impression of the molecular conformation is obtained. It is apparent that the methyl groups at C(8) and C(9) have different orientations with respect to the benzene ring. The positions adopted may be determined by the spatial requirement of the oxaziridine ring, but intermolecular forces may just as well exert the major influence.

The packing of the molecules in the cell does not appear very compact. One contact, however, is of an unusual character. The hydrogen atom attached to C(7) points towards an oxygen atom in the neighbouring unit cell in the **b** direction. It seems justified to describe this contact as an intermolecular C–H···O bridge for the following reasons. The carbon–hydrogen bond in question is very polar since the carbon is attached to three electron withdrawing ligands, *i.e.* oxygen, nitrogen and a substituted phenyl group. The distances involved are C···O 3·34 Å, C–H 1·05 Å, H···O 2·30 Å, and this particular H···O distance is about 0·5 Å shorter than any other intermolecular distance found in this structure between hydrogen and one of the other kinds of atom. Furthermore the angles N–O···C and C–O···C are 100 and 116° respectively, in good accordance with the conception of oxygen as acceptor atom in a hydrogen bridge.

My thanks are due to the Dean of the Institute of Medical Biochemistry, University of Göteborg, Professor S. Ställberg-Stenhagen, for hospitality during my six weeks' stay at the Institute; also to Dr Sixten Abrahamsson and all the members of his group for discussions and kind helpfulness, and especially to Maureen Innes and Anders Westerdahl for generous and efficient assistance with the computations. Financial support has been obtained from the Swedish Natural Science and Swedish Medical Research Councils and the U.S. Public Health Service, (GM-11653).

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The Crystal Structure Determination of the Complex $(C_6H_5)_3P{\rightarrow}Au{\rightarrow}Mn(CO)_4P(OC_6H_5)_3$

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(*Received* 16 *February* 1967 *and in revised form* 8 *April* 1967)

Diamagnetism and the short Au–Mn distance of 2·57 ± 0·01 Å found in the complex $(C_6H_5)_3P{\rightarrow}Au{-}Mn(CO)_4P(OC_6H_5)_3$ indicate a direct metal to metal bonding between the dissimilar metal atoms. The crystals are triclinic, space group $P\bar{1}$, with two molecules in a cell of dimensions $a=10·76$, $b=10·63$, $c=16·74$ Å, $\alpha=93·6°$, $\beta=97·0°$, $\gamma=77·8°$. The structure consists of discrete molecules. The manganese is octahedrally coordinated. Taking the metal to metal bond direction along the Z axis, the carbonyl groups on the Z plane are in a staggered configuration and are bent towards the metal to metal bond direction. The Mn–P bond of length 2·33 ± 0·01 Å appears to be multiple in nature. The P–Au–Mn bond angle of 165·5 ± 0·3° is significantly non-linear.

Introduction

As a part of a study of metal to metal bonds, the structure determination of the complex triphenylphosphinegold–tetracarbonyltriphenoxyphosphinemanganese, $(C_6H_5)_3P{\rightarrow}Au{-}Mn(CO)_4P(OC_6H_5)_3$, was undertaken.

Complexes of the type $Ph_3P{\rightarrow}Au{-}Mn(CO)_4L$ have been prepared, where Ph ≡ phenyl, L ≡ pyridine, $AsPh_3$ or PPh_3. The carbonyl stretching frequencies for all these complexes have been studied. It has been found that the mean carbonyl stretching frequency is practically constant at about 1935 cm^{-1}. For $L \equiv P(OPh)_3$ this increases to 1969 cm^{-1}. This fact has been attributed to the greater π-bonding capacity of the $P(OPh)_3$ group competing with the CO group (Coffey, Lewis & Nyholm, 1964).

Experimental

The crystal belongs to the triclinic system. Cell constants obtained from three zero-layer Weissenberg photographs around each axis with Cu $K\alpha$ radiation are:

$$a=10·76 \pm 0·01,\quad b=10·63 \pm 0·01,\quad c=16·74 \pm 0·014\ \text{Å};$$
$$\alpha=93·6 \pm 0·1°,\quad \beta=97·0 \pm 0·1°,\quad \gamma=77·8 \pm 0·1°.$$

The observed density measured by flotation is $1·68_5$ $g.cm^{-3}$. Thus there are two molecules in the unit cell.

