Crystal Structure and Ligand Mobility in Solution of *cis*-Dimethyl-bis(trimethylphosphine)gold(III) Complexes

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Complexes $[Me_2Au(PMe_3)_2]^+ X^-$ with X = I and ClO_4 have been prepared by several conventional routes in good yields. The products are thermally stable and decompose above 130 °C with reductive elimination of ethane. The two salts crystallize as isomorphous orthorhombic dichloromethane solvates. The cations have the *cis*-configuration based on a crystallographically imposed C_{2v} symmetry. Owing to the *trans* influence of the tertiary phosphine ligands the Au-C bonds are significantly shorter than in standard reference cases. The cations are stacked in pairs of columns running parallel to the *c* axis of the unit cell with the Me_2Au units oriented in opposite directions and slightly interlocked. The anions are inserted into the pockets formed by the four Me_3P groups of each pair of neighbouring cations in the same column. The large channels between the double columns are filled by the solvent molecules, which could be localized for the perchlorate salt, but were disordered and deficient in the iodide case.

Key words: Gold(III) Complexes, Dimethylgold(III) Complexes, Ligand Exchange, *trans* Influence, Crystalline Solvates

Introduction

Although alkylgold(III) compounds were among the first organogold compounds to be prepared, their chemistry has developed rather slowly because only unsatisfactory preparative procedures are available for their synthesis [1 – 4]. The alkylation of $HAuCl_4$ or $AuCl_3$ with Grignard, alkyllithium, alkyltin, or other organometallic reagents gives only low yields of products, because side reactions lead to either gold(I) complexes of the types (L)AuR or (L)AuCl, or gold metal. As demonstrated in separate experiments with authentical compounds $R_2AuX(L)$ and $R_3Au(L)$, the former are the products of reductive elimination of alkane R_2. Similar observations were made with alkenyl- and alkynyl-gold(III) complexes.

Already the early preparative work [1] has shown very clearly that – among the family of complexes $R_xAuX_{3-x}(L)$ – the *di*alkylgold(III) halide complexes $R_2AuX(L)$ are among the most stable (R = alkyl, X = halogen, L = tertiary phosphine). Reductive elimination of alkane R_2 is observed at temperatures above 60 – 80 °C, depending on the nature of R and X. The stability is generally lowest with bulky groups R and L, and with the larger halogens.

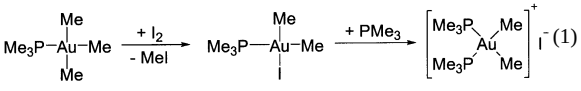
The cationic complexes $[R_2Au(L)_2]^+ X^-$, which are readily available by treatment of $R_2AuX(L)$ with one equivalent of L, are even more robust and undergo this reductive elimination only above 130 °C. Indirect evidence based on analytical and spectroscopic data of all previous work has suggested that the cations $[R_2Au(L)_2]^+$ have a *cis*-configuration in which the *trans*-influence of the two auxiliary ligands L stabilizes both Au-C bonds, but there was no detailed structural information [5 – 12].

In the context of recent preparative work in organogold(III) chemistry [13 – 15] we have revisited two simple prototypes $[Me_2Au(PMe_3)_2]^+X^-$, with the "soft" and "hard" counterions X = I, ClO_4, respectively, and investigated their crystal structure and their ligand mobility in solution.

Preparation and Characterization of the Complexes

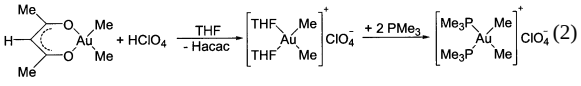
For the preparation of $[Me_2Au(PMe_3)_2]^+ I^-$, trimethyl(trimethylphosphine)gold(III) was treated with an equimolar quantity of elemental iodine in dichloromethane to give *cis*-dimethyl-iodo-(trimethylphosphine)gold(III) [16]. (Note that this compound

can also be prepared from *cis*-$Me_2AuCl(PMe_3)$ in a metathesis with NaI in acetone [5], or by oxidative addition of MeI to $MeAuPMe_3$ [17–19].) The complex was further reacted with a slight excess of trimethylphosphine in benzene or toluene to give the target complex (Eq. (1), 87% yield). The product crystallizes as a non-stoichiometric dichloromethane solvate from dichloromethane/pentane (colourless plates, m. p. 129–130 °C; lit. 126–130 °C [1, 7]).



