

Implications of the Results of a Routine Structure Determination: Tris(triphenylphosphine)gold(I) Chloride Bis(dichloromethane)

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Gold(I) Chloride, (Triphenylphosphine)gold(I) Complexes, Gold(I) Coordination

Tris(triphenylphosphine)gold(I) chloride was found to form a crystalline phase with two molecules of dichloromethane. In the crystal the chlorine atom is almost fully dissociated from the $[(\text{Ph}_3\text{P})_3\text{Au}]^+$ cation. The gold atom shows only a minor displacement from the plane of the phosphorus atoms (sum of the angles P-Au-P 355.35° ; $d(\text{Au}-\text{Cl})$ 2.7962(6) Å), very similar to the geometry of the solvent-free crystalline phase. The results are discussed in the context of all known structures for compounds $[(\text{Ph}_3\text{P})_3\text{MCl}]$, M = Cu, Ag, Au. The variations in structure appear to be dominated by electronic (relativistic) rather than steric effects.

Owing to strong relativistic effects (s-orbital contraction, d-orbital expansion and spin-orbit coupling), two-coordinate gold(I) complexes of the types L-Au-X and $[\text{L}-\text{Au}-\text{L}]^+$, where L is a neutral and X an anionic ligand, are poor acceptor molecules or ions, respectively. This general trend is obvious from the plethora of structural data available for complexes generated in the reactions with strong donor ligands like tertiary phosphines and arsines [1, 2]. The products are generally ionic in nature and feature linear or trigonal planar cations $[\text{L}_2\text{Au}]^+$ or $[\text{L}_3\text{Au}]^+$ together with independent counterions X^- . Cations of the stoichiometry $[\text{L}_4\text{Au}]^+$ more often than not show partial dissociation into $[\text{L}_3\text{Au}]^+$ and L depending on the nature of L and X [3]. This tendency is contrary to the behaviour of the corresponding silver(I) and copper(I) complexes, where tetracoordination is prevailing including the types $[\text{L}_3\text{MX}]$ and $[\text{L}_4\text{M}]\text{X}$ [4a, 4b].

In a report of 1982, a solvent-free crystalline phase of the composition $[(\text{Ph}_3\text{P})_3\text{AuCl}]$ was described [5], in which the gold atom appears to be quasi-four-coordinate but with a conspicuously elongated Au-Cl distance of 2.710(2) Å. Reference values for $[\text{Ph}_3\text{PAuCl}]$ and $[(\text{Ph}_3\text{P})_2\text{AuCl}]$ are 2.279 and 2.500 Å, respectively [6, 7]. In the solvent-free phase $[(\text{Ph}_3\text{P})_3\text{AuCl}]$ the three Au-P distances and P-Au-P angles are all significantly different with individual data of 2.395(2), 2.404(2) and 2.431(2) Å

and 119.6(1), 116.6(1) and $116.1(1)^\circ$, respectively. The sum of these angles [352.3°] indicates a significant deviation from planarity [360°] for the P_3Au core and an even larger deviation from the geometry of a tetrahedral structure [328°]. The bonding situation thus appeared to be intermediate between covalent $[(\text{Ph}_3\text{P})_3\text{AuCl}]$ and ionic $[(\text{Ph}_3\text{P})_3\text{Au}]\text{Cl}$.

The authors also have mentioned a crystalline phase containing dichloromethane, but the stoichiometry could not be elucidated and the structure could not be solved [5]. Solvated $[(\text{Ph}_3\text{P})_3\text{AuCl}]$ was also postulated as a component of solution equilibria [8].

Results

In the course of preparative studies in gold(I) coordination chemistry we required $[(\text{Ph}_3\text{P})_3\text{AuCl}]$ as a starting material. The compound is readily formed in the reaction of equimolar quantities of $[(\text{Ph}_3\text{P})_2\text{AuCl}]$ and Ph_3P in dichloromethane. However, the product was found to crystallize as the solvate $[(\text{Ph}_3\text{P})_3\text{AuCl}](\text{CH}_2\text{Cl}_2)_2$ (95% yield). The crystal structure analysis of this phase has shown that the constitution is again intermediate between molecular and ionic, but approaching even more closely the ionic extreme.