By the equi-inclination technique, nine layers along the a axis and three layers along the b axis were recorded, using Cu $K\alpha$ radiation. The total number of independent reflexions collected from these photographs amounted to 2760. The multiple film technique was adopted. Intensities were measured by visual comparison with an intensity scale prepared with a reflexion of the same crystal. Lorentz and polarization corrections were made. From extinctions the space group $P\bar{1}$ was assumed, and this was verified later by structure factor calculations.

The determination of the structure and refinement

Two-dimensional sharpened Patterson syntheses were calculated from $0kl$ and $h0l$ reflexions. These are shown in Figs. 1 and 2 respectively. The peak marked **a** is for the gold to gold vector, and that marked **b** is for the gold to manganese and gold to phosphorus vectors. These maps gave clear indications as to the positions of P–Au–Mn group.

On the basis of these three atomic positions, structure factors for all the reflexions were calculated. The R value was 0·62. Here, R is given by $\Sigma\,|(|F_o|-|F_c|)|/\Sigma\,|F_o|$.

Three rounds of block-diagonal isotropic least-squares refinements brought the R value down to 0·41.

Determination of the unknown part of the structure was carried out by several rounds of three-dimensional Fourier and difference Fourier syntheses. Refinement by the least-squares method was repeated until no further information could be obtained from the maps. In this way all the atoms except hydrogen were located, and the R value was reduced to 0·17 after several rounds of least-squares (block-diagonal approximations) with isotropic temperature factors.

The difference map at $R=0{\cdot}19$ revealed considerable anisotropic vibrations of the heavy and even of the lighter atoms. The crystals selected for the collection of data were sufficiently small for neglecting absorption corrections. The relative temperature factors for the heavy atoms may be fairly correct even though absorption corrections are neglected, while the temperature factors for the lighter atoms would naturally be inaccurate.

Use of anisotropic temperature factors for the heavy atoms and carbonyls brought the R value down to 0·16 in one round of least-squares. Two rounds of anisotropic least-squares for all the atoms reduced the R value to 0·14.

The atomic scattering factors used are those given in *International Tables for X-ray Crystallography* (1962). The values of $\Delta f'_j$ and $\Delta f''_j$ given by Cromer (1965) for gold, manganese, and phosphorus were used for anomalous dispersion corrections. Weights (w) used in the least-squares equations are given by

$$w = \frac{1}{1+\left\{\dfrac{|F_o|-b}{a}\right\}^2},$$

where, a and b are constants.

The value of b was so selected as to give unit weight for moderately intense reflexions, and the value of a determines the fractional weights to be given to weak and strong reflexions. Block-diagonal approximations were made in the least-squares equations.

The temperature factors are given by

$$2^{-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)}$$

In Table 1 the final atomic coordinates, and in Table 2 the corresponding thermal parameters are given. A full list of calculated and observed structure factors may be obtained from the author.