(1)

For the preparation of $[Me_2Au(PMe_3)_2]^+\ ClO_4^-$, dimethylgold(III) chloride was first treated with two equivalents of $HClO_4$ in tetrahydrofuran to give a solution of the complex $[Me_2Au(thf)_2]^+\ ClO_4^-$ [8]. Addition of a solution of PMe_3 (2 equivalents) in toluene gave a colourless precipitate of the target complex (Eq. (2)), which can be crystallized from dichloromethane as colourless plates of the 1:1 solvate (75% yield, m. p. 126–130 °C with decomposition).



(2)

The NMR spectra of solutions of the perchlorate salt in dichloromethane-d_2 at room temperature show a singlet $^{31}P\{^1H\}$ resonance at $\delta P = -6.0$ ppm and ^1H resonances at $\delta H = 1.05$ (t, $A_3XX'A'_3$, 6H) and 1.74 ppm (d, $A_9XX'A'_9$, 18H) for the MeAu and MeP protons, respectively. These multiplicities can be simulated with coupling constants $^2J_{P,H}$ 6.8/8.1 (MeAu) and $^2J_{P,H}$ 10.4 (MeP), indicating firm bonding of the PMe_3 ligand on the NMR time scale.

By contrast, the ^1H NMR spectrum of solutions of the iodide in dichloromethane-d_2 under the same conditions gives only a broad singlet resonance at $\delta H = 1.09$ (6H) and a broad doublet at 1.77 ($^2J_{P,H}$ 9.7 Hz, 18H). The signal at $\delta P = -11.5$, s, is also notably broadened, suggesting rapid ligand exchange. Temperatures as low as −90 °C in CD_2Cl_2 are required to sharpen the resonances ($\delta P = -8.6$) and recover the expected multiplicities. At this temperature the $^{13}C\{^1H\}$ signals are also observed for both types of carbon atoms: $\delta C = 11.9$, dd, $^2J_{P,C} = 108.3$ and 10.0 Hz, MeAu; $\delta C = 14.8$, t, AXX', MeP. Similar results are obtained for the iodide salt in aqueous solution (D_2O) at room temperature.

Table 1. Crystal data, data collection and structure refinement details.

	$[Me_2Au(PMe_3)_2]I$	$[Me_2Au(PMe_3)_2]ClO_4 \cdot CH_2Cl_2$
Empirical formula	$C_8H_{24}AuIP_2$	$C_9H_{26}AuCl_3O_4P_2$
M	506.08	563.55
Crystal system	orthorhombic	orthorhombic
Space group	*Cmcm*	*Cmcm*
a/Å	11.6285(19)	13.1865(4)
b/Å	19.7710(16)	17.6364(4)
c/Å	7.6701(11)	8.1742(2)
V/Å^3	1763.4(4)	1901.01(9)
ρ_{calc}/g cm^{-3}	1.906	1.969
Z	4	4
F(000)	936	1088
μ (Mo-K$_\alpha$) (cm^{-1})	102.43	83.33
T/K	143	143
Refls. measured	31548	26570
Refls. unique	935 [$R_{int} = 0.103$]	981 [$R_{int} = 0.051$]
Refined param./ restraints	38 / 3	63 / 2
*R*1 [$I \geq 2\sigma(I)$]	0.0448	0.0232
*wR*2[a]	0.1218	0.0592
Weighting scheme	$a = 0.0718$ $b = 0.0000$	$a = 0.0257$ $b = 10.8397$
σ_{fin}(max/min)/eÅ^{-3}	1.807/−1.538	1.359/−0.688

[a] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$.

These results show that in *dichloromethane* solutions the iodide anion intermittently competes successfully with the PMe_3 ligand for a coordination site at the gold(III) centre resulting in a rapid exchange process, while this is not true for the perchlorate anion. Notwithstanding, upon crystallization of the compounds from dichloromethane solution both anions are excluded from coordinating. However, efficient solvation of both the iodide *and* the perchlorate anion by *water* molecules reduces the reaction rate to such an extent, that the exchange is not discernible by NMR spectroscopy.

