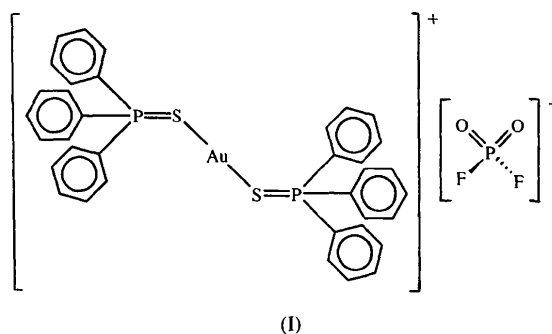


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The structure of such a complex, (I), with the triphenylphosphine sulfide ligand is reported here.



Structure solution was complicated by disorder of the anion. It was thought that the  $PF_6^-$  salt had been prepared, since a literature procedure (Jones, Maddock, Mays, Muir & Williams, 1977; Jones & Williams, 1977) and a reagent from a bottle labelled silver hexafluorophosphate (Aldrich Chemical Company) had been used. The crystallographic analysis and spectroscopic data (including IR,  $^{31}P$  and  $^{19}F$  NMR), however, suggested that hydrolysis had taken place and that the anion was actually  $PO_2F_2^-$ . The presence of the  $PO_2F_2^-$  ion instead of the expected  $PF_6^-$  has been reported several times before (Bruce *et al.*, 1988; Hirsch, Wilson & Moore, 1996; Kitagawa, Kawata, Nozaka & Munakata, 1993; Reger, Huff & Lebioda, 1991; Weidlein, 1968; White, Thompson & Maitlis, 1977) and it has been demonstrated that  $PF_6^-$  is readily hydrolyzed to  $PO_2F_2^-$  in the presence of a metal ion (Clark & Jones, 1970; Il'in, Maizel', Shcherbakova, Vol'f & Buslaev, 1982). A fairly satisfactory refinement was possible with an anion disorder comprised of three distorted tetrahedra.

The molecular cation is shown in Fig. 1. The ligating atoms form the expected almost linear arrangement around the Au atoms, with the Au atom on a crystallographic twofold axis and an S—Au—S angle of  $172.40(12)^\circ$ . The  $7.60(12)^\circ$  deviation from  $180^\circ$  is not caused by gold–gold interactions as there are no Au···Au distances less than  $7.4 \text{ \AA}$ . It may be caused by intramolecular  $\pi$ – $\pi$  interactions between phenyl rings (see below). The Au—S distance [ $2.277(2) \text{ \AA}$ ] is close to that observed for  $Ph_3PSAuCl$  [ $2.256(1) \text{ \AA}$ ] (Husain & Schlemper, 1987);  $2.264(2) \text{ \AA}$  (Jones & Bembenek, 1992)] and other bond lengths and angles are similar. The Au—S—P angle [ $103.27(12)^\circ$ ] is smaller, by about  $3^\circ$ , than the corresponding angle in  $Ph_3PSAuCl$  [ $106.35(6)^\circ$ ] (Husain & Schlemper, 1987);  $105.9(1)^\circ$  (Jones & Bembenek, 1992)], and the difference between the largest and smallest S—P—C angles is reduced from  $10.7^\circ$  in  $Ph_3PSAuCl$  to  $6.5^\circ$  in  $Au(PPh_3)_2$ . The P—S···S—P torsion angle is  $74.9(2)^\circ$ , relatively close to the  $90^\circ$  needed to maximize Au—S  $\pi$ -bonding. The three phenyl groups do not form a propeller conformation. Two of the phenyl rings are arranged so that

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## Bis(triphenylphosphine sulfide-S)gold(I) Difluorophosphate(V)

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### Abstract

The cation of the title compound,  $[Au(C_{18}H_{15}PS)_2]-(PO_2F_2)$ , lies with the Au atom on a twofold axis, with Au—S  $2.277(2) \text{ \AA}$  and S—Au—S  $172.40(12)^\circ$ . The deviation from linearity is not caused by Au···Au interactions. It may be caused by intramolecular  $\pi$ – $\pi$  interactions between phenyl rings. Bond lengths and angles are normal.

