F₅)₂Cl₂] (0.201 g, 0.24 mmol) and AgClO₄ (0.099 g, 0.48 mmol), was added PPh₂CH₂SPh (0.147 g, 0.48 mmol). After half an hour of stirring, the solvent was evaporated to *ca* 5 ml. Cooling the solution to 253 K led to the precipitation of the complex as a colourless solid that was collected by filtration (yield 75%). The compound was recrystallized from chloroform/hexane.

Crystal data

[Au(C ₆ F ₅) ₂ (C ₁₉ H ₁₇ PS) ₂]ClO ₄ ·CHCl ₃	<i>Z</i> = 4
<i>M_r</i> = 1366.62	<i>D_x</i> = 1.693 Mg m ^{−3}
Orthorhombic, <i>P</i> 2 ₁ 2 ₁ 2 ₁	Mo <i>K</i> α radiation
<i>a</i> = 11.290 (2) Å	<i>μ</i> = 3.16 mm ^{−1}
<i>b</i> = 13.795 (2) Å	<i>T</i> = 173 (2) K
<i>c</i> = 34.421 (4) Å	Prism, colourless
<i>V</i> = 5361.1 (14) Å ³	0.50 × 0.35 × 0.20 mm

Data collection

Siemens P4 diffractometer
ω scans
Absorption correction: ψ scan
(XEMP; Siemens, 1994)
*T*_{min} = 0.739, *T*_{max} = 0.834
(expected range = 0.471–0.532)
17522 measured reflections

11909 independent reflections
9376 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.030
*θ*_{max} = 27.5°
3 standard reflections
every 297 reflections
intensity decay: none

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.037
wR(*F*²) = 0.069
S = 0.92
11909 reflections
662 parameters
H-atom parameters constrained

w = 1/[σ²(*F*_o²) + (0.0289*P*)²]
where *P* = (*F*_o² + 2*F*_c²)/3
(Δσ)_{max} = 0.003
Δρ_{max} = 1.10 e Å^{−3}
Δρ_{min} = −0.77 e Å^{−3}
Absolute structure: Flack (1983),
5100 Friedel pairs
Flack parameter: −0.019 (4)

Table 1

Selected geometric parameters (Å, °).

Au–C71	2.079 (5)	P2–C51	1.806 (6)
Au–C81	2.083 (5)	P2–C41	1.818 (5)
Au–P1	2.3818 (14)	P2–C2	1.849 (5)
Au–P2	2.3990 (15)	S1–C31	1.769 (6)
P1–C21	1.804 (5)	S1–C1	1.823 (6)
P1–C11	1.820 (6)	S2–C61	1.778 (6)
P1–C1	1.837 (5)	S2–C2	1.810 (6)
C71–Au–C81	83.0 (2)	C11–P1–Au	109.54 (16)
C71–Au–P1	92.02 (14)	C1–P1–Au	113.56 (19)
C81–Au–P1	170.25 (15)	C51–P2–C41	105.4 (2)
C71–Au–P2	168.21 (15)	C51–P2–C2	107.7 (2)
C81–Au–P2	89.47 (15)	C41–P2–C2	105.5 (3)
P1–Au–P2	96.70 (5)	C51–P2–Au	118.44 (18)
C21–P1–C11	107.3 (2)	C41–P2–Au	113.36 (18)
C21–P1–C1	104.0 (2)	C2–P2–Au	105.71 (18)
C11–P1–C1	105.5 (3)	C31–S1–C1	103.7 (3)
C21–P1–Au	116.27 (18)	C61–S2–C2	101.9 (2)
C31–S1–C1–P1	144.2 (3)	Au–P2–C2–S2	32.8 (3)
Au–P1–C1–S1	−84.6 (3)	C1–S1–C31–C32	−162.8 (4)
C61–S2–C2–P2	−161.4 (3)	C2–S2–C61–C62	146.9 (4)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
C2–H2A···O3	0.99	2.49	3.118 (7)	121
C52–H52···O3	0.95	2.41	3.353 (8)	171
C66–H66···O3	0.95	2.61	3.473 (8)	152
C36–H36···O1 ⁱ	0.95	2.60	3.454 (8)	149
C1–H1A···O2 ⁱ	0.99	2.59	3.345 (8)	133
C26–H26···O2 ⁱ	0.95	2.67	3.605 (8)	167
C36–H36···O2 ⁱ	0.95	2.60	3.487 (7)	156
C14–H14···O2 ⁱⁱ	0.95	2.61	3.328 (7)	133
C15–H15···O4 ⁱⁱ	0.95	2.46	3.380 (8)	163

Symmetry codes: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x, y - \frac{1}{2}, -z + \frac{3}{2}$.

H atoms were included using a riding model with fixed C–H bond lengths of 0.95 (phenyl), 0.99 (methylene), 1.00 Å (CHCl₃); *U*_{iso}(H) values were fixed at 1.2 times *U*_{eq} of the parent atom. To improve refinement stability, a total of 562 restraints were applied to C atom displacement parameters (similarity and rigid-bond restraints) and local ring symmetry (planarity and similarity of distances). The Flack

(1983) parameter is unambiguous, but the compound is not chiral and crystallizes only by chance in a non-centrosymmetric space group. Displacement parameters of the solvent molecule are high and contacts to this molecule are therefore not included in Table 2. Significant difference peaks are in the solvent region or close to the Au atom. The largest peak is 0.61 Å from atom Cl4.

Data collection: *XSCANS* (Fait, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL97*.

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