Ground-state *trans*-Effect and Molecular Structure of Trichloro(triphenylphosphine)gold(III)

By **G. Bandoli, D. A. Clemente,** and **G. Marangoni,*** Laboratorio di Chimica e Tecnologia dei Radioelementi del C.N.R., Via Vigonovese 52, Padova
L. Cattalini, Facoltà di Chimica Industriale, Università di Venezia, Calle Larga, S. Marta, Venezia, Italy

The molecular structure of the title compound has been determined by a three-dimensional *X*-ray diffraction study. Crystals are triclinic, space group $P\bar{1}$, with $Z = 2$ in a cell of dimensions: a = 10·683(8), b = 9·109(6), c = 10·090(8) Å, α = 92·19(8)°, β = 69·68(8)°, γ = 91·69(8)°. The structure was solved by Patterson and Fourier methods.

Least-squares refinement gave R 0·050 for 2076 reflections, observed by counter methods.

The structure consists of well separated molecules. The co-ordination about the Au atom is nearly square-planar, with Au–P 2·335(4), and the Au–Cl 2·273(4), 2·282(4), and 2·347(4) Å.

The relatively large Au–Cl distance for the chlorine *trans* to the phosphine ligand and the small but significant deviation from complete planarity are discussed in relation to the general behaviour of the complex and to the relatively high *trans*-effect of the phosphine ligand.

The possibility of a critical discussion of the *trans*-effect based upon a comparison of the kinetic behaviour and molecular structure of planar four-co-ordinate complexes of d^8 transition-metal ions has been examined mainly for platinum(II) derivatives.[1] Such a comparison is obviously restricted by the fact that, whereas reactivity relates to the free-energy difference between the ground- and transition-states, the structural information refers to the ground-state configuration only. This difficulty was clearly pointed out [2] in the definition of a *trans*-influence of a ligand as being ' the extent to which that ligand weakens the bond *trans* to itself in the equilibrium state of a substrate.'

In order to extend the considerations already developed for platinum(II) complexes since the early works of Chatt *et al.*,[3-5] we have investigated the molecular structure of the complex $[Au(PPh_3)Cl_3]$. In spite of the foregoing comments about the differences between the *trans*-influence and the kinetic *trans*-effect, we have chosen this compound mainly on the basis of kinetic information, *i.e.* the dependence of the rate of substitution upon both bond-making and -breaking has been established for gold(III) complexes,[6] and preliminary kinetic studies indicated a very high lability of the chlorine in this complex.

EXPERIMENTAL

The complex was prepared according to the literature method.[7] Preliminary kinetic experiments were carried out by use of an Optica CF4 R spectrophotometer and a Durrum stopped-flow apparatus.

Crystal Data.—$C_{18}H_{15}AuCl_3P$, $M = 565{\cdot}6$, Triclinic, $a = 10{\cdot}683$ (8), $b = 9{\cdot}109$ (6), $c = 10{\cdot}090$ (8) Å, $\alpha = 92{\cdot}19$ (8)°, $\beta = 69{\cdot}68$ (8)°, $\gamma = 91{\cdot}69$ (8)°, $U = 919{\cdot}9$ Å^3, $D_m = 2{\cdot}06$ g cm^{-3} (by flotation), $Z = 2$, $D_c = 2{\cdot}04$ g cm^{-3}. Space group $P1$ or $P\bar{1}$, but the structural resolution assigned the latter. Cu-K_α radiation, $\lambda = 1{\cdot}54178$ Å; μ(Cu-K_α) = 200·2 cm^{-1}.

Data were collected on a Siemens AED-automated four-circle diffractometer with nickel-filtered Cu-K_α radiation and a Na(Tl)I scintillation counter. Lattice and orientation parameters were derived by use of the Busing and Levy procedure [8] on 30 reflections.

The intensities of 2310 independent non-zero reflections were taken to the limit θ 55° and 2076 (89%) reflections were assumed to have observable intensity.[9] Reflections with intensities below threshold were considered to be unobserved and omitted in the refinement.

A general reflection was remeasured every 20 reflections throughout the data collection and was used to normalize the intensities to a common basis, correcting for any systematic change in the instrument or the crystal. The normalization factor was essentially constant with time, with an overall variation of 2·9% in intensity. Lorentz polarisation corrections were applied to the intensities. The scale of the $|F_o|$ data and the overall temperature factor were estimated from a Wilson plot.

An unsharpened three-dimensional Patterson revealed the position of the gold, chlorine, and phosphorus, refinement of which gave R 0·16. The remaining non-hydrogen atoms were located from the resultant difference Fourier.

