$[\text{Au}(C_{18}H_{15}PS)_2](F_2PO_2)$

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^i	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$_2$F$_2^-$ 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 1.2U_{eq} 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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Pentacarbonyl(triphenylsilyl)manganese(I)

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Abstract

The title compound, $[\text{Mn}(C_{18}H_{15}Si)(CO)_5]$, crystallizes in the space group $P\bar{1}$ 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

(Nicholson, Simpson & Robinson, 1973). The Mn—Si bond length in this complex is 2.564 (6) Å, a value which is considered to be rather high in view of the sum of the covalent radii, leading to the conclusion that no bond shortening occurs, since the bulky tris(trimethylsilyl)silyl group prevents metal–ligand π-backbonding. Other Mn(CO)$_5$ complexes with group IV ligands include the triphenylgermanium (Kilbourn, Blundell & Powell, 1965) and triphenyltin complexes (Weber & Bryan, 1967) where the Ge and the Sn bond lengths to Mn are 2.54 (2) and 2.674 (4) Å, respectively. We report here the structure of the pentacarbonyl(triphenylsilyl)-manganese(I) complex, (I).
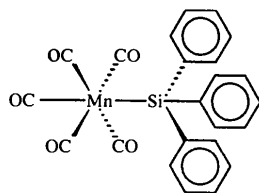
(I)

The two molecules in the asymmetric unit have near mirror planes of symmetry with regard to the orientation between the trigonal triphenylsilyl group and the square formed by the *cis* carbonyl ligands on manganese. The angles of rotation, as represented by the smallest C—Mn—Si—C torsion angles, are C2—Mn1—Si1—C11 11.1 (3) and C9—Mn2—Si2—C41 11.8 (3)° for molecules 1 and 2, respectively. The corresponding torsion angles, C5—Mn—Sn—C21, for the four independent molecules in the triphenyltin complex are in the range

10.3 (17)–13.5 (17)°. The four *cis* carbonyl groups show the typical behaviour of complexes of this type by being bent towards the Si atom, with Si—Mn—C bond angles in the range 81.5 (2)–89.2 (2)°.

The major difference between the two molecules in the asymmetric unit lies in the torsion angles involving the phenyl rings. For molecule 2, one of the torsion angles, Mn2—Si2—C51—C56, is only 20.7 (5)° compared with values of between 45.5 (5) and 69.9 (4)° for the phenyl rings in molecule 1. In the tin case, the Mn—Sn—C—C torsion angles fall into narrow ranges with average values of 41.2 (7), 60.0 (4) and 62 (4)° for phenyl rings 1, 2 and 3, respectively.

The Si—Mn bond lengths are 2.509 (2) and 2.498 (2) Å, which are significantly shorter than the bond length in the tris(trimethylsilyl)silyl complex, 2.564 (6) Å, and this indicates that appreciable π-backbonding does occur. In this context, it is interesting to note that the Mn—C bond distances in the tin complex (Weber & Bryan, 1967) have a mean value of 1.762 (10) Å and are significantly shorter than the mean value of 1.841 (7) found for the present triphenylsilyl case. A decrease in the metal–carbon distance should be accompanied by a longer C—O distance and the average C—O bond lengths are 1.184 (11) Å for the tin and 1.139 (7) Å for the silicon compounds. The weakening of the *trans* carbonyl bond in the silyl complex is reflected by the differences in the Raman frequencies for the a_1 (axial) mode in the solid state, as shown in Table 2.

Experimental

The title compound was synthesized according to the literature method of Jetz, Simons, Thomsom & Graham (1966). Colourless transparent rectangular-shaped crystals were obtained from a benzene/octane solvent mixture.

Crystal data

[Mn(C$_{18}$H$_{15}$Si)(CO)$_5$]	Mo $K\alpha$ radiation
$M_r = 454.36$	$\lambda = 0.7107$ Å
Triclinic	Cell parameters from 24
$P\bar{1}$	reflections
$a = 11.380 (2)$ Å	$\theta = 14$–17°
$b = 11.541 (2)$ Å	$\mu = 0.702$ mm^{-1}
$c = 17.111 (3)$ Å	$T = 295 (2)$ K
$\alpha = 104.95 (2)°$	Plate
$\beta = 98.20 (2)°$	$0.45 \times 0.36 \times 0.10$ mm
$\gamma = 91.10 (2)°$	Colourless
$V = 2145.4 (6)$ Å^3	
$Z = 4$	
$D_x = 1.407$ Mg m^{-3}	
D_m not measured	

Data collection

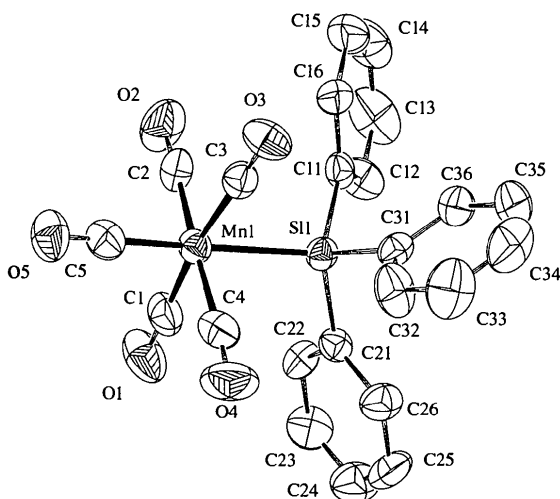|	
Rigaku AFC-6S diffractometer	3921 reflections with $I > 2\sigma(I)$