Crystals of $[(\text{Ph}_3\text{P})_3\text{AuCl}](\text{CH}_2\text{Cl}_2)_2$ are monoclinic, space group $P2_1/n$, with $Z = 4$ formula units in the unit cell. (The dimensions of the unit cell differ

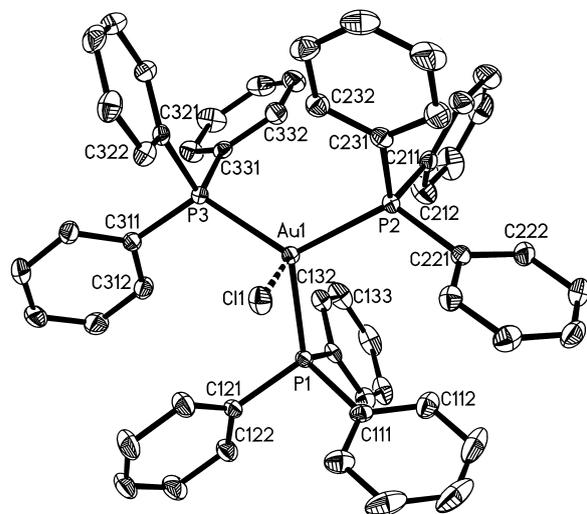


Fig. 1. Structure of the formula unit $[(\text{Ph}_3\text{P})_3\text{AuCl}]$ in the crystal with atomic numbering (ORTEP, 50% probability ellipsoids; hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Au1-P1 2.3795(6), Au1-P2 2.3911(6), Au1-P3 2.3666(6), Au1-Cl1 2.7962(6); P1-Au1-P2 114.82(2), P1-Au1-P3 118.23(2), P2-Au1-P3 122.30(2), Cl1-Au1-P1 90.31(2), Cl1-Au1-P2 90.31(2), Cl1-Au1-P3 105.27(2).

from the data given for the solvent-free phase and also for a phase containing an unknown quantity of dichloromethane [5].) The asymmetric unit contains one formula unit of the complex with no crystallographically imposed symmetry (Fig. 1), and two solvent molecules. The gold atom is surrounded by three phosphorus atoms and the chlorine atom in an irregular geometry. The three independent Au-P distances are not grossly different [2.3666(6), 2.3795(6) and 2.3911(6) Å for P1, P2 and P3, respectively], but the Au-Cl distance is much longer at 2.7962(6) Å. Referring to the solvent-free phase, all three Au-P distances are shorter and the Au-Cl distance even longer.

The three P-Au-P angles are 114.82(2), 118.23(2) and 122.30(2)° for P1/P2, P1/P3 and P2/P3, respectively [average 118.45(3)°], and thus add up to a sum of 355.35°, only 4.65° from the 360° standard for a trigonal planar arrangement.

An inspection of the unit cell shows a geometry suggesting weak hydrogen-bonding of the “chloride anion” to one of the hydrogen atoms of one dichloromethane molecule (Fig. 2), but it is unlikely that this C-H...Cl contact is a significant factor in determining the structure.

Table 1. M-P and M-Cl distances [Å] in complexes of the type $[(\text{Ph}_3\text{P})_3\text{MCl}]$.

Cu-P	2.318(2) ^b	2.348(2) ^a 2.351(2) 2.355(2)
Cu-Cl	2.347(3)	2.320(4) 2.336(4) 2.350(4)
Ag-P	2.558(5) ^c	2.520(1) ^a 2.552(1) 2.556(1)
Ag-Cl	2.533(4)	2.552(1)
Au-P	2.3666(6) ^d	2.395(2) ^a 2.404(2) 2.431(2)
Au-Cl	2.7962(6)	2.710(2)

^a Solvate-free: Cu [4b], Ag [10], Au [5]; ^b tetrahydrofuran solvate [14]; ^c acetone solvate [4a]; ^d dichloromethane solvate (this work).

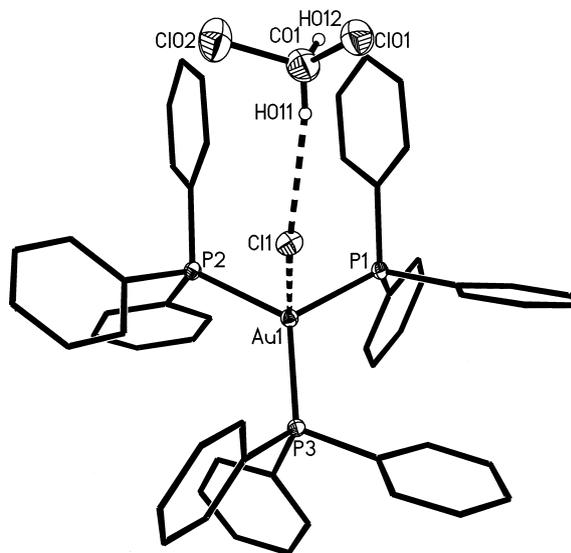


Fig. 2. Interactions between the components $[(\text{Ph}_3\text{P})_3\text{Au}]^+$, Cl^- and CH_2Cl_2 in the crystal. Hydrogen bond: C01-H011 0.926 Å, H011...Cl1 2.608 Å, C01...Cl1 3.521 Å; C01-H001...Cl1 169.2°.