Two cycles of least-squares refinement with the neutral atom scattering factors of ref. 10, corrected for the real part of the dispersion effect for heavy atoms, and using the weighting scheme of ref. 11 and individual isotropic temperature factors, reduced R to 0·10.

A weighting scheme based on counter statistics was unsuccessful probably owing to systematic errors.[12]

A weighting function $w^{-1} = A|F_o|^2 + B|F_o| + C$ with $A = 0{\cdot}11111$, $B = 0{\cdot}0025$, and $C = 0{\cdot}00001$ was checked by plotting $w(|F_o| - |F|_c)^2$ *vs.* $|F_o|$. At this stage, ani-

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sotropic temperature factors of the form, $\exp\,|-\tfrac{1}{4}(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl)|$ were assigned to heavy atoms and refinement of the structure proceeded to R 0·050 with full-matrix least-squares method. A difference-Fourier showed no significant peaks except at the positions of the hydrogen atoms. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20634 (4 pp., 1 microfiche).* Final atomic positional and thermal parameters are given in Table 1, and bond lengths, bond angles, and least-squares equations for selected planes within the molecule, and the angles between these planes, in Tables 2 and 3. Standard deviations for the atomic parameters are derived from the full matrix least-squares program.

TABLE 1

Final fractional co-ordinates, with estimated standard deviations in parentheses

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Au	0·2178(1)	0·2714(1)	0·1713(1)	1·98(2)	1·89(2)	2·67(2)	0·06(2)	−0·22(2)	−0·12(2)
Cl(1)	0·3895(4)	0·1390(4)	0·0217(4)	3·19(15)	3·24(16)	4·84(18)	0·75(12)	−0·70(14)	−1·09(13)
Cl(2)	0·0462(4)	0·4203(5)	0·2967(5)	2·75(16)	5·40(21)	5·78(21)	1·15(14)	−0·56(15)	−2·15(17)
Cl(3)	0·0722(4)	0·1338(4)	0·0844(4)	3·40(16)	4·08(18)	4·95(18)	−0·27(13)	−1·49(14)	−1·10(14)
P	0·3482(3)	0·3823(4)	0·2922(4)	2·57(14)	1·88(13)	2·84(14)	0·23(11)	−0·58(11)	0·02(11)

Atom	x/a	y/b	z/c	B	Atom	x/a	y/b	z/c	B
C(1)	0·3061(12)	0·5731(14)	0·3339(13)	2·63(23)	C(10)	0·8075(15)	0·3709(17)	0·0888(16)	3·96(29)
C(2)	0·3085(15)	0·6632(17)	0·2280(15)	3·78(28)	C(11)	0·7416(15)	0·5076(17)	0·1235(16)	4·03(29)
C(3)	0·2744(16)	0·8130(18)	0·2539(17)	4·43(32)	C(12)	0·5995(14)	0·5101(15)	0·1843(14)	3·32(26)
C(4)	0·2398(19)	0·8662(21)	0·3900(20)	5·41(38)	C(13)	0·3066(13)	0·2825(15)	0·4571(14)	3·16(25)
C(5)	0·2375(16)	0·7782(18)	0·4994(17)	4·36(31)	C(14)	0·1757(15)	0·2604(17)	0·5333(16)	4·06(30)
C(6)	0·2709(14)	0·6299(16)	0·4734(15)	3·62(27)	C(15)	0·1377(17)	0·1830(19)	0·6648(17)	4·76(34)
C(7)	0·5267(13)	0·3784(15)	0·2084(14)	3·05(24)	C(16)	0·2353(18)	0·1314(21)	0·7033(19)	5·38(37)
C(8)	0·5943(14)	0·2416(15)	0·1750(14)	3·34(26)	C(17)	0·3717(18)	0·1514(20)	0·6249(19)	5·15(36)
C(9)	0·7314(15)	0·2415(17)	0·1101(16)	3·76(27)	C(18)	0·4041(15)	0·2320(17)	0·5014(16)	4·09(30)

TABLE 2

Bond lengths (Å) and bond angles (°), with estimated standard deviations in parentheses

(*a*) Distances

Au–Cl(1)	2·273(4)	C(7)–C(8)	1·43(2)
Au–Cl(2)	2·282(4)	C(7)–C(12)	1·39(2)
Au–Cl(3)	2·347(4)	C(8)–C(9)	1·38(2)
Au–P	2·335(4)	C(9)–C(10)	1·39(2)
P–C(1)	1·806(13)	C(10)–C(11)	1·42(2)
P–C(7)	1·799(16)	C(11)–C(12)	1·43(2)
P–C(13)	1·836(15)	C(13)–C(14)	1·36(2)
C(1)–C(2)	1·37(2)	C(13)–C(18)	1·37(2)
C(1)–C(6)	1·41(2)	C(14)–C(15)	1·45(3)
C(2)–C(3)	1·41(2)	C(15)–C(16)	1·34(3)
C(3)–C(4)	1·37(3)	C(16)–C(17)	1·41(2)
C(4)–C(5)	1·38(3)	C(17)–C(18)	1·40(2)
C(5)–C(6)	1·40(2)		