Fig. 1. *PLATON* (Spek, 1990) displacement ellipsoid plot of molecule 1 showing the numbering scheme. Ellipsoids are shown at 30% probability. For molecule 2, the carbonyl groups are numbered 6 to 10 in the same sequence as in molecule 1, the C atoms in the phenyl rings are numbered Cn1 to Cn6 with $n = 4$, 5 and 6.

$\omega/2\theta$ scans
Absorption correction:
  ψ scan (NRCVAX; Gabe,
  LePage, Charland, Lee &
  White, 1989)
  T_{min} = 0.804, T_{max} = 0.932
15 186 measured reflections
7558 independent reflections

R_{int} = 0.071
θ_{max} = 25.0°
$h = -13 \rightarrow 13$
$k = -13 \rightarrow 13$
$l = -20 \rightarrow 19$
3 standard reflections
  every 200 reflections
  intensity decay: 1.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.069$
$wR(F^2) = 0.108$
$S = 0.918$
7558 reflections
542 parameters
H atoms riding, C—H =
  0.93 Å
$w = 1/[\sigma^2(F_o^2)]$
$(\Delta/\sigma)_{max} = -0.008$

$\Delta\rho_{max} = 0.36$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}
Extinction correction:
  SHELXL93 (Sheldrick,
  1993)
Extinction coefficient:
  0.0009 (2)
Scattering factors from
  International Tables for
  Crystallography (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Mn1—C5	1.827 (6)	Mn2—C7	1.834 (7)
Mn1—C1	1.839 (6)	Mn2—C8	1.835 (6)
Mn1—C4	1.846 (6)	Mn2—C10	1.837 (6)
Mn1—C3	1.850 (6)	Mn2—C6	1.844 (6)
Mn1—C2	1.852 (6)	Mn2—C9	1.846 (6)
Mn1—Si1	2.509 (2)	Mn2—Si2	2.498 (2)
Si1—C21	1.882 (5)	Si2—C61	1.879 (5)
Si1—C11	1.890 (5)	Si2—C41	1.880 (5)
Si1—C31	1.898 (5)	Si2—C51	1.892 (5)
Mn1—Si1—C11—C16	59.2 (4)	Mn2—Si2—C41—C42	64.9 (4)
Mn1—Si1—C21—C22	68.9 (4)	Mn2—Si2—C51—C56	20.7 (5)
Mn1—Si1—C31—C32	45.5 (5)	Mn2—Si2—C61—C66	71.5 (5)

Table 2. *Carbonyl stretching frequencies (cm^{-1}) for the pentacarbonyl(triphenylsilyl)manganese(I) and triphenyltin(pentacarbonyl)manganese(I) complexes*

Assignment	Mn(CO)$_5$(SiPh$_3$)		Mn(CO)$_5$(SnPh$_3$)	
	IR	Raman	IR	Raman
a_1 (equatorial)	2095 (m)	2096 (m)	2092 (ms)	2093 (m)
b_1	2030 (mw)	2029 (s)	2029 (sh)	2024 (ms, sh)
e	2010 (br)	2010 (mw)	2013 (ms)	2014 (s)
			1998 (ms)	1991 (mw)
a_1 (axial)	1988 (s)	1992 (ms)	1983 (s)	1975 (mw)
	1970 (s)	1980 (s)	1976 (s)	

IR spectra were recorded for Nujol mulls on KBr plates, Raman spectra were measured on powders packed into a 2 mm diameter sampling cup.

Data collection: MSC/AFC Diffractometer Control Software (Molecular Structure Corporation, 1985). Cell refinement: MSC/AFC Diffractometer Control Software. Data reduction: modified versions of NRC2 and NRC2A (Ahmed, Hall, Pippy & Huber, 1966). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1985). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: ORTEPII in NRCVAX94 (Johnson, 1976) and PLATON96 (Spek, 1990). Software used to prepare material for publication: SHELXL93 and NRCVAX94.

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5-(o-Chlorophenyl)-1,3-dithia-2,4-diazolylium Hexafluoroarsenate

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Abstract

The structure of the title compound, (C$_7$H$_4$ClN$_2$S$_2$)[AsF$_6$], has four crystallographically independent cations, in each of which, attractive S$\cdots$Cl interactions enhance the intrinsic electronic tendency of the two rings to coplanarity. The C—C—C—S torsion angles about the bond joining the rings are 1.4 (11), 9.0 (11), 9.5 (11) and 5.0 (12)°, and in each cation the S$\cdots$Cl distance is close to 2.9 Å.