Crystal structures of chloro(trimethylphosphine)gold(I), chloro(tri-^{i}propylphosphine)gold(I) and bis(trimethylphosphine)gold(I) chloride *

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Abstract

The crystal structures of chloro(trimethylphosphine)gold(I), chloro(tri-^{i}propylphosphine)gold(I) and bis(trimethylphosphine)gold(I) chloride · 2CHCl$_3$ have been determined by single crystal X-ray diffraction studies. The monomeric units of the molecular complexes (Me$_3$P)AuCl (1) and (^{i}Pr$_3$P)AuCl (2) have linear P–Au–Cl axes. However, the monomers of (Me$_3$P)AuCl are aggregated to form a helical chain through fairly short alternating Au $\cdots$ Au contacts of 327.1(1), 335.6(1), and 338.6(1) pm and Au–Au–Au angles of 141.6(1), 141.8(1) and 141.9(1)°. By contrast, the monomers of compound 2 show no such Au $\cdots$ Au contacts in the lattice. This distinction between the two structures of the two analogous species is attributed to the different steric requirements of the phosphines. The crystals of bis(trimethylphosphine)gold(I) chloride (3) · 2CHCl$_3$ consist of layers of (Me$_3$P)$_2$AuCl complexes separated by layers of solvent molecules. The P–Au–P coordination is almost linear, with a chlorine atom at right angles (Au–Cl = 316.7(1) pm, Cl–Au–P = 92.3(1)°).

Key words: Gold; Phosphine; Chloride; Crystal structure

1. Introduction

Halido(phosphine)gold(I) complexes are amongst the most stable coordination compounds of univalent gold. They attracted considerable interest as starting materials for sulfido(phosphine)gold(I) compounds, the most potent drugs for the treatment of rheumatoid arthritis [1]. Since the 1980s (2,3,4,6-tetraacetyl-1-thioglucosyl)-(triethylphosphine)gold(I) has been used under the trade mark Auranofin™ as a cure for rheumatic diseases.

On the basis of only a limited amount of structural data, it has been tacitly assumed that R$_3$PAuX compounds are monomers with a linear coordination geometry at the gold atoms. Though this is true for a few compounds with large or medium-sized phosphine ligands, very recent studies have shown, that short intermolecular Au $\cdots$ Au contacts, representing weak sec-

ond order metal–metal bonding, can lead to an aggregation of the monomeric units into a whole range of structural motifs, including dimers [2–5], tetramers [6] or even polymers [7,8].

The important prerequisite for this novel type of aggregation ("aurophilicity") is the presence of structurally non-demanding ligands R$_3$P and X. Any overcrowding of the molecules can prevent the Au $\cdots$ Au contacts with their rather small bond energies. The latter have been estimated to be of the order of 6–9 kcal/mole from studies of binuclear gold(I) complexes of 1,1'-bis(diphenylphosphino)bicyclopropyl, 2,3-bis(diphenylphosphino)-1,3-butadiene and bis(diphenylphosphino)methylene-trimethylphosphorane [9]. This value is comparable with that for hydrogen bonding.

The AuX complexes for which extended aggregation has been detected are those of the primary phosphine 2-MeC$_6$H$_4$PH$_2$ (X = Br) [8] and of the smallest tertiary phosphine, Me$_3$P (X = CN) [7]. With the somewhat larger phosphines 2,4,6-(Me$_3$C)$_3$C$_6$H$_2$PH$_2$ (X = Cl) [3], Ph$_2$PH (X = Br) [4] and (CH$_2$)$_6$N$_3$P (X = Cl) [5] dimers (LAuX)$_2$ are observed in the crystals, while

complexes with standard phosphines with larger cone angles such as Et_3P, $^tBu_2PH$ and Ph_3P, have a monomeric structure [10–12]. The aggregation of the LAuX monomers can occur with the P–Au–X moieties parallel (head-to-tail, or head-to-head) [3,4,8] or in a crossed fashion (perpendicular) [2,5,8]. In the extended structures these modes of association can appear together as structural motifs of helical or zig-zag frameworks.