(*b*) Angles

Cl(1)–Au–Cl(3)	88·5(1)	P–C(1)–C(2)	119·2(10)
Cl(1)–Au–P	93·8(1)	P–C(1)–C(6)	121·1(11)
Cl(2)–Au–Cl(3)	89·8(2)	P–C(7)–C(8)	120·4(10)
Cl(2)–Au–P	89·1(1)	P–C(7)–C(12)	119·4(10)
Cl(1)–Au–Cl(2)	172·7(2)	P–C(13)–C(14)	117·7(13)
Cl(3)–Au–P	169·9(1)	P–C(13)–C(18)	121·2(10)
Au–P–C(1)	110·8(5)		
Au–P–C(7)	117·9(5)		
Au–P–C(13)	105·4(5)		

None of the eighteen C–C–C angles in the phenyl rings is significantly different from 120°.

A projected drawing of the molecule is presented in Figure 1 which also shows the arbitrary numbering scheme adopted. The arrangement of the molecules in the unit cell as viewed along the b^* axis is shown in Figure 2.

TABLE 3

Least-squares planes with the deviations (Å) of the relevant atoms in square brackets

(*a*) Equations of the planes in direct space are in the form: $Px + Qy + Rz = S$

	P	Q	R	S
(1): Au, Cl(1)—(3), P	0·4261	−6·4019	7·0638	−0·4090
[Au −0·026, Cl(1) −0·162, Cl(2) −0·166, Cl(3) 0·179, P 0·174]				
(2): Au, Cl(3), P	−6·7272	6·0341	1·7191	0·4668
(3): Au, Cl(1), Cl(2)	7·8820	5·7651	3·9425	3·9569
(4): Cl(1)—(3)	1·6652	−5·7404	7·9507	0·0232
[Au 0·143, P 0·685]				
(5): C(1)—(6) *	10·2249	1·9749	1·8254	4·8760
(6): C(7)—(12) *	4·3555	−0·5516	10·0662	4·1909
(7): C(13)—(18) *	1·7975	7·6193	5·2025	5·0858

(*b*) Angles (°) between the planes

(1,4)	8·5	(1,7)	77·3
(2,3)	88·4	(5,6)	76·3
(1,5)	75·9	(6,7)	60·3
(1,6)	45·7	(5,7)	73·2

* The benzene rings are planar within 0·01 Å.

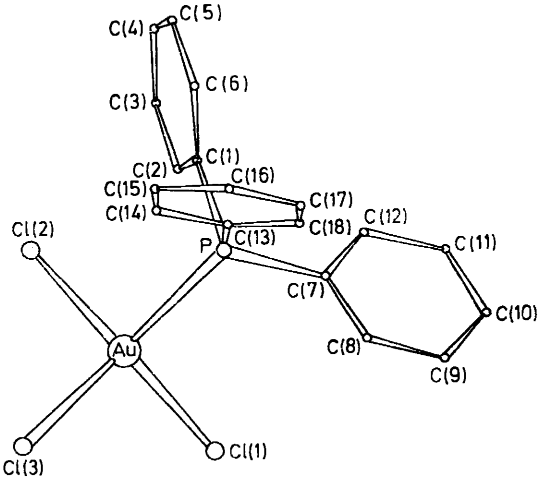

FIGURE 1 Projection on the mean co-ordination plane

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

RESULTS AND DISCUSSION

The main point which will be taken into account in the discussion are (i) the relatively large Au–Cl distance for the chlorine *trans* to phosphine and (ii) the small but significant deviation from planar geometry.

It is clear that the Au–Cl(3) bond distance (2·347 Å) is longer than the Au–Cl(1) and Au–Cl(2) distances (2·273 and 2·282 Å) which are equal. Examination of the molecular structure also indicates that such a difference in the Au–Cl bond distances cannot be due to any kind of hydrogen bonding or crystal packing effects. In fact, if the Bondi's [13] van der Waals radii are 1·70 for chlorine and 1·77 Å for carbon, the closest Cl · · · Cl and Cl · · · C approaches are within a few σ of the sum of van der Waals radii (Figure 2). As far as the deviation from complete planarity is concerned the Cl(1)–Au–Cl(2) angle (172·7°) is 7·3° away from linearity while the Cl(3)–Au–P angle (169·9°) is 10·1° away from linearity. The distortion observed in the complex could be also correlated with the fact that [Au(PPh$_3$)Cl$_3$] exhibits a medium halogen-sensitive band in the i.r. spectrum at 340 cm^{-1}, which has been related to the ' symmetric ' stretch of the group Cl(1)–Au–Cl(2).[14] It is implied that this type of distortion is not expected for the similar complexes [AuLCl$_3$] mentioned in ref. 14 which do not show this extra i.r. band.