Discussion

At this stage, a new discussion [4] of the data is justified, because two independent sets of results are now available for the complexes of all three coinage metals (Table 1).

The new results suggest that the crystal structures of the solvent-free [5] and the new bis(solvate)

phase reflect the same bonding situation for the gold(I) complex, where the chloride anion has already left the coordination sphere of the metal such that its presence leads to only marginal distortions of the trigonal planar core geometry of the cation $[(\text{Ph}_3\text{P})_3\text{Au}]^+$. The situation is also similar to that in the related thiocyanide complex $[(\text{Ph}_3\text{P})_3\text{AuSCN}]$ [9a, b]. To our knowledge there is generally no compound known of the type $[(\text{Ph}_3\text{P})_3\text{AuX}]$ with a regular tetrahedral structure and a short contact between Au and X that would be indicative of standard coordinative bonding [9c]. The structural motif thus appears to be *intrinsic*, and it is highly unlikely that the “distortions” of the structures are determined by packing forces. Analogous results have been reported for phenyl-dibenzophosphole complexes [9c].

By contrast, the corresponding silver(I) complex $[(\text{Ph}_3\text{P})_3\text{AgCl}]$ shows a structure much closer to the standard tetrahedral geometry both in a solvent-free crystal [10] and in a bis(acetone) solvate [4a]. In the former there are four almost equal Ag-P/Cl bond lengths in the range 2.520(1) - 2.556(1) Å and a sum of the P-Ag-P angles of 345.19(3)°, while in the latter these distances are between 2.533(4) and 2.582(4) Å with a sum of P-Ag-P angles of 334.3(1)°. For both phases the *average* P-Ag-P angle is exactly the same at 115(1)°. Note that these sums of P-Ag-P angles are now only *ca.* 16.5° from the tetrahedron reference, but 25.3° from the trigonal-planar reference.

It is tempting to ascribe the structural differences to the larger cationic radius of silver(I) as compared to gold(I), which has recently been confirmed for several independent series [4a, 11, 12, 13]. However, a comparison with data of the copper(I) complex $[(\text{Ph}_3\text{P})_3\text{CuCl}]$ makes this *steric* argument doubtful:

For $[(\text{Ph}_3\text{P})_3\text{CuCl}]$ (three independent molecules with threefold symmetry in the trigonal unit cell) the Cu-P/Cl distances are all very similar [in the range 2.3200(2) - 2.355(2) Å] and all P-Cu-P/Cl angles are within the narrow range 109.11(6) - 110.51(6)° clearly indicating a regular tetrahedral structure [4a]. In a tetrahydrofuran solvate, the structure of the $[(\text{Ph}_3\text{P})_3\text{CuCl}]$ unit (C_3 symmetry) is also quasi-tetrahedral, but with a larger spread of the P-Cu-P angles [14].

As known from previous measurements [4a, [11 - 13], and as obvious from the M-P/Cl distances

in this work (Table 1), the ionic radius of copper(I) is the smallest of the coinage metal radii (regardless of the coordination number). Therefore, based solely on *steric* arguments, any increase in the coordination number by addition of a phosphine or a halide ligand would be expected to lead to the most severe steric hindrance for the *copper* complex, less so for *gold*, and least for *silver*.