Chloro(trimethylphosphine)gold(I) is not only a very simple prototype of the R_3PAuX family, but also an important starting material for gold cluster chemistry [13]. Based on the evidence outlined above, we expected this standard compound also to exhibit an extended association in the solid state, which could shed further light on the general principles governing the auriophilicity phenomenon, and we therefore set out to determine its structure, together with that of the related 2:1 complex, another valuable synthon in gold coordination chemistry. Chloro(tri-^{i}propylphosphine)-gold(I) was also included, because it should provide a simple monomeric reference structure owing to the bulk of its ligand.

2. Experimental details

All experiments were carried out under dry, pure nitrogen. Solvents were dried and saturated with nitrogen. NMR-spectrometers: Jeol GX 400 and GX 270.

Chloro(trimethylphosphine)gold(I) (1) and bis(trimethylphosphine)gold(I) chloride (3) were made as previously described [14]. Chloro(tri-^{i}propylphosphine)gold(I) (2) was prepared by the procedure previously described for analogous compounds, *i.e.* by treating a methanolic solution of tetrachlorogold(III) acid with tri-^{i}propylphosphine [15]. Single crystals were grown from methylene chloride (1) or chloroform (2 and 3), respectively.

2.1. Spectroscopic data

2.1.1. Chloro(trimethylphosphine)gold (1)
^{1}H-NMR (400 MHz, $CDCl_3$, 25°C): $\delta = 1.6$ ppm (d, $^2J_{PH} = 11.3$ Hz). ^{13}C-NMR (100.54 MHz, $CDCl_3$, 25°C): $\delta = 16.1$ (q/d, $^1J_{PC} = 40.4$, $^1J_{CH} = 131.0$ Hz). ^{31}P{^{1}H}-NMR (161.83 MHz, $CDCl_3$, 25°C): $\delta = -9.7$ (s).

2.1.2. Chloro(tri-^{i}propylphosphine)gold(I) (2)
^{1}H-NMR (400 MHz, $CDCl_3$, 25°C): $\delta = 1.3$ (CHCH_3, d/d, $^3J_{PH} = 16.5$, $^3J_{HH} = 7.3$ Hz), 2.3 (CHCH$_3$, d/sept, $^2J_{PH} = 9.5$, $^3J_{HH} = 7.3$ Hz). ^{13}C{^{1}H}-NMR (100.54 MHz, $CDCl_3$, 25°C): $\delta = 24.2$ (PC, d, $^1J_{PC} = 31.3$ Hz), 20.4 (CH$_3$, s). ^{31}P{^{1}H}-NMR (161.83 MHz, $CDCl_3$, 25°C): $\delta = 64.8$ (s).

2.1.3. Bis(trimethylphosphine)gold(I) chloride (3)
^{1}H-NMR (400 MHz, $CDCl_3$, 25°C): $\delta = 1.6$ (s). ^{31}P{^{1}H}-NMR (161.83 MHz, $CDCl_3$, 25°C): $\delta = 3.4$ (s).

