

Fig. 1. The structure of Mo₂Cl₄O₂(hfac)₂.

seems no good reason for the range of Mo—Cl_b distances though perhaps there is some tendency towards five-coordination in the dimer.

The terminal Mo—O and Mo—Cl bond lengths [1.648 (9); 2.305 (5) Å] are comparable to values in MoOCl₃·SPPPh₃ [1.647 (3); 2.305 (1)–2.342 (1) Å] (Boorman, Garner, Mably & King, 1974) and in MoOCl₃L₂, L = PO(NMe₂)₃ [1.669 (5); 2.368 (2)–2.381 (2) Å] (Khodadad, Viossat & Rodier, 1977). The two bonds to hfac are significantly different [2.07 (1), 2.17 (1) Å], the longer bond being *trans* to terminal O. This difference of 0.10 Å is a common feature of molecules containing terminal O, for example 0.099 Å in MoOCl₃L₂, 0.11 Å in ReOCl₂(acac)(PPh₃) (Lock & Wan, 1975).

Least-squares-planes calculations for the dimer show

that the six-membered ring is almost planar, the maximum deviation of a contributing atom being 0.05 Å. The metal atom is 0.34 Å above the plane of Cl(1), Cl(1'), Cl(2) and O(1) towards the terminal O(3). The dimensions of the hfac ligand are as expected, although the F atoms are undergoing severe thermal motion.

No intermolecular distance is shorter than the sum of the van der Waals radii; the shortest being an O...F contact of 3.0 Å.

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Bis(dimethylphenylphosphine)trichlorostannioiodine

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Abstract. [P(C₆H₅)(CH₃)₂]₂AuSnCl₃, monoclinic, *P*2₁/*m*, *a* = 11.954 (2), *b* = 9.925 (2), *c* = 10.059 (1) Å, β = 111.40 (2)°, *Z* = 2, *D*_o = 2.05, *D*_c = 2.08 g cm⁻³. The Au atom is coordinated by the two phosphine ligands [Au—P, 2.310 (4), 2.318 (4) Å] and the SnCl₃ ligand [Au—Sn, 2.881 (1) Å], in a trigonal geometry distorted considerably towards linear

P—Au—P and an uncoordinated SnCl₃⁻ anion [P—Au—P, 153.8 (2)°].

Introduction. Initial cell dimensions were determined from precession photographs (Mo *K*_α radiation). Systematic absences (0*k*0 for *k* odd) indicated space group *P*2₁/*m* or *P*2₁; the centrosymmetric *P*2₁/*m*

(imposing crystallographic mirror symmetry on the molecule) was confirmed by the successful structure determination.

A thin plate (*ca* 0.01 mm thick, dominant faces {302}) was sealed in a Lindemann-glass tube and mounted on a Hilger & Watts Y290 four-circle diffractometer, with **b** misaligned slightly from the spindle (φ) axis. Cell parameters and the orientation matrix were refined by least squares from 12 reflexions ($38^\circ < 2\theta < 47^\circ$) (Busing & Levy, 1967). Intensities were collected for all unique reflexions with $2\theta \leq 55^\circ$ (Mo $K\alpha$ radiation, Zr filter, $\lambda = 0.71069$ Å, θ - 2θ scan mode). No reflexions were sufficiently intense to require the insertion of attenuators into the beam. Three standard reflexions showed steady decays of about 50% of original intensity over the two-week collection; linear decay functions were calculated from their periodic measurements and applied. Absorption corrections were made by a method based on that of Sheldrick & Sheldrick (1970), adapted for four-circle geometry [$\mu = 84.19$ cm $^{-1}$; a well defined minimum in the residual $R_w = (\sum w\Delta^2 / \sum wF_o^2)^{1/2}$ was obtained for $\mu t = 0.125$, corresponding to a thickness of 0.0148 mm]. Of the 2226 independent reflexions with positive net recorded intensity, 1766 with $I > 2.5\sigma(I)$ were used for structure solution and refinement. Non-hydrogen atoms were located by Patterson and Fourier techniques, and refined by full-matrix least squares to a minimum value of $\sum w\Delta^2$ [$\Delta = |F_o| - |F_c|$, $w = k/[\sigma^2(F_o) + gF_o^2]$, k and g refined to final values of 1.98 and 0.002025], with anisotropic temperature factors. H atoms were placed in geometrically calculated positions on the external bisectors of C-C-C angles (phenyl H) or staggered with respect to substituents on P (methyl H), with C-H 0.95 Å (Churchill, 1973), and constrained to these positions