Crystal Structures

Crystals of the iodide and the perchlorate obtained from dichloromethane solutions are both orthorhombic, space group *Cmcm*, with $Z = 4$ molecules in unit cells of very similar dimensions (Table 1). The crystals of the perchlorate were found to contain stoichiometric quantities of dichloromethane (1:1). The solvent molecules could be localized in the refinement of the structure of the perchlorate salt, while the dichloromethane contents of the crystals of the iodide salt was substoichiometric with the remaining solvent molecules disordered. Both crystals were found to wither quickly

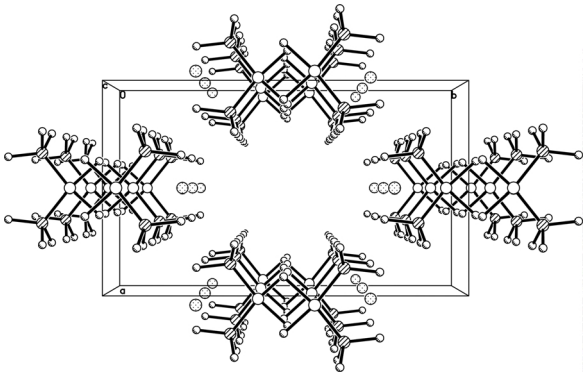


Fig. 1. Projection of the unit cell of crystals of the compound $[cis\text{-}Me_2Au(PMe_3)_2]^+ I^-$ along the *c* axis. (Arbitrary atomic radii; disordered and deficient intercalated dichloromethane solvate molecules are not shown).

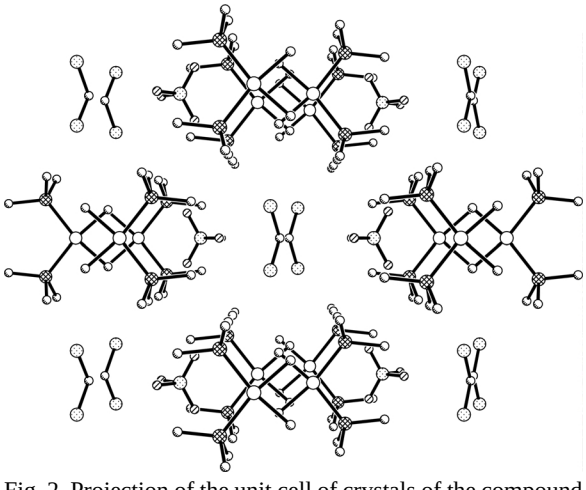


Fig. 2. Projection of the unit cell of crystals of the compound $[cis\text{-}Me_2Au(PMe_3)_2]^+ ClO_4^- \cdot (CH_2Cl_2)$ along the *c* axis with arbitrary atomic radii.

upon exposure to the atmosphere owing to loss of solvent.

The cations of the compounds are stacked in double columns along the *c* axis of the crystals. The Me_2Au parts of the cations in neighbouring columns are oriented in opposite directions and slightly interlocked, but the gold atoms of each column are placed on straight lines (Figures 1 and 2).

The iodide anions are placed above the rectangles formed by the four phosphorus atoms of each pair of adjacent cations in the same column (Fig. 1). The chlorine atoms of the perchlorate tetrahedra are in analogous positions, the two perpendicular O-Cl-O planes being in the *ab* and *ac* planes of the unit cell, respectively (Fig. 2). There are only van der Waals contacts between the hydrogen atoms of the PMe_3 ligands and the iodine or perchlorate oxygen atoms, respectively.