2.2. Crystal and structure solution data

1, C_3H_9AuClP: $0.02 \times 0.05 \times 0.40$ mm, $M_r = 308.49$, triclinic, $a = 9.142(1)$, $b = 9.271(1)$, $c = 13.586(1)$ Å, $\alpha = 79.12(1)$, $\beta = 76.34(1)$, $\gamma = 74.93(1)°$, space group $P\bar{1}$ (No. 2), $V = 1065.1$ Å^3, $Z = 6$, $D_c = 2.858$ g cm^3, $T = 25°$C, μ(Mo–Kα) = 212.0 cm^{-1}, λ(Mo–Kα) = 0.71069 Å, CAD4 diffractometer, 4176 reflections measured, 3545 unique, and 2725 observed [$F_0 \geq 4\sigma(F_0)$]; empirical absorption correction applied. Structure solution by direct methods, with missing non-hydrogen atoms located by successive difference Fourier syntheses; refinement of 164 parameters converged at $R = 0.037$ ($R_w = 0.033$) ($R = [\Sigma \parallel F_0 \mid - \mid F_c \parallel /\Sigma \mid F_0 \mid]$, $R_w = [\Sigma w(\mid F_0 \mid - \mid F_c \mid)^2/\Sigma w \mid F_0 \mid^2]^{1/2}$ with $w = [\sigma^2(F_0) + 0.000283 \ F_0^2]^{-1}$), including hydrogens in fixed idealized positions; maximum and minimum residual electron densities in the difference Fourier map were 0.95 and -1.31 e Å^{-3}, respectively.
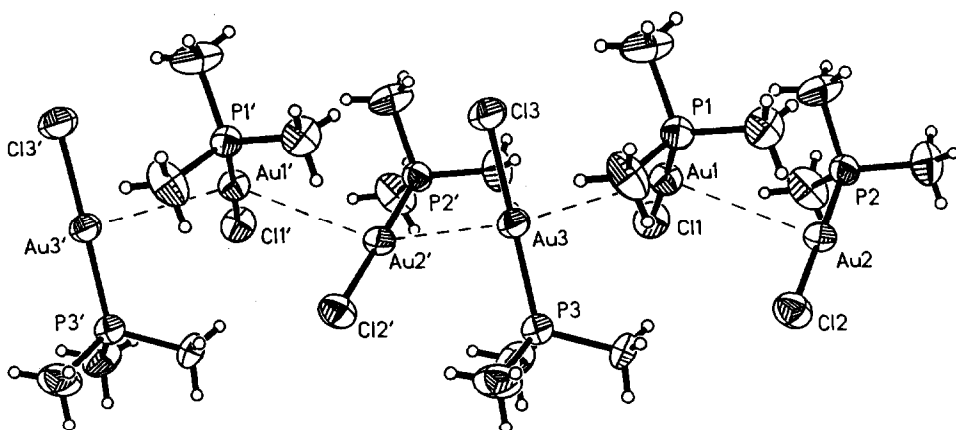

Fig. 1. Section of the helical chain-structure of chloro(trimethylphosphine)gold(I).

2, $C_9H_{21}AuClP$: $0.15 \times 0.30 \times 0.35$ mm, $M_r = 392.64$, orthorhombic, $a = 14.885(1)$, $b = 7.562(1)$, $c = 11.528(2)$ Å, space group $Pna2/_1$ (No. 33), $V = 1297.6$ Å^3, $Z = 4$, $D_c = 2.010$ g cm^{-3}, $T = 25°$ C, μ(Mo − Kα) $= 116.2$ cm^{-1}, λ(Mo − Kα) $= 0.71069$ Å, CAD4 diffractometer, 2816 reflections measured, 2617 unique, and 2289 observed [$F_o \geq 4\sigma(F_o)$]; empirical absorption correction applied. Structure solution by direct methods, with missing non-hydrogen atoms located by successive difference Fourier syntheses; carbon atoms refined with isotropic thermal parameters using a split model for one carbon site half occupied (SOF = 0.5). Refinement of 67 parameters converged at $R = 0.037$ ($R_w = 0.044$) ($R = [\Sigma \| F_o | - | F_c \| / \Sigma | F_o |]$, $R_w = [\Sigma w (| F_o | - | F_c |)^2 / \Sigma w | F_o |^2]^{1/2}$ with $w = [\sigma^2(F_o) + 0.006740 \ F_o^2]^{-1}$); attempted structure solution and refinement in space group Pnam proved unsuccessful; maximum and minimum residual electron densities in the difference Fourier map were 1.10 and −2.66 e Å^{-3}, respectively.

3 · 2CHCl$_3$, $C_8H_{20}AuCl_7P_2$: $0.20 \times 0.30 \times 0.40$ mm, $M_r = 623.98$, tetragonal, $a = 9.394(1)$, $b = 9.394(1)$, $c = 11.909(2)$ Å, space group $P4^-$(No. 81), $V = 1051.0$ Å^3, $Z = 2$, $D_c = 1.972$ g cm^{-3}, $T = -71°$ C, μ(Mo − Kα) $= 76.4$ cm^{-1}, λ(Mo − Kα) $= 0.71069$ Å, CAD4 diffractometer, 5904 reflections measured, 5677 unique, and 5307 observed [$F_o \geq 4\sigma(F_o)$]; empirical absorption correction applied. Structure solution by direct methods, with missing non-hydrogen atoms located by successive difference Fourier syntheses; hydrogen atoms of the solvate molecules included in fixed idealized positions, the disordered trimethylphosphine group refined with isotropic thermal parameters for carbon atoms using a split model with carbon sites partially occupied (SOF = 0.33). Refinement of 94 parameters converged at $R = 0.033$ ($R_w = 0.034$) ($R = [\Sigma \| F_o | - | F_c \| / \Sigma | F_o |]$, $R_w = [\Sigma w (| F_o | - | F_c |)^2 / \Sigma w | F_o |^2]^{1/2}$ with $w = [\sigma^2 (F_o) + 0.000552 \ F_o^2]^{-1}$); maximum and minimum residual electron densities in the difference Fourier map were 2.47 and −8.63 e Å^{-3}, respectively.

