(Triphenylarsine)gold(I) Complexes: Synthesis of an Oxonium Salt and Redistribution of the Arsine Ligands

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Gold(I) Complexes, Arsine Complexes, Oxonium Salts, Gold Clusters

The reaction of ([Ph₃As)AuCl] with Ag₂O in the presence of NaBF₄ in tetrahydrofuran affords three products, identified as ([Ph₃As)Au]BF₄ (40.3%), ([Ph₃As₂)Au]BF₄ (16.4%) and {[(Ph₃As)Au]O}BF₄ (17.3%). The properties of the main product agree well with recent literature data. The other two compounds are new and have been identified by their analytical, spectroscopic, and crystallographic data. The structures are isomorphous with those of the analogous Ph₃P complexes. Variations in the stabilities are discussed in terms of kinetic and thermodynamic effects.

Introduction

Tertiary phosphines are the most common ligands in modern coordination chemistry of univalent gold [1]. Labile gold-element bonds are readily stabilized by phosphines as auxiliary donors at two-, three- or four-coordinate gold(I) centers. Clustering of gold(I) at Main Group and Transition Elements as heteroatoms is also most common for systems with terminal phosphine ligands [2], while several attempts to obtain similar compounds with other auxiliary ligands than phosphines have often met with failure.

In the present work we therefore undertook a study of some simple arsenic analogues in order to delineate further the stability borderlines determined by the ligands L for compounds of the type [(LAu)ₓE]⁺, with L = Ph₃As, E = N (n = 4) and E = O (n = 3). The corresponding phosphorus compounds (L = PPh₃) are classics of gold heterocluster chemistry [2, 3].

Results and Discussion

When the method established for the synthesis of {tris[(triorganophosphine)gold(I)]oxonium} salts [2-7] was applied to the preparation of the triphenylarsine analogue starting from silver oxide, chloro(triphenylarsine)gold(I) and sodium tetrafluoroborate in tetrahydrofuran, mixtures of products were obtained in all experiments. This result indicated that bonding of the arsenic ligand to the gold center was much more labile, and that redistribution of ligands is a major complication not observed with the phosphate analogues.

Extraction of the reaction mixtures with dichloromethane followed by layering of the solutions with diethyl ether gave a crop of crystals composed of three different components, which could be separated under a microscope. Red needles, pale yellow plates and colourless prisms were isolated in 17.3, 16.4 and 40.3% yield, respectively (calculated relative to the arsenic content). There is also a large amount of dark insoluble material containing the excess of the silver oxide and sodium tetrafluoroborate, and finely devided gold metal.

The main product (1) was identified as [tetakis(triphenylphosphine)gold(I)] tetrafluoroborate, m.p. 268–269 °C, through its analytical, spectroscopic and crystallographic data (Experimental Part). The compound has just recently been fully characterized [8].

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Crystal data

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<td>12.731(2)</td>
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<td>12.853(4)</td>
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<td>c (Å)</td>
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Table I. Crystal data, data collection, and structure refinement for compounds 2 and 3.

[a] R = Σ(|F_o| - |F_c|) / Σ|F_o|;
[b] wR2 = {Σ[w(F_o^2 - F_c^2)^2] / Σ[w(F_o^2)^2]}^{1/2}; w = 1/[σ(σ(F_o^2) + (ap)^2 + bp)]; p = (F_o^2 + 2F_c^2)/3;

The analytical data of the pale yellow crystals (2), m. p. 211 - 212 °C, suggested the presence of the corresponding 1:2 complex of Au^+BF_4^- and triphenylarsine, which had not been reported in the literature. The structure of the compound was determined by a single crystal X-ray diffraction study. The crystals are monoclinic, space group C2/c, with 8 formula units in the unit cell. The compound is thus isomorphous with the corresponding triphenylphosphine complex [9]. The lattice contains bis(triphenylarsine)gold(I) cations loosely associated with the tetrafluoroborate anions (Fig. 1, Table I).

The ion pair has no crystallographically imposed symmetry owing to an irregular orientation of the six phenyl groups. Under the influence of the approaching anion the As1-Au-As2 axis is significantly bent [166.07(2)°], but the Au-As bonds are equivalent within the accuracy limits of the experiment (Caption to Fig. 1). The anion is crystallographically disordered, but the positioning of the fluorine atoms could be resolved in a split model calculation. The situation is similar for the phosphorus analogue [9]. The main difference between the two structures (with Ph_3P and Ph_3As ligands) is the variation in the Au-E and C-E distances (E = P, As). The data reflect the difference in the covalent radii of phosphorus and arsenic in good agreement with previously tabulated values.

The red needles (3), m. p. 228 - 229°C, were identified as the tris[(triphenylarsine)gold(I)]oxonium tetrafluoroborate by the analytical, spectroscopic and structural data. The compound crystallizes in the monoclinic space group P2_1/c with 4 formula units in the unit cell. It is isomorphous with the corresponding phosphorus compound (Fig. 2) [2, 3].

The lattice is composed of dimeric cations and tetrafluoroborate anions. The two components of
the cation dimers are related by a crystallographically imposed center of inversion in the center of the square of gold atoms \( \text{Au}1\text{Au}3\text{-Au}1'\text{-Au}3' \). The core of the dication is an aggregate of two \( \text{O} \text{Au}_3 \) pyramids facing edges (\( \text{Au}1\text{-Au}3 \) versus \( \text{Au}1'\text{-Au}3' \)). The gold atoms thus form a six-membered ring in a chair conformation with \( \text{Au}--\text{Au} \) contacts in the narrow range from 3.0208(7) to 3.1553(8) Å. These short contacts are responsible for the dimerization and contribute considerably to the overall stability of the hexanuclear dication \( 2 \).

