Crystal Structures of Iodo(triphenylphosphine)gold(I) and Bis[iodo(trimethylphosphine)gold(I)]

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The structures of the title compounds have been determined at room temperature with a four-circle X-ray diffractometer. Both compounds are orthorombic, the space groups being $P2_12_12_1$ and $Pnca$, respectively. The triphenylphosphine compound is composed of discrete complexes $Au(Ph_3P)I$, with P–Au–I almost linearly arranged; the compound is isostructural with the analogous chloro and cyano complexes. In the trimethylphosphine compound, the $Au(Me_3P)I$ units form dimers by metal–metal interaction [Au–Au distance =3.168(1) Å]. Both structures are completely different from those of the stoichiometrically analogous pyridine and tetrahydrothiophene complexes of gold(I) iodide.

The halido(tetrahydrothiophene)gold(I) compounds $Au(THT)X$ (X = Cl, Br or I) all possess structures containing infinite arrays of gold atoms. In the chloride and bromide compounds which are isostructural,[1] mixed neutral complexes $[Au(THT)X]°$ are present, while in the iodide[2] cationic solvates $Au(THT)_2^+$ and AuI_2^- anions alternate along the chain. All these units are linear. In chloro(triphenylphosphine)gold(I), on the other hand, the neutral linear $Au(Ph_3P)Cl$ molecules are well separated.[3] Moreover, a preliminary investigation has indicated that the iodo complex $Au(Ph_3P)I$ is isostructural with the chloro complex.[4] The structural conditions thus seem to be different in the formally analogous tetrahydrothiophene and phosphine series of gold(I) halido complexes. It was therefore of interest to carry out a complete structure determination on $Au(Ph_3P)I$, and also to investigate whether an aliphatic phosphine provokes a structure different from that with the aromatic Ph_3P. To this end, the structures of the two title compounds have been determined.

Experimental

The compounds were prepared according to published methods.[5,6] Single crystals were obtained from dichloromethane solutions by slow addition of diethyl ether and cooling to 0 °C. Both compounds are stable at room temperature.

An Enraf-Nonius CAD-4 four-circle single crystal diffractometer was used for all X-ray diffraction measurements. The unit cell dimensions were refined by a least-squares treatment of 25 θ-values determined as $\theta_{hkl} = (\omega_{hkl} - \omega_{\bar{h}\bar{k}\bar{l}})/2$. The intensities were measured with the ω–2θ scan technique. The scan interval was extended 25 % at both ends for the background measurements. Three standard reflections were recorded every hour; no systematic variation in their intensities was observed. The values of I and $\sigma_c(I)$ were corrected for Lorentz, polarization and absorption effects [$\sigma_c(I)$ is based on counting statistics]. The transmission factors were evaluated by numerical integration.

Both compounds belong to Laue class mmm. The systematic extinctions indicated the orthorombic $P2_12_12_1$ and $Pnca$ as possible space groups for the triphenylphosphine and the trimethylphosphine compound, respectively.

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Table 1. Summary of crystal and intensity data. Results of the least-squares refinements.

Compound	[AuI{P(CH_3)_3}]_2	[AuI{P(C_6H_5)_3}]
mol. wt.	399.95	586.16
Space group	Pnca	P2_12_12_1
a/Å	11.615(2)	10.182(2)
b/Å	11.641(2)	12.536(4)
c/Å	12.031(3)	13.872(2)
V/Å³	1626.6(4)	1770.5(4)
Z	4 (dimers)	4
D_x/g cm^{-3}	3.28	2.20
Crystal size/mm	0.36×0.15×0.10	0.17×0.26×0.12
Radiation (graphite monochromatized)	MoKα	MoKα
θ-interval/°	3–28	3–25
ω-2θ scan width, Δω/°	0.6+0.5 tan θ	0.7+0.5 tan θ
σ(I)/I required in a scan	0.030	0.028
Maximum recording time/s	180	150
μ/cm^{-1}	218.9	100.8
Range of transmission factor	0.0511–0.1565	0.2726–0.3696
Number of measured reflections	1946	3159
Number of refl. with zero weight ($I < 2\sigma(I)$)	715	516
Number of refl. used in the final refinements, m	1231	2643
Number of parameters refined, n	40	190
C1 in weighting function	0.04	0.017
C2 in weighting function	0.5	1.0
$R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$	0.042	0.027
$R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$	0.056	0.031
$S = [\Sigma w(|F_o|-|F_c|)^2/(m-n)]^{1/2}$	1.12	0.99
δR-plot, slope	0.97	1.12
δR-plot, intercept	−0.07	−0.06

The structure of the triphenylphosphine complex was solved by Patterson and difference – Fourier methods, and that of the trimethylphosphine complex by direct methods[7] and difference – Fourier synthesis.