Supplementary data for all three structures have been deposited at the Cambridge Crystallographic Data Centre.

3. Description and discussion of the structures

3.1. The complexes R_3PAuCl (R = Me (1); R = ^{i}Pr (2))

The asymmetric unit in the crystals of chloro(trimethylphosphine)gold(I), **1**, contains three crystallographically independent molecules. These units are not fully separated *i.e.* with only standard van der Waals interactions between the molecules, but show an aggregation via Au ··· Au contacts to form a polymeric chain-structure. Clearly the short gold-gold contacts
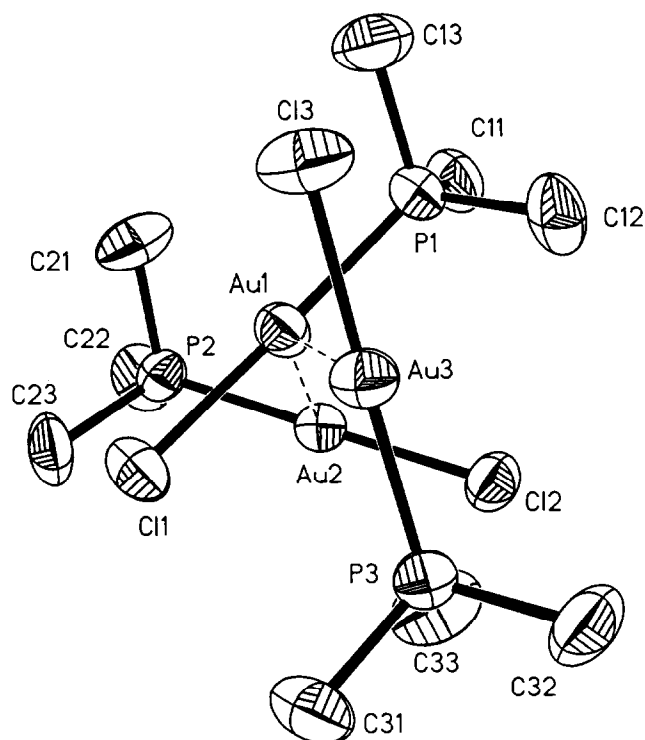

Fig. 2. A sequence of molecules 1 projected in the direction of the polymeric chain.

represent conformation-determining forces, which have a marked influence on the arrangements of the complex molecules in the lattice.

Along the chain, the P–Au–Cl axes of monomeric molecules are ordered in a crossed way, with dihedral angles P3–Au3–Au1–P1, P2–Au2–Au1–P1 and P2'–Au2'–Au3–P3 at 143.3, 141.7 and 137.6°, respectively. The angles formed by triples of adjacent gold atoms (Au3–Au1–Au2, Au2–Au3–Au1 and Au1–Au2–Au3) have nearly identical values of 141.8(1), 141.9(1) and 141.6(1)°, respectively. This is also true for the distances Au ··· Au (Au1–Au3, Au1–Au2 and Au2'–Au3), which are found in the narrow range of 327.1(1), 335.6(1) and 338.6(1) pm, respectively. By crystallographically-imposed symmetry, the chains are helical, with both rotatory directions present in the lattice, and also related by symmetry.

The Au–Cl and Au–P distances are in the range found for standard reference compounds. The three trimethylphosphine groups have an approximate threefold symmetry, and the environment of the phosphorus atoms is quasi-tetrahedral, with P–C distances of about 180 pm. The angles of the gold atoms (P–Au–Cl) are all close to linear. Selected values are listed in Table 1.