### Comment

Although a number of gold–thiol complexes have been used as drugs for the treatment of rheumatoid arthritis for more than sixty years (Sadler & Sue, 1994), some of the drugs are surprisingly poorly characterized and have resisted all crystallization attempts. The gold drug myochrysin, gold sodium thiomalate, for example, has been shown to be a mixture of at least five components, none of which have yet been conclusively characterized. During attempts to prepare and characterize gold–thiol complexes which may serve as models to the drug compounds, several 1:2 complexes have been isolated.

† Deceased.

they are almost coplanar with their S—P—C plane [dihedral angles, C11 4.4 (6) and C31 11.2 (3)°], whereas the other ring is at a right angle to its S—P—C plane [C21 89.7 (3)°]. A similar situation was claimed for Ph<sub>3</sub>PSAuCl by Husain & Schlemper (1987) but an examination of their results did not confirm this. The use of their parameters, or of the later re-determination by Jones & Bembenek (1992), showed that only one phenyl ring is almost coplanar with the corresponding S—P—C plane and none are at right angles [6.5, 49.0, 68.7° (Husain & Schlemper, 1987); 5.7, 49.1, 69.1° (Jones & Bembenek, 1992)]. All are canted in the same direction towards a propeller arrangement.

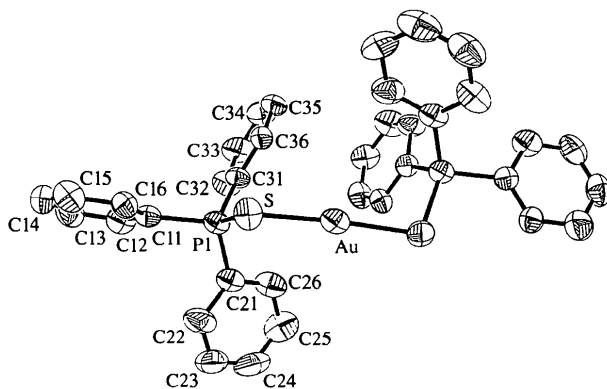


Fig. 1. The title cation drawn with 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

Despite the presence of so many phenyl rings there is only an internal  $\pi$ – $\pi$  interaction [3.45 (2)–3.96 (1) Å] between the C31 and C31A rings, related by a twofold axis, and a further external interaction [5.07 (9)–5.58 (7) Å] between these rings and those in adjacent molecules along the *z* direction, related by the *c* glide. There are no other  $\pi$ – $\pi$  interactions between phenyl rings because the cations stack in the *bc* plane and the remaining phenyl rings encapsulate the disordered PO<sub>2</sub>F<sub>2</sub><sup>−</sup> anions that lie in the  $y = \frac{1}{2}$  plane.

## Experimental

The title compound was prepared by a method similar to that of Jones *et al.* (1977) and Jones & Williams (1977) for the hexafluorophosphate salt. Colourless crystals were obtained from a dichloromethane/diethyl ether solution by filtration; yield 0.12 g (50%). <sup>1</sup>H NMR:  $\delta$  7.74–7.45 [*m*, Ar–H(*s*)]; <sup>13</sup>C NMR:  $\delta$  134.0 (*s*, *para*-C atoms), 132.9 (*d*,  $J_{PC}^2 = 10.8$  Hz, *ortho*-C atoms), 129.8 (*d*,  $J_{PC}^2 = 13.4$  Hz, *meta*-C atoms), 128.3 (*d*,  $J_{PC}^2 = 85.7$  Hz, substituted C atoms); <sup>31</sup>P NMR:  $\delta$  44.5 [*s*, Au(Ph<sub>3</sub>PS)<sub>2</sub>], −14.9 (*t*,  $J_{PF} = 955$  Hz, PO<sub>2</sub>F<sub>2</sub><sup>−</sup>); <sup>19</sup>F NMR:  $\delta$  −82.8 (*d*,  $J_{PF} = 960$  Hz, PO<sub>2</sub>F<sub>2</sub><sup>−</sup>).