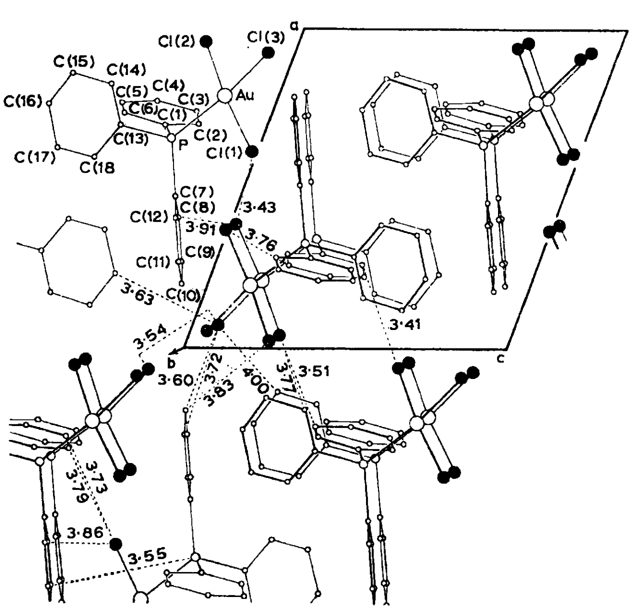

FIGURE 2 The arrangement of the molecules in the unit cell viewed along the b^* axis. Displacement of successive layers can be seen for a few of the molecules. Important intermolecular distances are indicated by dashes

The lengthening of the Au–Cl bond *trans* to phosphine can be related to the high reactivity of the complex. [Au(PPh$_3$)Cl$_3$] undergoes ligand substitution in methanol at 25 °C with poor nucleophiles such as pyridine at a rate which is too fast to follow even by the stopped-flow technique. According to the known *trans*-labilizing effect of the ligands in square planar complexes [1] Cl(3) can be assumed to be the most labile group. Indeed, the departure from Beer's law for methanol solution indicated a rapidly attained solvolytic equilibrium as was apparent from our preliminary experiments. The rates of displacement of the neutral ligand from [Au(amine)Cl$_3$] and [Au(thioether)Cl$_3$] as well as the replacement of chlorine in [AuCl$_4$]$^-$ by a range of neutral and anionic nucleophiles, while being relatively fast, can be and have been followed by conventional techniques.[2,15]

The possible relationship between the lability of the ligand Cl(3) and the Au–Cl(3) distance is not inconsistent with the little information available for platinum(II) complexes.

For instance complexes of the type *cis*-[Pt(PR$_3$)$_2$Cl$_2$] are known to undergo a relatively fast chlorine substitution as compared with the corresponding *trans*-[Pt(PR$_3$)$_2$Cl$_2$], in accordance with the large *trans*-effect of PR$_3$.[16]

Structural data are available for the *trans*-[Pt(PEt$_3$)$_2$Cl$_2$] [17] and *cis*-[Pt(PMe$_3$)$_2$Cl$_2$] [18] complexes. The Pt–Cl bond distance is 2·294 in the *trans*- and 2·376 Å in the *cis*-complex. The observed difference is said to be due [18] to the fact that the chloride is *trans* to a strongly labilizing ligand in the *cis*-complex. There are examples from platinum(II) complexes,[19,20] even if agreement is often only qualitative.

As far as the distortion from complete planarity is concerned this is not the only example in planar four-co-ordinate complexes. For instance in the structure of chlorobis(ethyldiphenylphosphine)hydridoplatinum-(II), the platinum, phosphorus, and chlorine atoms deviate slightly, but significantly, from coplanarity.[21] A possible explanation is the intramolecular repulsion of phosphorus and chlorine.

If, as already stated, the distortion from planarity does not arise from crystal packing effects, it might be maintained in solution and the high reactivity may be related to this distortion by following the suggestion of Oleari *et al.*: [22] the approach of a nucleophile toward one of the faces of the planar substrate will induce a transfer of negative charge from the metal to the ligands and the pair of mutually *trans* ligands which can be most easily distorted from the initial planar structure will occupy

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two of the three equatorial positions in the trigonal-bipyramidal transition state, the third being taken up by the entering group. In the present case the P–Au–Cl(3) axis is already on the way to the trigonal-bipyramid.

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