during refinement. Four overall isotropic temperature factors were refined for the H atoms, one for each phenyl or methyl group. Scattering factors for uncharged atoms were those of Cromer & Waber (1974) and Cromer & Ibers (1974). The final value of R was 5.93% ('observed' reflexions only), and R_w 7.35%. The number of parameters refined was 128. All shift/e.s.d. ratios in the last cycle were < 0.01 , and a final difference map contained no significant peaks except close to the metal atoms. Coordinates of non-hydrogen atoms are given in Table 1.*

Discussion. The compound (Fig. 1) was prepared from $\text{PhMe}_2\text{PAuCl}$, PhMe_2P and SnCl_4 in acetone solution (Bailey, 1972). It was recrystallized by slow diffusion of diethyl ether vapour into a chloroform solution; other attempted methods resulted in decomposition. The structure was investigated in order to determine whether the SnCl_3 group is bonded to the Au atom or exists as a separate anion. Recent ^{197}Au Mössbauer spectroscopic results suggest that Au is three-coordinate in this compound (Jones, Jones, Maddock, Mays, Vergnano & Williams, 1977), but this conflicts with previous ^{119}Sn Mössbauer results, which indicate the presence of SnCl_3^- anions (Mays & Sears, 1974). The coordination of Au is found to be intermediate between linear and trigonal planar.

Unconstrained bond lengths and angles are shown in Fig. 2. Phenyl ring 2 is planar within ± 0.02 Å. Crystallographic symmetry requires that phenyl ring 1 and the Au coordination are strictly planar and that

* Lists of structure factors, thermal parameters and H atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33056 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Atomic coordinates ($\times 10^4$) for non-hydrogen atoms

	x	y	z
Au	2293 (1)	2500	1771 (1)
Sn	-38 (1)	2500	-485 (1)
Cl(1)	73 (6)	2500	-2855 (6)
Cl(2)	-1554 (3)	708 (3)	-971 (5)
P(1)	3570 (4)	2500	515 (4)
P(2)	1867 (4)	2500	3842 (4)
C(10)	3414 (13)	1053 (14)	-641 (14)
C(11)	5157 (15)	2500	1696 (23)
C(12)	5480 (16)	2500	3135 (19)
C(13)	6698 (19)	2500	4032 (21)
C(14)	7570 (17)	2500	3451 (28)
C(15)	7227 (16)	2500	1925 (21)
C(16)	6050 (16)	2500	1105 (21)
C(20)	1044 (12)	1061 (14)	4084 (15)
C(21)	3321 (15)	2500	5268 (17)
C(22)	3906 (12)	1285 (14)	5772 (14)
C(23)	5085 (12)	1285 (17)	6706 (15)
C(24)	5628 (19)	2500	7149 (21)

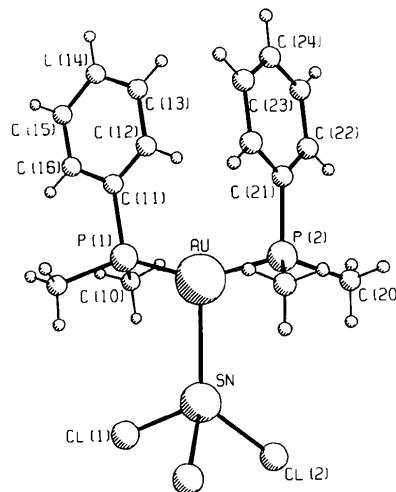


Fig. 1. Perspective view of the molecule.

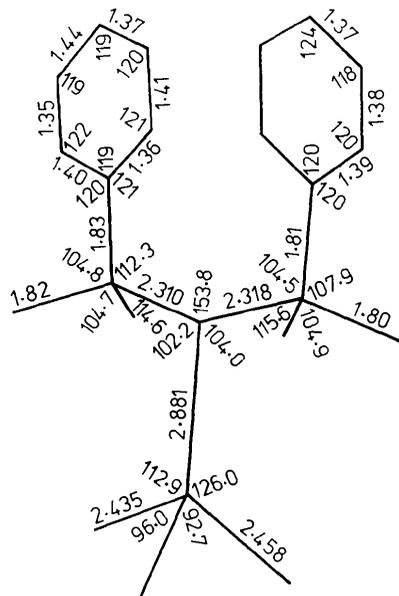


Fig. 2. Unconstrained bond lengths (Å) and angles (°). E.s.d.'s in bond lengths are: Au—Sn 0.001, Au—P and Sn—Cl 0.003–0.005, P—C 0.01–0.02, C—C 0.02–0.03 Å; in angles: at Au or Sn 0.1–0.2, at P 0.5–1.0, at C 1–2°.