Table 1. *Fractional positional parameters*

	x	y	z
Au(1)	0·4837	0·2003	0·1656
Mn(1)	0·3034	0·2818	0·2555
P(1)	0·6510	0·1770	0·0860
P(2)	0·3380	0·1090	0·3350
O(1)	0·0830	0·4010	0·3420
O(2)	0·5060	0·4060	0·3340
O(3)	0·1680	0·1300	0·1420
O(4)	0·2390	0·4830	0·1370
O(5)	0·4590	0·0160	0·3330
O(6)	0·2370	0·0140	0·3230
O(7)	0·3510	0·1270	0·4290
C(1)	0·1720	0·3580	0·3110
C(2)	0·4260	0·3540	0·3060
C(3)	0·2230	0·1700	0·1890
C(4)	0·2720	0·3950	0·1770
C(5)	0·7530	0·0190	0·0820
C(6)	0·8810	0·0180	0·0870
C(7)	0·9610	−0·1060	0·0940
C(8)	0·9040	−0·2080	0·0750
C(9)	0·7850	−0·2080	0·0700
C(10)	0·7000	−0·0920	0·0700
C(11)	0·7510	0·2850	0·1180
C(12)	0·8330	0·3590	0·0730
C(13)	0·8940	0·4360	0·0900
C(14)	0·9130	0·4640	0·1690
C(15)	0·8410	0·4070	0·2270
C(16)	0·7720	0·3250	0·1980
C(17)	0·6010	0·2200	−0·0180
C(18)	0·5200	0·3240	−0·0300
C(19)	0·4770	0·3670	−0·1100
C(20)	0·5310	0·2830	−0·1740
C(21)	0·6180	0·1670	−0·1650
C(22)	0·6540	0·1340	−0·0770
C(23)	0·5770	0·0200	0·3400
C(24)	0·6460	0·1100	0·3680
C(25)	0·7620	0·1140	0·3820
C(26)	0·8630	0·0360	0·3660
C(27)	0·8020	−0·0540	0·3450
C(28)	0·6690	−0·0660	0·3210
C(29)	0·2450	−0·1010	0·3470
C(30)	0·3360	−0·1610	0·4170
C(31)	0·3370	−0·2790	0·4370
C(32)	0·2650	−0·3450	0·3910
C(33)	0·1860	−0·2910	0·3160
C(34)	0·1750	−0·1650	0·3010
C(35)	0·2620	0·2070	0·4740
C(36)	0·1510	0·1800	0·4920
C(37)	0·0660	0·2620	0·5330
C(38)	0·1060	0·3610	0·5630
C(39)	0·2300	0·3880	0·5460
C(40)	0·3020	0·3060	0·5010

Discussion

A view of the molecule as seen on the a face is shown in Fig. 3. The atoms are labelled following Table 1.

The molecules in the crystal are discrete. In the molecule $(C_6H_5)_3P \rightarrow Au\text{–}Mn(CO)_4P(OC_6H_5)_3$ the Mn

Table 2. *Thermal parameters* ($B_{ij} \times 10^5$)

	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Au(1)	1089	1470	577	−200	400	70
Mn(1)	1440	1460	630	−300	300	100
P(1)	1600	1000	600	−200	500	100
P(2)	2300	2000	600	100	300	500
O(1)	1100	3200	100	−20	300	2600
O(2)	1700	2300	1500	−900	−1000	1200
O(3)	2800	6000	700	−1500	−1100	−3200
O(4)	9000	2500	1000	600	300	−1400
O(5)	3500	12000	400	1300	−900	−5000
O(6)	1000	2000	1500	−1000	−200	−900
O(7)	2000	3000	1000	600	−2000	700
C(1)	1700	2000	1000	−300	−1400	−2300
C(2)	2100	1800	600	−600	500	−1300
C(3)	3000	2600	300	2000	600	−4000
C(4)	2500	3600	1100	2300	700	−600
C(5)	2000	1400	400	300	700	2000
C(6)	900	1700	600	600	1000	600
C(7)	1300	4000	900	−700	−400	1000
C(8)	2600	1500	1200	−700	700	400
C(9)	9800	3900	1000	−80	800	−8700
C(10)	5000	1300	1000	−140	−300	−2000
C(11)	1900	1400	1000	−200	−1300	2300
C(12)	2400	4000	900	−90	700	−3100
C(13)	5600	600	1600	30	−400	−1000
C(14)	4700	600	1100	−600	−2300	800
C(15)	1600	3000	1100	−700	300	−300
C(16)	2700	1400	800	−300	900	1000
C(17)	1700	1100	700	70	200	400
C(18)	4500	4500	600	−2000	900	−2700
C(19)	3800	2500	1800	100	90	−1200
C(20)	4900	6200	400	−1900	700	800
C(21)	3200	1700	1400	−600	2600	−1900
C(22)	4700	1700	400	−500	−1200	−800
C(23)	4500	90	400	70	400	2900
C(24)	1800	1500	2400	700	−2000	900
C(25)	5000	2400	400	−300	−1800	−900
C(26)	5100	5000	800	2400	1200	6000
C(27)	3500	3500	1000	50	−2200	700
C(28)	1900	3200	1000	1500	100	1000
C(29)	5100	2300	1300	300	1600	−90
C(30)	6800	3800	1000	900	500	−5800
C(31)	5500	3400	1500	−200	500	−3500
C(32)	3800	2400	1100	−400	2000	1600
C(33)	3700	2500	1000	−500	−400	−2700
C(34)	6400	2900	1100	2100	−1400	−700
C(35)	2600	3100	300	−1700	600	1000
C(36)	3100	3800	1800	3000	800	1300
C(37)	3000	9000	800	1800	700	400
C(38)	5100	2500	1400	−200	−500	1500
C(39)	3700	3500	1300	−2800	500	500
C(40)	6400	1100	700	−200	1400	300