The structure of **1** closely resembles that of cyano-(trimethylphosphine)gold(I) [7], which also shows a

TABLE 1. Selected distances [pm] and angles [°] in (Me₃P)AuCl, **1**

Au1–P1	223.3(3)	C11–Au1–P1	177.5(2)
Au2–P2	223.4(4)	C12–Au2–P2	179.4(1)
Au3–P3	223.3(3)	C13–Au3–P3	178.4(2)
Au1–C11	230.6(4)	Au1′–Au2′–Au3	141.6(1)
Au2–C12	231.0(4)	Au2–Au1–Au3	141.8(1)
Au3–C13	231.0(1)	Au2′–Au3–Au1	141.9(1)
Au1–Au2	335.6(1)	P3–Au3–Au1–P1	143.3
Au1–Au3	327.1(1)	P2–Au2–Au1–P1	141.7
Au2′–Au3	338.6(1)	P2′–Au2′–Au3–P3	137.6

TABLE 2. Selected bond distances [pm] and angles [°] in (ᶦPro₃P)AuCl, **2**

Au–P	223.9(2)	Cl–Au–P	178.0(2)
Au–Cl	228.4(3)	C11–P–Au	113.5(3)
P–C11	183(1)	C21–P–Au	109.0(7)
P–C21	189(2)	C311–P–Au	115.2(7)
P–C311	183(2)	C312–P–Au	107.8(7)
P–C312	186(2)		

TABLE 3. Selected bond distances [pm] and angles [°] in [(Me₃P)₂Au]Cl, **3**

Au–P	230.4(1)	P–Au–P	175.4(1)
Au–Cl	316.7(1)	Cl–Au–P	92.3(1)

TABLE 4. Positional and equivalent thermal parameters for the non-hydrogen atoms of Me₃PAuCl, **1**, with e.s.d.s in parentheses

Atom	x	y	z	U_{eq}
Au1	0.13777(6)	0.29833(6)	0.70508(4)	0.038
Au2	0.28261(6)	0.59763(6)	0.70059(4)	0.038
Au3	0.18791(6)	−0.06318(6)	0.78592(5)	0.041
C11	0.3238(4)	0.2270(4)	0.5648(3)	0.051
C12	0.3498(4)	0.4896(4)	0.8561(3)	0.051
C13	−0.0635(4)	−0.0457(5)	0.7724(4)	0.061
P1	−0.0485(4)	0.3611(4)	0.8394(3)	0.038
P2	0.2151(4)	0.7018(4)	0.5509(3)	0.039
P3	0.4293(4)	−0.0824(4)	0.8038(3)	0.039
C11	−0.074(2)	0.545(2)	0.870(1)	0.051
C12	−0.022(2)	0.238(2)	0.956(1)	0.058
C13	−0.238(2)	0.353(2)	0.825(1)	0.072
C21	0.018(2)	0.699(2)	0.553(2)	0.076
C22	0.225(2)	0.893(2)	0.511(1)	0.061
C23	0.324(2)	0.610(2)	0.443(1)	0.060
C31	0.576(2)	−0.174(2)	0.704(1)	0.056
C32	0.468(2)	−0.187(2)	0.924(1)	0.072
C33	0.486(2)	0.093(2)	0.800(2)	0.062

chain-like arrangement of the molecules, with gold–gold distances between 324 and 332 pm and Au–Au–Au angles between 138 and 140°. By contrast, the structure of iodo(trimethylphosphine)gold(I) is built up from pairs of molecules [2] with a gold–gold distance of 316.8 pm.

TABLE 5. Positional and equivalent/isotropic thermal parameters for the non-hydrogen atoms of (ᶦPro₃P)AuCl, **2**, with e.s.d.s in parentheses

Atom	x	y	z	U_{eq}/U_{iso}
Au	0.26198(2)	0.08159(4)	0.4804(1)	0.052
P	0.1602(1)	0.2996(3)	0.4802(7)	0.049
Cl	0.3687(2)	−0.1353(4)	0.485(1)	0.084
C11	0.0443(8)	0.221(1)	0.467(1)	0.063
C12	0.035(1)	0.124(2)	0.346(1)	0.082
C13	0.021(1)	0.091(21)	0.573(1)	0.069
C21	0.159(2)	0.407(2)	0.332(2)	0.080
C22	0.097(1)	0.562(2)	0.315(2)	0.061
C23	0.254(1)	0.457(3)	0.295(2)	0.072
C311 [a]	0.190(2)	0.493(3)	0.567(2)	0.049
C312 [a]	0.174(1)	0.426(3)	0.617(2)	0.029
C32	0.111(1)	0.609(2)	0.607(2)	0.082
C33	0.271(1)	0.471(3)	0.639(2)	0.077

[a] Split carbon atom (SOF = 0.5).