rings 1 and 2 are mutually perpendicular. The geometry of the phosphine ligands is unexceptional. There are no unusually short intermolecular contacts.

We have previously discussed the distortion toward linear twofold coordination in three-coordinate Au^I complexes (Clegg, 1976). In this structure, the severe distortion is evident in the wide P—Au—P angle and in the mean Au—P bond length of 2.314 (4) Å, which is similar to the Au—P distances of 2.316 (4) Å in the two-coordinate [(Ph₂MeP)₂Au]⁺PF₆[−] (Guy, Jones & Sheldrick, 1976) and 2.31 (1) Å in the two-coordinate [(C₆H₁₁)₃P]₂Au⁺SCN[−] (Muir & Muir, 1977), but shorter than the mean of 2.331 Å in the distorted three-coordinate (Ph₃P)₂AuCl (Baenziger, Dittmore & Doyle, 1974) and much shorter than the mean of 2.382 Å in the three-coordinate [(Ph₃P)₃Au]⁺ ion (Guggen-

Table 2. Geometry of SnCl₃ ligands and anions

Compound	Mean Sn—Cl	Mean Cl—Sn—Cl	Reference
(OC) ₅ MnSnCl ₃	2.344 Å	100.6°	(a)
(C ₃ H ₃)Fe(CO) ₂ SnCl ₃	2.360	98.3	(b)
(C ₇ H ₉)(PMe ₂ Ph) ₂ IrSnCl ₃	2.406	95.5	(c)
(C ₇ H ₇)Mo(CO) ₂ SnCl ₃	2.411	95.0	(d)
(PPhMe ₂) ₂ AuSnCl ₃	2.450	94.9	This work
[Co(depe) ₂ Cl][SnCl ₃]	2.444	94.5	(e)
Cs[SnCl ₃]	2.52	89.8	(f)

References: (a) Onaka (1975). (b) Greene & Bryan (1970). (c) Churchill & Lin (1974). (d) Ziegler, Sasse & Nuber (1975). (e) Stalick, Corfield & Meek (1973). (f) Poulsen & Rasmussen (1970).

berger, 1974). The weakness of the Au—Sn bond is also suggested by the geometry of the SnCl₃ ligand. The mean Sn—Cl bond length (2.450 Å) and Cl—Sn—Cl angle (94.9°) fall between values for uncoordinated SnCl₃[−] anions and SnCl₃ ligands attached to metal atoms (Table 2), and closely resemble those for the SnCl₃[−] anion in [Co(depe)₂Cl][SnCl₃] (Stalick, Corfield & Meek, 1973). If covalent radii are taken as 1.40 Å for Sn (Onaka, 1975) and 1.33 Å for Au (Mannan, 1967; Blundell & Powell, 1971), the Au—Sn distance of 2.881 Å is considerably longer than the expected single-bond value of 2.73 Å; the assignment of covalent radii for metal atoms in low oxidation states and the interpretation of metal—metal bond lengths in terms of the strength of the interaction between the atoms are, however, notoriously hazardous.

It appears that the bonding of the SnCl₃ ligand to the Au atom is sufficiently strong to produce a ¹⁹⁷Au Mössbauer spectrum suggesting three-coordinate Au, but not strong enough to perturb the ¹¹⁹Sn Mössbauer parameters greatly from values typical of an uncoordinated SnCl₃[−] anion.

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catena-Bis(phosphinato)(2,2'-bipyridyl)manganese(II)

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Abstract. $C_{10}H_{12}MnN_2O_4P_2$, $C2/c$; $a = 16.827$ (15), $b = 10.745$ (20), $c = 7.170$ (5) Å, $\beta = 91.46$ (3)°, $Z = 4$, $D_x = 1.75$ g cm $^{-3}$, $\lambda(Cu K\alpha) = 1.5418$ Å, $\mu = 105.3$ cm $^{-1}$. The crystal contains chains along c . Each six-coordinate Mn atom is bonded to a bipyridyl ligand and is linked through two bridging phosphinate groups to each of the Mn atoms related to it by the c glide.