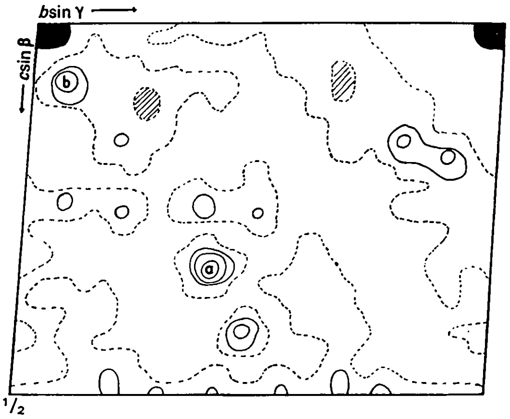

Fig. 1. Patterson projection on the *a* face.

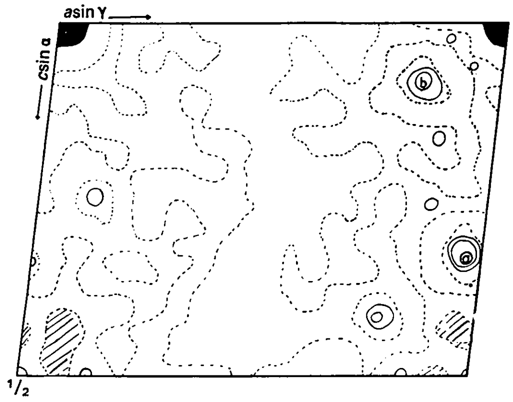

Fig. 2. Patterson projection on the *b* face.

atom is octahedrally coordinated. Each of the four CO groups and one $P(OC_6H_5)_3$ group contribute two electrons on the Mn atom, and the resultant $Mn(CO)_4$-$P(OPh)_3$ group requires just one electron to complete a closed-shell configuration. It appears that this is achieved by direct Au–Mn covalent bond formation ($d^{10}s^1 - d^7$). The P atom in the $P(C_6H_5)$ group is tetrahedrally bonded to the three C_6H_5 rings and the Au atom. The P atom in the $P(OPh)_3$ group is also tetrahedrally bonded to three O atoms and the Mn atom.

The important bond lengths and bond angles, and their estimated standard deviations (e.s.d.), are listed in Table 3. The e.s.d.'s are calculated from the equations of Cruickshank & Robertson (1953) and Darlow (1960), taking account of the variances and $\Sigma w\Delta^2$ from the last round of least-squares refinement.

Taking the radius of Cl as 0·994 Å and the Au–Cl (terminal) distance as 2·33 ± 0·03 Å (*International Tables for X-ray Crystallography*, 1962), the single covalent Au radius is expected as 1·34 ± 0·03 Å. The phosphorus radius can be derived as 1·06 ± 0·01 Å from the distances P–H, 1·43 ± 0·01 Å and H–H, 0·74 Å; the Mn radius similarly may be derived as 1·36 Å from the Mn–H distance of 1·73 Å (*Tables of Interatomic Distances and Configuration in Molecules and Ions*, 1965). Standard deviations when negligible up to the second decimal place are not quoted.