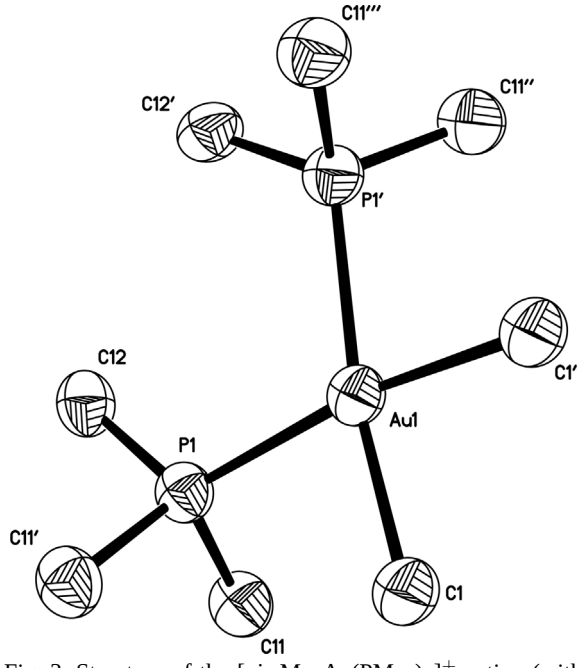


Fig. 3. Structure of the $[cis\text{-}Me_2Au(PMe_3)_2]^+$ cation (with crystallographic C_{2v} symmetry) in the perchlorate 1:1 dichloromethane solvate. Selected bond lengths [Å] and angles [°]: Au1-P1 2.3677(15), Au1-C1 2.084(6), Au1–Au1' 4.849; P1-Au1-C1 86.5(2), P1-Au1-P1' 104.11(8), C1-Au1-C1' 82.8(4).

It is obvious from the projections of both structures along the *c* axis of the crystals that there are large channels between the stacks of cations and their counterions. It is in these channels that the solvent molecules are intercalated. Their positions are ordered in the perchlorate salt (Fig. 2), but virtually random in the iodide salt, and the dichloromethane molecules have therefore been omitted in Fig. 1.

The $[Me_2Au(PMe_3)_2]^+$ cations have crystallographically imposed C_{2v} symmetry (Fig. 3). The metal atom is in a square planar environment C_2AuP_2 with Au-C and Au-P bond lengths of 2.089(13) / 2.084(6) and 2.350(3) / 2.367(1) Å for the iodide / perchlorate, respectively. Probably owing to steric crowding the P-Au-P' angles are widened to 103.20(17) / 104.11(8)° and the C-Au-C' angles compressed to 84.7(7) / 82.8(4)°. For the same reason the conformation of the PMe_3 group relative to the *cis*-MeAu unit is staggered.

Conclusions

The results of the present study have confirmed that the title compounds have the *cis*-structure originally proposed on the basis of earlier investigations. The *trans*-isomers are still unknown even though a variety of preparative routes have been probed. It therefore appears that the mutual *trans*-influence between a methyl and a trimethylphosphine ligand leads to paramount stability of the *cis*-isomer. This idea is supported by the significantly shorter Au-C bond lengths (average 2.087 Å) and by the increased thermal stability (> 130 °C) as compared to reference compounds in which one or both methyl groups are *trans* to other ligands, as *e.g.* methyl groups (2.15 Å) [20], ylides (2.10 Å) [21, 22] or halogen atoms (2.12 Å) [23]. It should also be noted that the reaction of $Me_3Au(PMe_3)$ with elemental iodine leads exclusively to the *cis*-product showing that a methyl group is retained in a position *trans* to the phosphine [16].

The Me_3P ligands are nevertheless susceptible to substitution by strong (soft) nucleophiles like I^- as demonstrated by the temperature- and solvent-dependent solution NMR experiments. Polar solvents reduce the substitution rate very considerably due to efficient solvation of the nucleophile. Weak (hard) nucleophiles like ClO_4^- do not induce a ligand exchange detectable on the NMR time scale.

In the crystal structures there is no evidence for metallophilic interactions between square-planar (d^8) metal centers. Recent experimental data [24] and results of quantum-chemical calculations [25, 26] have shown that such interactions have to be taken into account in a meaningful, comprehensive description of intermolecular interactions between gold(I) and gold(III) complexes, even though these weak forces may often be overruled by other types of chemical bonding, by steric hindrance, or by Coulomb repulsion. It should also be noted that stacking of square-planar platinum(II) complexes – which are isoelectronic with gold(III) complexes – is very common [27]. In the present case, cation aggregation which leads to short Au–Au contacts is probably prohibited by the bulk of the tertiary phosphines which is too great even for a stacking with the components in a staggered conformation. To our knowledge, the crystal and molecular structure of the isoelectronic complex molecule $Me_2Pt(PMe_3)_2$ is not known.

Experimental Section

General: All reactions and measurements were routinely carried out in an atmosphere of dry, pure nitrogen. Solvents were distilled, dried and kept under nitrogen. Glassware was oven-dried and filled with nitrogen. The starting materials were prepared following literature methods: $Me_3Au(PPh_3)$ [16]; *cis*-$Me_2Au(acac)$ [28],

NMR: Jeol JNM-GX 270 and 400; δH/C values in [ppm] relative to residual resonances of the deuterated solvents converted to TMS, δP relative external 85% aqueous H_3PO_4; J in [Hz]. ^{31}P and ^{13}C spectra were $\{^1H\}$-decoupled.