Although the structure of chloro(tri-ᶦpropylphosphine)gold(I), **2**, is complicated by disorder of the alkyl groups in the crystal, the positions of all heavy elements could be unambiguously determined. The lattice contains individual molecules clearly separated at long van der Waals distances. The coordination of the gold(I) atom is linear, with Au–Cl and Au–P distances of 228.4(3) and 223.9(2) pm, respectively. There are no short gold-gold contacts. The steric bulk of the ligands apparently rules out any close approach of the molecules for metal-metal bonding.

Our results with trimethylphosphine, the smallest trialkylphosphine as a ligand, confirm that it is indeed the steric requirements of the substituents, that govern the oligomerisation of R₃PAuX compounds. In the

TABLE 6. Positional and equivalent/isotropic thermal parameters for the non-hydrogen atoms of [(Me₃P)₂Au]Cl, **3**, with e.s.d.s in parentheses

Atom	x	y	z	U_{eq}/U_{iso}
Au	0.00000	−0.50000	−0.12639(1)	0.034
P	−0.3267(1)	0.1733(1)	0.13422(1)	0.035
Cl	−0.50000	0.00000	−0.13951(8)	0.035
C12	−0.2178(2)	0.2817(2)	0.6984(1)	0.072
C13	−0.2437(4)	0.0407(2)	0.5552(2)	0.122
C14	−0.4599(2)	0.2537(4)	0.5546(2)	0.124
C4	−0.6653(7)	−0.1669(7)	−0.3621(4)	0.055
C11 [a]	−0.254(2)	0.222(1)	−0.002(1)	0.032
C12 [a]	−0.162(2)	0.118(2)	0.209(2)	0.050
C13 [a]	−0.392(2)	0.343(2)	0.196(2)	0.049
C21 [a]	−0.392(2)	0.309(2)	0.239(2)	0.056
C22 [a]	−0.154(2)	0.098(2)	0.156(2)	0.064
C23 [a]	−0.306(2)	0.274(2)	0.001(2)	0.053
C31 [a]	−0.398(3)	0.340(3)	0.122(2)	0.086
C32 [a]	−0.203(2)	0.162(2)	0.250(2)	0.061
C33 [a]	−0.189(3)	0.150(3)	0.021(2)	0.071

[a] Split carbon atom (SOF = 0.33).

crystal structure of chloro(triethylphosphine)gold(I) [10], the next symmetrical trialkylated phosphine in the series, gold-gold interactions are also observed, but only dimers are formed with a comparatively large intermetallic distance of 361.5 (2) pm. For chloro(tri-^{i}propylphosphine)gold(I) and chloro(tri-^{t}butylphosphine)gold(I) [16] intermetallic contacts are no longer discernible. The surmise of Ahrland that gold-gold bonding in halido(phosphine)gold(I) compounds is preferred with "soft" substituents (I, CN, etc.) is not valid [7]. The observation, that cyano(trimethylphosphine)-gold(I) and chloro(trimethylphosphine)gold(I) give rise to nearly the same chain structures rules out this hypothesis, and provides evidence that steric effects are of prime importance.

3.2. The complex (Me₃P)₂AuCl (3)

The 2:1 complex of AuCl with PMe₃ is obtained from compound 1 upon reaction with a second equivalent of phosphine.