The expected single Au–Mn distance turns out to be 2·70 ± 0·03 Å; some other estimates would make it significantly larger. This expected value differs significantly from the observed Au–Mn distance of 2·57 ± 0·01 Å. This observed Au–Mn distance agrees with the Au–Mn distance of 2·52 ± 0·03 Å found in the complex $(C_6H_5)_3P \rightarrow Au\text{-}Mn(CO)_5$ (Powell, Mannan, Kilbourn & Porta, 1964). This suggests that the Au–Mn bond is multiple in nature. Diamagnetism and the short Au–Mn distance suggest a metal to metal bonding in the present complex.

The expected Au–P distance is 2·40 ± 0·03 Å. The Au–P bond of length 2·33 ± 0·01 Å is possibly multiple

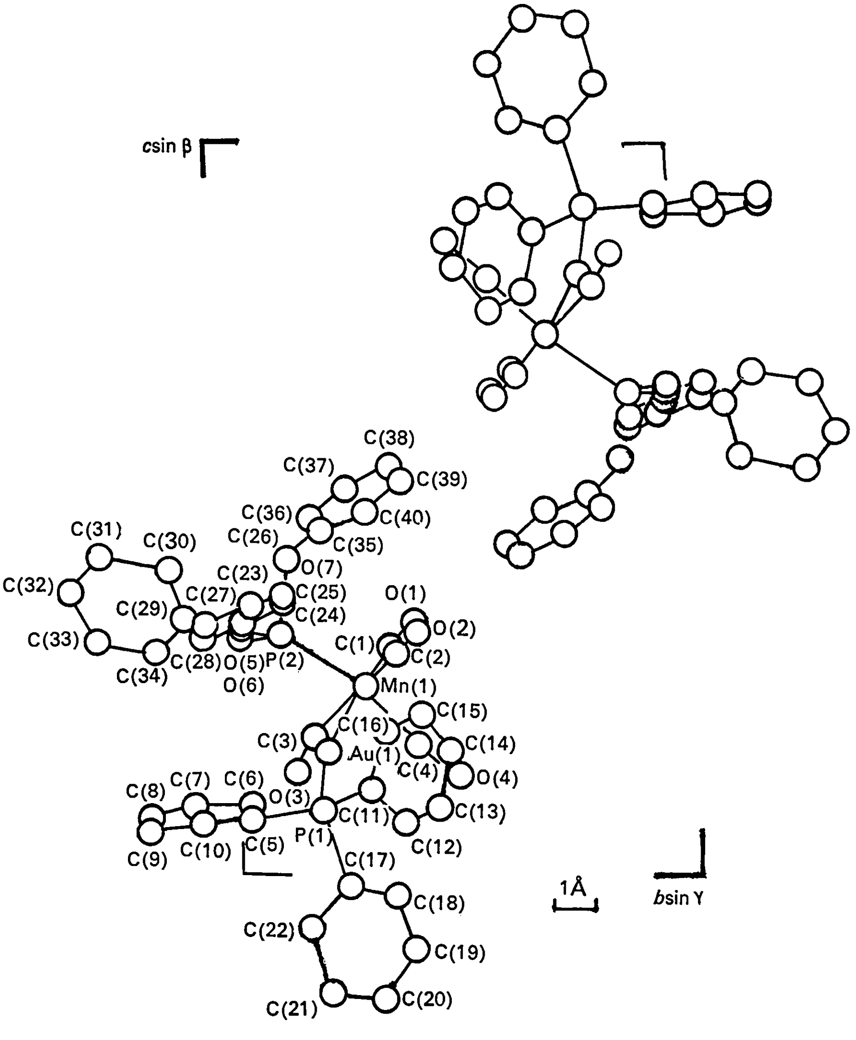

Fig. 3. Projection of the structure along the *a* axis.