### Crystal data

[Au(C<sub>18</sub>H<sub>15</sub>PS)<sub>2</sub>](F<sub>2</sub>PO<sub>2</sub>) Ag *K* $\alpha$  radiation  
*M<sub>r</sub>* = 886.60  $\lambda$  = 0.56086 Å

### Monoclinic

*P*2/*c*  
*a* = 13.847 (3) Å  
*b* = 9.232 (2) Å  
*c* = 14.681 (3) Å  
 $\beta$  = 108.57 (3)°  
*V* = 1779.0 (7) Å<sup>3</sup>  
*Z* = 2  
*D<sub>x</sub>* = 1.655 Mg m<sup>−3</sup>  
*D<sub>m</sub>* = 1.69 (1) Mg m<sup>−3</sup>  
*D<sub>m</sub>* measured by suspension  
 in CCl<sub>4</sub>/CH<sub>2</sub>I<sub>2</sub>

### Cell parameters from 20

reflections  
 $\theta$  = 7.7–13.5°  
 $\mu$  = 2.409 mm<sup>−1</sup>  
*T* = 296 (2) K  
 Irregular plate  
 0.50 × 0.20 × 0.10 mm  
 Colourless

### Data collection

Siemens P3 diffractometer  
 $\omega$ –2 $\theta$  scans  
 Absorption correction:  
 empirical, via  $\psi$  scans  
 (SHELXTL; Sheldrick,  
 1994)  
 $T_{\min} = 0.615$ ,  $T_{\max} = 0.786$   
 3071 measured reflections  
 2939 independent reflections

2122 reflections with  
 $I > 2\sigma(I)$

$R_{\text{int}} = 0.030$   
 $\theta_{\text{max}} = 19.05^\circ$   
 $h = 0 \rightarrow 16$   
 $k = 0 \rightarrow 10$   
 $l = -17 \rightarrow 16$   
 3 standard reflections  
 every 97 reflections  
 intensity decay: −0.7%

### Refinement

Refinement on  $F^2$   
 $R = 0.050$   
 $wR(F^2) = 0.1164$   
 $S = 0.912$   
 2939 reflections  
 242 parameters  
 H atoms riding: see below

$w = 1/[\sigma^2(F_o^2) + (0.0662P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = -0.003$   
 $\Delta\rho_{\text{max}} = 1.479 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -1.890 \text{ e \AA}^{-3}$   
 Extinction correction: none  
 Scattering factors from  
 International Tables for  
 Crystallography (Vol. C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U^{ij}a_i^*a_j^* \cdot \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U<sub>eq</sub></i>
Au	0	0.57392 (6)	1/4	0.0467 (2)
S	0.0715 (2)	0.5576 (3)	0.1305 (2)	0.0540 (6)
P1	0.1712 (2)	0.7246 (2)	0.1584 (2)	0.0417 (6)
C11	0.2311 (6)	0.7233 (10)	0.0645 (6)	0.043 (2)
C12	0.3023 (7)	0.8286 (10)	0.0663 (8)	0.058 (3)
C13	0.3418 (8)	0.8343 (13)	−0.0077 (9)	0.069 (3)
C14	0.3110 (8)	0.7389 (14)	−0.0829 (8)	0.071 (3)
C15	0.2427 (8)	0.6337 (13)	−0.0821 (8)	0.070 (3)
C16	0.2014 (7)	0.6257 (10)	−0.0082 (7)	0.051 (2)
C21	0.2677 (6)	0.7113 (9)	0.2740 (7)	0.047 (2)
C22	0.3567 (8)	0.6349 (11)	0.2835 (9)	0.066 (3)
C23	0.4274 (9)	0.6224 (15)	0.3716 (10)	0.083 (4)
C24	0.4101 (9)	0.6768 (15)	0.4499 (10)	0.086 (4)
C25	0.3233 (10)	0.7530 (13)	0.4429 (8)	0.078 (3)
C26	0.2516 (8)	0.7676 (12)	0.3537 (8)	0.067 (3)
C31	0.1077 (6)	0.8960 (9)	0.1541 (6)	0.041 (2)
C32	0.1666 (7)	1.0198 (10)	0.1852 (7)	0.054 (3)
C33	0.1190 (8)	1.1546 (11)	0.1738 (8)	0.066 (3)
C34	0.0168 (8)	1.1637 (11)	0.1380 (7)	0.059 (3)
C35	−0.0417 (7)	1.0428 (10)	0.1083 (7)	0.056 (3)
C36	0.0045 (6)	0.9074 (10)	0.1154 (6)	0.046 (2)
P2	1/2	0.8354 (6)	3/4	0.0784 (13)
O1†	0.398 (4)	0.714 (7)	0.723 (5)	0.051 (6)
O2†	0.504 (5)	0.838 (7)	0.647 (5)	0.051 (6)
F1†	0.429 (4)	0.964 (5)	0.772 (4)	0.056 (5)
F2†	0.617 (6)	0.787 (7)	0.815 (4)	0.056 (5)