Full matrix least-squares refinement minimizing $\Sigma w(|F_o|-|F_c|)^2$ with weights $w^{-1} = \sigma_c^2/4|F_o|^2 + C1|F_o|^2 + C2$ was performed. All non-hydrogen atoms except the carbon atoms in trimethylphosphine were refined anisotropically. For the triphenylphosphine compound, the positions of the H atoms were calculated from geometrical criteria (C–H distance =0.95 Å) and included in the structure factor calculations before the last cycles of refinement. Neither positional nor temperature parameters ($U_{iso} = 0.08$ Å) were refined for the H atoms. Scattering factors with corrections for anomalous dispersion were taken from Ref. 8. For Au(Ph₃P)I, both absolute configurations were tested against the data. A better fit is obtained with the model of Table 2 than with the mirror related model ($R = 0.061$, $R_w = 0.079$). Computer programs used were those compiled and amended by Lundgren.[9] Tables of $|F_o|$, $\sigma(|F_o|)$, $|F_c|$ and anisotropic temperature factors are available on request from the authors.

Crystal data and information on the collection and reduction of the intensity data sets, as well as on the subsequent refinements, are collected in Table 1. The final positional parameters are listed in Table 2, and selected interatomic distances and angles in Table 3.

Description and discussion of the structures

It has been confirmed that iodo(triphenylphosphine)gold(I) (Fig. 1) is isostructural with the analogous chloro complex.[3,4] Contrary to what has been found previously for the formally analogous THT complexes, the structure of the iodo complex thus does not differ from that of the

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Table 2. Final positional and thermal parameters for the non-hydrogen atoms. Estimated standard deviations in the last significant digit(s) are given in parentheses.

Atom	x/a	y/b	z/c	$U_{iso}^{a} \cdot 10^2/\text{Å}^2$
Bis[iodotrimethylphosphinegold(I)]				
Au	0.14375(5)	0.08534(5)	0.14846(4)	0.0418(2)
I	0.02878(9)	−0.05803(8)	0.26897(9)	0.0551(3)
P	0.23129(30)	0.21641(29)	0.03919(27)	0.0407(10)
C1	0.1343(14)	0.2942(16)	−0.0534(14)	0.066(4)
C2	0.3052(13)	0.3312(14)	0.1156(13)	0.054(3)
C3	0.3376(12)	0.1567(15)	−0.0532(14)	0.058(4)
Iodotriphenylphosphinegold(I)				
Au	0.66527(3)	0.42807(3)	0.73796(2)	0.0418(1)
I	0.90018(6)	0.48647(5)	0.70125(5)	0.0516(2)
P	0.46024(22)	0.37437(16)	0.77387(16)	0.0398(7)
C10	0.3467(8)	0.4846(7)	0.7957(6)	0.044(3)
C11	0.3297(10)	0.5572(7)	0.7224(7)	0.057(3)
C12	0.2431(11)	0.6446(7)	0.7361(9)	0.065(4)
C13	0.1806(10)	0.6565(8)	0.8208(10)	0.068(4)
C14	0.1987(11)	0.5857(10)	0.8952(10)	0.077(5)
C15	0.2834(10)	0.5006(9)	0.8824(8)	0.062(4)
C20	0.3811(8)	0.2947(7)	0.6799(6)	0.039(3)
C21	0.2476(10)	0.2957(8)	0.6689(7)	0.056(4)
C22	0.1893(11)	0.2323(10)	0.6003(8)	0.068(4)
C23	0.2634(13)	0.1668(9)	0.5445(8)	0.068(5)
C24	0.3975(13)	0.1655(8)	0.5546(8)	0.062(4)
C25	0.4566(10)	0.2298(8)	0.6236(7)	0.051(3)
C30	0.4570(9)	0.2900(7)	0.8804(6)	0.041(3)
C31	0.3855(10)	0.1984(8)	0.8849(6)	0.054(4)
C32	0.3880(12)	0.1345(8)	0.9659(8)	0.065(4)
C33	0.4652(13)	0.1631(9)	1.0435(7)	0.070(4)
C34	0.5395(14)	0.2553(11)	1.0396(8)	0.083(5)
C35	0.5358(12)	0.3179(9)	0.9588(8)	0.072(4)

[a]These values have been calculated from the average of the anisotropic temperature factors, except for C1, C2 and C3 which were refined isotropically.