Preparations

cis-Dimethyl-bis(trimethylphosphine)gold(III) iodide: $Me_3Au(PMe_3)$ (95 mg, 0.30 mmol) was dissolved in 10 ml of dichloromethane and elemental I_2 (76 mg, 0.3 mmol) was added with stirring. Small amounts of gas were evolved. After 1 h the solvent was removed from the reaction mixture in a vacuum and the residue recrystallized from dichloromethane/pentane; 78 mg *cis*-$Me_2AuI(PMe_3)$ (61% yield). – 21 mg of this product (0.05 mmol) were dissolved in 2 ml of benzene and 0.1 ml of a 1 M solution of Me_3P (0.1 mmol) in toluene was added. A colourless solid precipitated, which was filtered and recrystallized from dichloromethane/pentane; 22 mg (87% yield), m. p. 129 – 130 °C (lit. 126 – 130 °C [1, 7]). NMR, D_2O, 25 °C: δH = 1.04, br.s, 6H, MeAu; 1.74, br.s., 18H, MeP; δP = −7.9, s. CD_2Cl_2, 25 °C: δH = 1.09, br.s, 6H, MeAu; 1.77, d, J = 9.7, 18H, MeP; δP = −11.5, br.s; δC = 14.8, d, J = 30, MeP; MeAu not observed. CD_2Cl_2, −90 °C: δH = 0.88, br.s, 6H, MeAu; 1.72, d, J = 10.0, 18H, MeP; δP = −8.6, s; δC = 11.9, dd, J = 108.3 and 10.0, MeAu; 14.8, t, AXX', MeP. $C_8H_{24}AuIP_2$ (506.08) found / calcd. C 19.48 / 18.99, H 4.35 / 4.78% (CH_2Cl_2 removed from the sample in a vacuum).

cis-Dimethyl-bis(trimethylphosphine)gold(III) perchlorate: Dimethylgold(III) acetylacetonate (16 mg, 0.05 mmol) was treated with 0.1 ml of a 0.5 M solution of $HClO_4$ (0.05 mmol) in diethylether/tetrahydrofuran. To the resulting solution containing $[Me_2Au(thf)_2]^+$ ClO_4^- was added 0.1 ml of a 1.0 M solution of Me_3P (0.1 mmol) in toluene. The mixture was stirred for 1 h and the precipitate filtered off and recrystallized from dichloromethane/pentane; 18 mg (75% yield), m. p. 126 – 139 °C with decomposition. NMR, CD_2Cl_2, 25 °C: δH = 1.05, t, $A_3XX'A'_3$, 6H, MeAu; 1.74, d, $A_9XX'A'_9$, 18H, MeP; δC = 12.0, t, AXX', MeAu; 14.0, br.t, AXX', MeP; δP = −6.0, s. $C_8H_{24}AuClO_4P_2$ (563.55) found / calcd. C 20.00 / 20.07, H 4.91 / 5.05% (CH_2Cl_2 removed from the sample in a vacuum).

Crystal structure determination

Specimens of suitable quality and size were mounted on the ends of quartz fibers in F06206R oil and used for intensity data collection on a Nonius DIP2020 diffractometer, employing graphite-monochromated Mo-K_α radiation. Intensity data were corrected for absorption effects (DELABS from PLATON). The structures were solved by a combination of direct methods (SHELXS-97) and difference-Fourier syntheses and refined by full matrix least-squares calculations on F^2 (SHELXL-97) [29]. The thermal motion of all non-hydrogen atoms was treated anisotropically. Apart from the alkene hydrogen atom of **1** which was found and refined isotropically, all hydrogen atoms were calculated and allowed to ride on their parent atoms with fixed isotropic contributions. During the structure refinement of $[Me_2Au(PMe_3)_2]I$ the atoms of a severely disordered solvent molecule were observed. Because these atoms could not be modelled satisfactorily, the SQUEEZE routine in PLATON [30] was applied. Further information on crystal data, data collection and structure refinement are summarized in Table 1. Important interatomic distances and angles are shown in the corresponding Figure Captions. Anisotropic displacement parameters and tables of 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-291991/291992.

Acknowledgements

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