$$Me_3PAuX + Me_3P \rightarrow (Me_3P)_2AuX$$
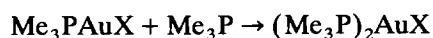
The product, 3, crystallizes with two equivalents of CHCl₃. The crystal lattice is a layer structure with a stacking parallel to the crystallographic X,Y-plane. Layers containing cations and anions are separated by
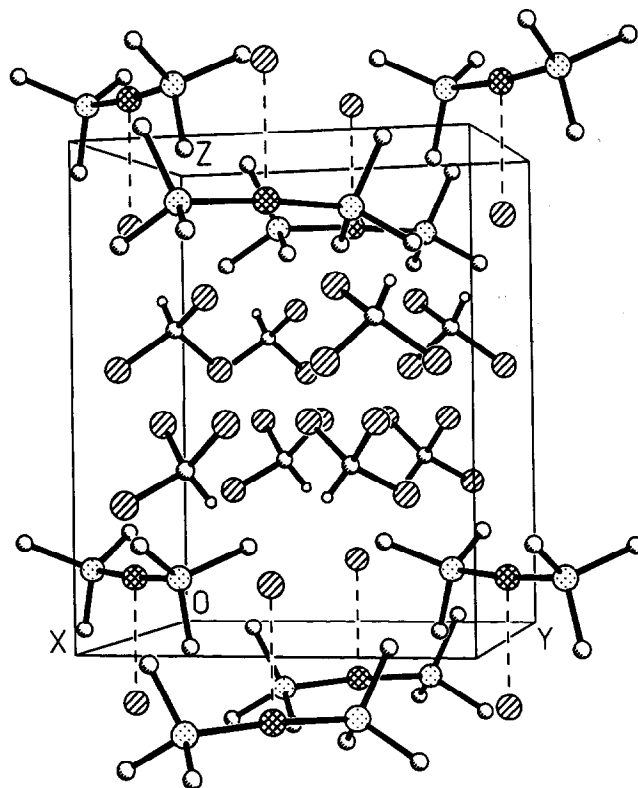

Fig. 4. Section of the crystal lattice of 3·2CHCl₃.

double layers of solvent molecules. The orientation of the chloroform molecules in the solvent layers of the lattice shows no preference for contacts with the substrate layers and appears to be governed by van der Waals and dipole packing.

The Me₃PAuPMe₃Cl units have crystallographic C_{2v} symmetry, with a twofold rotation axis passing through the Au and Cl atoms. The trimethylphosphine ligands are disordered, but this distribution was accounted for by using three rotational sites with a carbon occupancy factor SOF = 0.33.

The P–Au–P axis is nearly linear (P–Au–P = 175.4(1)°) with Au–P distances of 230.4(1) pm. The Au ··· Cl distance of 316.7(1) pm indicates a weak interaction, best interpreted as an ion pair contact. This is in agreement with the small deviation of the P–Au–P linkage from linearity. The species thus adopts a T-shape geometry with P–Au–Cl angles of 92.3(1)°. In the analogous Ph₃P complex the distortion is much larger, with the P–Au–P and P–Au–Cl angles approaching 120° [17].

Acknowledgments
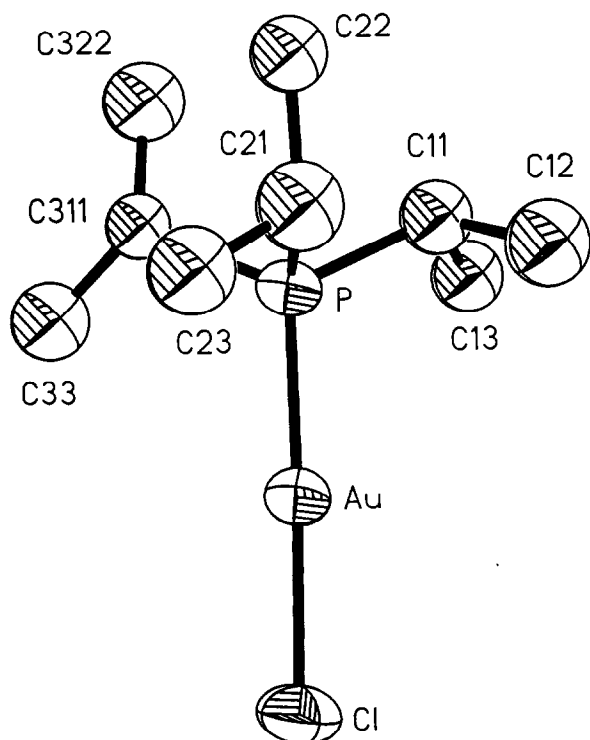
Fig. 3. Molecular structure of chloro(tri-^{i}propylphosphine)gold(I), 2.

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