Table 3. Selected interatomic distances (Å) and angles (°), with estimated standard deviations in the last digit given in parentheses. A primed atom denotes a transformation $^1/_2-x$, $−y$, z.

A. Coordination geometry around the gold and phosphorus atoms

Bis[iodotrimethylphosphinegold(I)]

Au–Au'	3.168(1)	Au'–Au–I	89.86(3)
Au–I	2.583(1)	Au'–Au–P	94.19(9)
Au–P	2.256(3)	I–Au–P	175.65(9)
P–C1	1.83(2)	Au–P–C1	114.4(6)
P–C2	1.84(2)	Au–P–C2	114.3(5)
P–C3	1.80(2)	Au–P–C3	114.1(6)
		C1–P–C2	103.5(8)
		C1–P–C3	103.8(8)
		C2–P–C3	105.6(7)

Iodotriphenylphosphinegold(I)

Au–I	2.553(1)		
Au–P	2.249(2)	I–Au–P	178.46(6)
P–C10	1.827(9)	Au–P–C10	113.5(3)
P–C20	1.829(8)	Au–P–C20	114.5(3)
P–C30	1.817(9)	Au–P–C30	111.9(3)
		C10–P–C20	104.6(4)
		C10–P–C30	107.1(4)
		C20–P–C30	104.7(4)

B. Carbon–carbon distances in the phenyl rings of iodotriphenylphosphinegold(I)

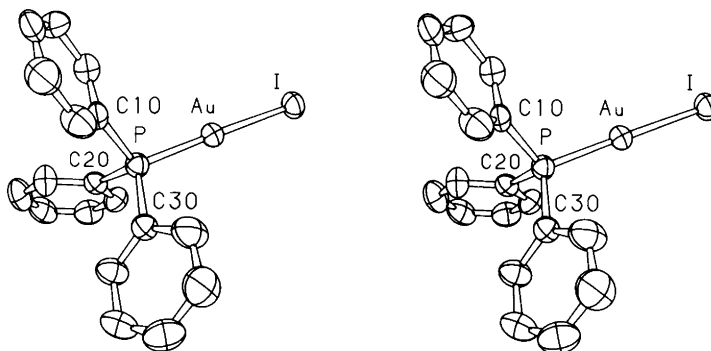|					
C10–C11	1.38(1)	C20–C21	1.37(1)	C30–C31	1.36(1)
C11–C12	1.42(1)	C21–C22	1.38(2)	C31–C32	1.38(1)
C12–C13	1.35(2)	C22–C23	1.36(2)	C32–C33	1.38(1)
C13–C14	1.37(2)	C23–C24	1.37(2)	C33–C34	1.38(2)
C14–C15	1.38(2)	C24–C25	1.39(2)	C34–C35	1.37(2)
C15–C10	1.38(1)	C25–C20	1.37(1)	C35–C30	1.40(1)

Fig. 1. A stereoscopic view of the coordination around gold in the triphenylphosphine compound.

chloro (and, most probably, the bromo complex). Furthermore, the cyano complex of this series is, in fact, isostructural with the halido species.[10] All these compounds have structures containing well-separated Au(Ph₃P)X units; in the iodide compound, the shortest Au–Au distances are 7.12 and 7.37 Å.

The coordination around gold(I) is practically linear for the iodide and chloride compounds; the angle P–Au–X is very close to 180° (Table 3, Ref. 3). In the cyanide compound, a larger deviation has been reported (angle P–Au–C = 169°). For the triethylphosphine cyano complex, however, the coordination has been found to be almost linear[11] (angle P–Au–C = 176.6°). One reason for this difference may be that it is notoriously difficult to locate the light carbon atom in the vicinity of the heavy gold atom. In the triphenylphosphine complexes, the Au–P distances

seemingly increase in the sequence chloride (2.23 Å) < iodide (2.25 Å) < cyanide (2.27 Å), i.e. in the order of increasing softness of the ligand X. Evidently, this reflects a weakening of the Au–P bond with increasing competition from X for the bonding capacity of the gold atom.