The experimental data are at variance with this prediction and therefore must be based on *effects other than steric*. Distortions of the tetrahedral structure are seen to increase steadily in the direction Cu-Ag-Au and thus follow the trend of increasing relativistic effects: s-Orbital contraction and d-orbital expansion favour chemical bonding in compounds with low coordination numbers and bonds of low polarity (high s-character of the bonding orbitals). Complexes of the type $[(\text{Ph}_3\text{P})_3\text{MCl}]$ will therefore partly dissociate to give ion pairs $[(\text{Ph}_3\text{P})_3\text{M}]^+ \text{Cl}^-$ rather than pairs of neutral molecules, $[(\text{Ph}_3\text{P})_2\text{MCl}]$ and Ph_3P . It is only for the cations $[(\text{Ph}_3\text{P})_4\text{Au}]^+$ that facile dissociation of Ph_3P is observed [15]. Cations $[(\text{Ph}_3\text{P})_4\text{M}]^+$ with $\text{M} = \text{Ag}, \text{Cu}$ are stable. It is also in agreement with this argument that $[(\text{Ph}_3\text{P})_3\text{AgBr}]$ and even $[(\text{Ph}_3\text{P})_3\text{AgI}]$ with their much larger, but less electronegative halide anions have less distorted tetrahedral structures than $[(\text{Ph}_3\text{P})_3\text{AgCl}]$ [4a]. For $[(\text{Ph}_3\text{P})_3\text{AuBr/I}]$ structures with cations $[(\text{Ph}_3\text{P})_3\text{Au}]^+$ more distorted towards a tetrahedral structure than $[(\text{Ph}_3\text{P})_3\text{AuCl}]$ are predicted. Quantum-chemical calculations on the dianion $[\text{Au}(\text{GeCl}_3)_3]^{2-}$ with its T-shaped structure have also confirmed the strong influence of relativistic effects [16].

Experimental Part

The experiment needed no special precautions regarding the exclusion of air, but the reaction was nevertheless conducted under nitrogen and the solvents and glassware were dried to avoid the formation of hydrates (water of crystallization) and the oxidation of the phosphine. Conventional equipment was used throughout.

Tris(triphenylphosphine)gold(I) chloride bis(dichloromethane)

Bis(triphenylphosphine)gold(I) chloride (710 mg, 0.94 mmol) [6] and triphenylphosphine (246 mg, 0.94 mmol) were dissolved in dry acetonitrile and the reaction mixture heated to reflux for 1 h under nitrogen. The

solvent was removed in a vacuum and the residue crystallized from dry dichloromethane; yield 1.06 g (95%). The crystals slowly lose dichloromethane when left at room temperature. After drying of the crystals in a vacuum the white powder melts at 223 °C.

$C_{56}H_{49}AuCl_5P_3$ (1189.08) calcd. C 56.56, H 3.98; found C 55.81, H 4.06. NMR ($CDCl_3$, 20 °C), 1H : 7.25 - 7.72, m, Ph. $^{13}C\{^1H\}$: 126.85, 129.80, 132.40, and 134.18, all d, $J = 65, 12, 4, \text{ and } 14$ Hz, for *i/m/p/o-C*. $^{31}P\{^1H\}$: 23.05, s. MS (FAB) m/z 993 $[Au(PPh_3)_3]^+$, 721 $[Au(PPh_3)_2]^+$, 459 $[AuPPh_3]^+$.

Crystal structure determination

The crystalline sample was placed in inert oil, mounted on a glass pin, and transferred to the cold gas stream of the diffractometer. Crystal data were collected and integrated using a Nonius DIP2020 system with monochromated Mo- K_α ($\lambda = 0.71073$ Å) radiation at -130 °C. The structure was solved by direct methods using SHELXS-97 and refined by full matrix least-squares calculations on F^2 using SHELXL-97. Non-hydrogen atoms were refined with anisotropic displacement parameters. Phenylhydrogen atoms were placed in idealized positions and

refined using a riding model with fixed isotropic contributions, whereas the hydrogen atoms of the solvent CH_2Cl_2 were located and refined isotropically. Selected interatomic distances and angles are given in the corresponding figure captions. Complete lists of displacement parameters and interatomic distances and angles have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. The data are available on request on quoting CCDS-185354. E-mail: deposit@ccdc.cam.ac.uk.

Crystal data for $C_{56}H_{49}AuCl_5P_3$: $M = 1189.08$, monoclinic, $a = 11.0788(1)$, $b = 22.7308(2)$, $c = 20.3203(2)$ Å, $\beta = 93.320(1)^\circ$, space group $P2_1/c$, $Z = 4$, $V = 5108.7(1)$ Å³, $\mu(\text{Mo-K}\alpha) = 32.72$ cm⁻¹, 107553 measured and 10441 unique reflections [$R_{\text{int}} = 0.038$], 602 refined parameters, $wR2 = 0.0464$, $R = 0.0219$. The function minimized was $wR2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; $a = 0.0113$, $b = 7.80$.

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