Table 3. *Important bond lengths, bond angles, and e.s.d.'s*

Au(1)–Mn(1)	2·573 ± 0·007 Å
Au(1)–P(1)	2·33 ± 0·01
Mn(1)–P(2)	2·27 ± 0·02
Mn(1)–C(1)	1·81 ± 0·06
Mn(1)–C(2)	1·78 ± 0·05
Mn(1)–C(3)	1·76 ± 0·05
Mn(1)–C(4)	1·16 ± 0·07
O(1)–C(1)	1·13 ± 0·06
O(2)—C(2)	1·15 ± 0·06
O(3)—C(3)	1·17 ± 0·06
O(4)—C(4)	1·16 ± 0·07
P(1)—C(5)	1·79 ± 0·05
P(1)—C(11)	1·76 ± 0·05
P(1)—C(17)	1·78 ± 0·05
P(2)—O(5)	1·46 ± 0·06
P(2)—O(6)	1·62 ± 0·03
P(2)—O(7)	1·57 ± 0·04
Mn(1)–Au(1)–P(1)	166·5 ± 0·3°
Au(1)–Mn(1)–C(1)	172·5 ± 1·8
Au(1)–Mn(1)–C(2)	78·9 ± 1·5
Au(1)–Mn(1)–C(3)	77·0 ± 1·6
Au(1)–Mn(1)–C(4)	76·0 ± 1·7

in nature. The Au–P distance of 2·21 ± 0·04 Å found in the complex $(C_6H_5)_3P \rightarrow Au–Mn(CO)_5$ differs significantly from the value found in this complex.

The single covalent Mn–P distance should be 2·42 ± 0·01 Å. The observed Mn–P distance of 2·27 ± 0·02 Å differs significantly from the expected single covalent distance at the 0·1% level of significance. This indicates that the observed Mn–P bond is multiple in nature, the $P(OC_6H_5)_3$ group competing with the carbonyl groups in π-bonding.

The P–Au–Mn angle of 166·5 ± 0·3° in the present complex and that of 168 ± 1° in $Ph_3P \rightarrow Au–Mn(CO)_5$ do not differ significantly at the 5% level of significance. Such distortion in the P–Au–Mn bond angle has been found from various complexes of a similar nature. No explanation can be put forward.

In the complex studied, and in similar metal carbonyls, *e.g.* $(C_6H_5)_3P \rightarrow Au–Mn(CO)_5$, $(C_6H_5)_2Sn[Mn(CO)_5]$, (Powell, Mannan, Kilbourn & Porta, 1964), and $Mn_2(CO)_{10}$ (Dahl & Rundle, 1963) the carbonyl groups on the plane perpendicular to the metal to metal bond direction are in a staggered configuration. Taking the metal to metal bond direction along the Z axis, the carbonyl groups on the Z plane may be called the equatorial carbonyls. In the first two complexes studied by Powell *et al.*, the equatorial carbonyls are bent towards the metal to metal bond direction; whereas in $Mn_2(CO)_{10}$ these are bent away. It has been suggested by Mason & Bennett (1965) that mixing of p-character with the non-bonding d_{xz} and d_{yz} orbitals decreases the repulsion between orbitals. The repulsion between the non-bonded carbonyl groups, while playing an important role in $Mn_2(CO)_{10}$, is completely absent in the complexes $Ph_3P \rightarrow Au–Mn(CO)_5$, $Ph_3P \rightarrow Au–Mn(CO)_4P(OPh)_3$ and $Ph_2Sn[Mn(CO)_5]$. Mixing greater p-character with the non-bonding d_{xz} and d_{yz} orbitals decreases repulsion between non-bonding orbitals, and the metal to metal bond is stabilized. Unlike $Mn_2(CO)_{10}$, the metal to metal bonds in all these complexes may be expected to be shorter as there is no repulsion between the non-bonded equatorial carbonyl groups. The metal to metal bonds in all these complexes except $Mn_2(CO)_{10}$ are rather shorter than expected single-bond lengths. In $Ph_2Sn[Mn(CO)_5]$, the Sn–Mn bond length of 2·70 ± 0·01 Å is multiple in nature.

In $Ph_3P \rightarrow Au–Mn(CO)_4P(OPh)_3$ the phosphorus of the phenoxyl group is bent away from the metal to metal bond direction. This appears to be due to steric hindrance of the large phenoxyl group.

My thanks are due to Prof. H. M. Powell for his guidance during the course of this work. All the computations were done at Oxford on the Ferranti Computer. Prof. R. S. Nyholm kindly supplied the crystals for X-ray investigation.

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