In the structure of the trimethylphosphine compound, on the other hand, the Au(Me₃P)I units are arranged in dimers, most probably held together by a weak Au–Au bond of length 3.168(1) Å; there are no bridging ligands. In the dimer, the two I–Au–P moieties are arranged so that the least-squares planes through Au', Au, P and I, and through Au, Au', P' and I' are at an angle of 69.7(6)° (Fig. 2). The Au–Au' distance is within the range 2.97–3.35 Å found in the chains of the gold(I)–THT complexes referred to above.[1,2] In other structures in which gold atoms are close (without being joined by bridging li-
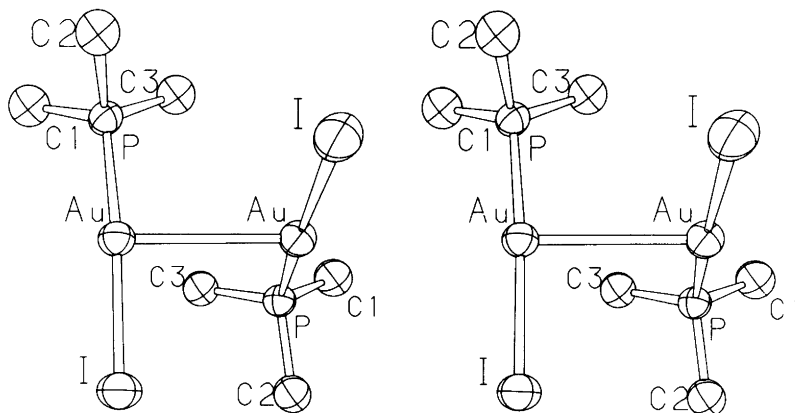

Fig. 2. A stereoscopic view of the coordination around gold in the trimethylphosphine dimer, showing the gold–gold bond. Half of the atoms correspond to the symmetry transformation ½ − x, −y, z.

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gands), as e.g. in the pyridine compounds[12,13] Au
(py)₂ClO₄ and Au(py) X (X = Cl, Br or I), the
Au–Au distances are within this range, or are
·slightly longer.

Strong evidence that an Au–Au interaction in-
deed occurs is also provided by the observation
that the Au–I bond is significantly longer than in
the monomeric triphenylphosphine complex
(Table 3). This is to be expected if the gold atom
has a higher coordinatin number in the dimeric
trimethylphosphine complex. Furthermore, the
I–Au–P configuration is more bent in the dimer
and in such a direction as would be expected if an
Au–Au bond really exists in this compound. A
comparable lengthening of Au–I bonds by gold–
gold interactions is found in the iodo–THT com-
plex.[2] In the AuI_2^- present in this compound, the
Au–I bond-length is 2.565(2) Å, while in the
tetra-n-butylammonium salt[14] of AuI_2^-, in which
no such special interactions occur, the Au–I bond
length is 2.529(1) Å. The Au–P bond is also
longer in the dimeric phosphine than in the
monomeric one, although the difference is slight.
The length of this bond is evidently also influen-
ced by the donor strength of the phosphorous
atom, which is higher in the aliphatic phosphine
than in the aromatic one.[15] This tends to compen-
sate for the lengthening of the Au–P bond due to
dimerization.

The trimethylphospine complex thus provides
another example of an compound in which an
Au–Au interaction results in a dimer. Several
such compounds were discussed in a theoretical
study by Jiang, Alvarez and Hoffmann,[16] who
concluded that a bond, although weak, may be
formed by mixing of s, p_z and d_{x^2} orbitals. In these
calculations, however, all the dimers considered
have the gold atoms joined also by two ligand
bridges. In our compound, in which no such
bridges exist, the Au–Au bond is, of course, im-
perative for the formation of the dimer. In the
compound $[Au_2\{S_2P(OC_3H_7)_2\}_2]_\infty$, however, in
which bridged dimers are joined to a chain only
by Au–Au bonds,[16,17] the conditions for the inter-
dimeric bonds are much the same as in our dimer,
although the distances are somewhat shorter, viz.
3.05 and 3.11 Å.

The reason why dimers are not formed for any
of the triphenylphosphine complexes discussed
above might simply be that the larger bulk of the
ligand prevents the gold atoms from coming
within bonding range.

For both phosphines, the C–P–C angles are sig-

nificantly larger in the complexes than in the free
ligands (Table 3; Refs. 18 and 19). This is evi-
dently a consequence of the donation of the free
electron pair on P to the metal acceptor. Other-
wise the phosphine ligands have their normal
geometries; not even the lengths of the P–C
bonds are significantly changed.

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