O3‡	0.460 (4)	0.677 (5)	0.713 (4)	0.051 (6)
O4‡	0.391 (3)	0.878 (6)	0.724 (4)	0.051 (6)
F3‡	0.604 (3)	0.865 (5)	0.824 (3)	0.056 (5)
F4‡	0.515 (4)	0.946 (5)	0.670 (3)	0.056 (5)
O5§	0.453 (3)	0.912 (6)	0.823 (4)	0.051 (6)
O6§	0.630 (4)	0.816 (7)	0.790 (4)	0.051 (6)
F5§	0.478 (3)	0.891 (4)	0.644 (3)	0.056 (5)
F6§	0.513 (3)	0.673 (3)	0.723 (2)	0.056 (5)

‡ Site occupancy = 0.124 (8). † Site occupancy = 0.179 (9). § Site occupancy = 0.203 (10).

Table 2. Selected geometric parameters (Å, °)

Au—S	2.277 (2)	P1—C21	1.799 (9)
S—P1	2.023 (3)	P1—C31	1.802 (8)
P1—C11	1.821 (9)		
S—Au—S <sup>i</sup>	172.40 (12)	C21—P1—C31	107.5 (4)
P1—S—Au	103.27 (12)	C11—P1—S	106.7 (3)
C11—P1—C21	109.5 (4)	C21—P1—S	113.2 (3)
C11—P1—C31	108.3 (4)	C31—P1—S	111.6 (3)

Symmetry code: (i)  $-x, y, \frac{1}{2} - z$ .

Analysis of the systematic absences, with the *XPREP* program (*SHELXTL*; Sheldrick, 1994), suggested two possible space groups, *P2/c* and *Pc*. The structure was solved with both space groups, but refinement suggested that *P2/c* was the proper choice. The PO<sub>2</sub>F<sub>2</sub><sup>-</sup> anion was highly disordered. In the initial stages of refinement, three tetrahedra (O1, O2, F1, F2; O3, O4, F3, F4; and O5, O6, F5, F6), constrained to be identical and to conform to previously published geometric parameters (Eriks *et al.*, 1985), were fitted to peaks surrounding P2. The occupancy of each tetrahedron was set at 0.16667 so that the sum of the occupancies was 0.5 (the twofold axis increases the site occupancy to 1). Constraints were removed in a stepwise manner so that the three tetrahedra were refined independently. With the isotropic displacement parameters of all F and O atoms constrained to be equivalent, the occupancy of each tetrahedron was allowed to refine, with the constraint that they must sum to 0.5. The occupancies were then fixed at the refined values and all of the atoms were refined anisotropically. Although the disorder treatment appeared to result in a satisfactory refinement (both the residuals and the errors in the cation's bond lengths improved), the geometric parameters for the anion tetrahedra have very high errors and are unreliable. The largest maxima/minima in the final difference map occur within 1.2 Å of the Au atom. H atoms were added at calculated positions and allowed to ride on the atoms to which they were attached. Their isotropic displacement parameters (*U*'s) were set to 1.2*U*<sub>eq</sub> of the atom to which they were attached.

Data collection: *P3/PC Diffractometer Program* (Siemens, 1989). Cell refinement: *P3/PC Diffractometer Program*. Data reduction: *P3/PC Diffractometer Program*. Program(s) used to solve structure: *SHELXTL*. Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1269). Services for accessing these data are described at the back of the journal.

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## Pentacarbonyl(triphenylsilyl)manganese(I)

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### Abstract

The title compound, [Mn(C<sub>18</sub>H<sub>15</sub>Si)(CO)<sub>5</sub>], crystallizes in the space group *P1* with two molecules in the asymmetric unit. It is a strong covalent 'bimetallic' complex with partial multiple-bond character in the 'metal-metal' bond as evidenced by the short (average) Mn—Si distance of 2.504 (6) Å.

### Comment

The full structure of only one silicon complex with a manganese pentacarbonyl moiety appears to have been reported, that of the tris(trimethylsilyl)silyl complex