Introduction. The title compound was studied during an investigation of the structural role of the phosphinate anion, $H_2PO_2^-$, in a number of salts. It was obtained by the method of Sala-Pala, Kergoat & Everchais (1972) as yellow laths elongated along c . Equi-inclination multifilm Weissenberg photographs of the levels $h0-l$ and $hk0-6$ were recorded from two crystals each $0.1 \times 0.2 \times 0.5$ mm, and were scanned by the SRC Microdensitometer Service, Rutherford Laboratory. The systematic absences indicated the space group Cc or $C2/c$. The intensities were corrected for absorption. The structure was solved by the heavy-atom method. Refinement was initiated in space group Cc , and was continued in $C2/c$ after the diad axis had become apparent. A difference synthesis at $R = 0.065$ showed

Table 2. Interatomic distances (Å) and angles (°)

Mn—O(1)	2.170 (4)	N—C(5)	1.334 (7)
Mn—O(2 ^l)	2.140 (4)	C(1)—C(2)	1.404 (7)
Mn—N	2.311 (4)	C(2)—C(3)	1.378 (8)
P—O(1)	1.494 (4)	C(3)—C(4)	1.370 (8)
P—O(2)	1.489 (4)	C(4)—C(5)	1.384 (8)
N—C(1)	1.342 (7)	C(1)—C(1 ⁱⁱ)	1.497 (10)
O(1)—Mn—O(2 ^l)	90.2 (2)	Mn—N—C(5)	123.1 (4)
O(1)—Mn—O(1 ⁱⁱ)	175.4 (2)	C(1)—N—C(5)	118.3 (5)
C(2 ⁱⁱ)—Mn—O(2 ⁱⁱⁱ)	107.3 (2)	N—C(1)—C(2)	122.0 (5)
O(1)—Mn—N	87.2 (2)	C(1)—C(2)—C(3)	118.1 (5)
O(2 ^l)—Mn—N	90.9 (2)	C(2)—C(3)—C(4)	120.0 (5)
N—Mn—N ⁱⁱ	70.8 (2)	C(3)—C(4)—C(5)	118.4 (5)
O(2 ⁱⁱⁱ)—Mn—N	161.6 (2)	C(4)—C(5)—N	123.1 (5)
O(1)—P—O(2)	119.5 (2)	N—C(1)—C(1 ⁱⁱ)	116.1 (5)
Mn—N—C(1)	118.6 (4)	C(2)—C(1)—C(1 ⁱⁱ)	122.0 (5)

Distances between atoms in adjacent chains

P—C(2^{iv}) 3.77 (1) O(1)—C(2^{iv}) 3.37 (1) C(1)—C(2^{iv}) 3.47 (1)

Symmetry code

(i) $x, -y, \frac{1}{2} + z$
 (ii) $-x, y, \frac{1}{2} - z$

(iii) $-x, -y, -z$
 (iv) $x, 1 - y, \frac{1}{2} + z$

Table 1. Atomic coordinates ($\times 10^4$)

	x	y	z
Mn	0	1536 (1)	2500
P	1037 (1)	993 (1)	-1349 (2)
O(1)	367 (2)	1606 (4)	-377 (6)
O(2)	988 (2)	-357 (3)	-1803 (7)
N	770 (3)	3290 (4)	3012 (6)
C(1)	430 (3)	4412 (5)	2798 (7)
C(2)	849 (3)	5520 (5)	3156 (8)
C(3)	1643 (3)	5435 (6)	3655 (9)
C(4)	1996 (3)	4291 (5)	3847 (9)
C(5)	1536 (3)	3241 (6)	3530 (8)

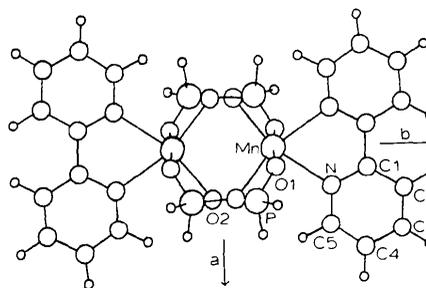


Fig. 1. Axial (c) projection of one chain.