The angles at the gold atoms are all close to 180° showing that the gold-gold contacts do not perturb significantly the geometry of the \( \text{O} \text{-Au-As} \) bonding. However, the angles at the oxygen atoms are all smaller than the tetrahedral standard and reflect very nicely the influence of \( \text{Au}--\text{Au} \) bonding at the basis of the \( \text{O} \text{Au}_3 \) pyramids.

These observations are all very similar to those reported for the corresponding triphenylphosphine complex [3]. Again, major differences are only found for the \( \text{Au-P/As} \) and \( \text{P-C/As} \) distances which are mainly determined by the covalent radii of phosphorus and arsenic. The results therefore suggest that structure and bonding in the trigoldoxonium compounds with phosphine/arsine ligands is not very different and dominated by the core elements [2].

The difficulties encountered in the synthesis of the arsenic compound can be ascribed to a greater kinetic lability of the (arsine)gold compounds which release their ligands readily in substitution reactions with other nucleophiles in the reaction mixture. The results also suggest, however, that the salt \( [(\text{Ph}_3\text{As})_4\text{Au}] \text{BF}_4 \) is an energy sink and draws arsenic ligands away from all other components of the system. (After long reaction times at ambient temperature only this product can be isolated and no oxonium salt is left in the reaction mixture.) This is surprising since there is no such tendency for the related triphenylphosphine systems. It therefore appears that geometrical factors (the ratio of the element radii \( \text{Au/As} \) versus \( \text{Au/P} \) ) play a significant role in determining the thermodynamics of the reactions, which together with the kinetic effects make the preparation of (arsine)gold(I) clusters a much more delicate task. Thus all attempts to prepare the tetrakis[(triphenylarsine)gold(I)] ammonium tetrafluoroborate failed [10], while the analogous triphenylphosphine complex is well established [2, 11 - 13].

**Experimental Part**

**General:** All experiments were carried out in an atmosphere of dry nitrogen. Solvents were distilled and saturated with nitrogen. \( (\text{Ph}_3\text{As})\text{AuCl} \) was prepared following the literature procedure [14]. NMR spectra: Jeol GX 400. Mass spectra: Finnigan MAT 90 (FAB, 4-nitrobenzyl alcohol matrix). Microanalysis was by in-house equipment for combustion and atomic absorption spectroscopy techniques.
Preparation of the Compounds: Silver oxide was prepared from KOH (5.63 g, 100 mmol) and AgNO₃ (8.54 g, 50 mmol) in water, washed till alkali-free, and dried in a vacuum. This material was suspended in tetrahydrofuran (500 ml) and treated with (Ph₃As)AuCl (3.01 g, 5.59 mmol) and NaBF₄ (3.68 g, 33.53 mmol) with stirring at room temperature. After 3 h all volatiles were removed in a vacuum at room temperature to leave a dark brown residue, which was washed three times with benzene (20 ml) to remove unreacted (Ph₃As)AuCl and then extracted three times with dichloromethane (20 ml). The volume of the extract was reduced to 10 ml in a vacuum and layered with diethyl ether (30 ml). After 2 d a crop of crystals was obtained, the components of which were carefully separated under a microscope.

a) Colourless prisms (1), 0.85 g (40.3 % based on As), m.p. 268-269 °C; analytical, spectroscopic, and X-ray data are in agreement with those reported for [(Ph₃As)Au]BF₄ [8].
b) Pale yellow plates (2), 0.41 g (16.4 %), m.p. 211-212 °C.

Elemental analysis for C₃₆H₃₀Au₂BF₄ (896.22).
Calcd C 34.02 H 2.74 Au 21.4%. Found C 34.01 H 2.75 Au 21.4%.

1H NMR (CDCl₃): δ 6.70 - 7.53, m, Ph. 13C{¹H} NMR (CDCl₃): δ 133.27, 132.16, 130.34, 129.92 (s, Ph for o, p, m, and ipso, respectively). MS (FAB): m/z = 809.3 (100%, [M⁺]).

C) Red needles (3), 0.52 g (17.3 %), m.p. 228-229°C (decomposition).

Elemental analysis for C₅₄H₄₅Au₂BF₄O (1612.37).
Calcd C 30.23 H 3.34 Au 21.98%. Found C 30.21 H 3.34 Au 21.98%.

1H NMR (CDCl₃): δ 7.60 - 7.53, m, Ph. 13C{¹H} NMR (CDCl₃): δ 133.27, 132.16, 130.34, 129.92 (s, Ph for o, p, m, and ipso, respectively). MS (FAB): m/z = 1525.5 (15% [{(Ph₃As)Au}⁺]).

Structure determinations

Suitable crystals of 2 and 3 were mounted in glass capillaries and used for measurements of precise cell constants and intensity data collection. During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed for both compounds. Diffraction intensities were corrected for Lp and for absorption effects (psi-scans). The thermal motion of all non-hydrogen atoms of compound 2 was treated anisotropically, whereas the phenyl rings and the BF₄⁻ anion of compound 3 were refined with isotropic contributions. All hydrogen atoms were placed in idealized calculated positions and allowed to ride on their corresponding carbon atom with Uiso (C) = 1.5 Ueq (C). The anion of 2 was disordered and refined in split positions with site occupation factors of 50/50. Further information on crystal data, data collection, structure solution and refinement is summarized in Table I. Important interatomic distances and angles are summarized in the corresponding figure captions. Anisotropic thermal parameters, tables of distances and angles, and atomic coordinates have been deposited with Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen. The data are available on request on quoting CSD No. 408769 (2) and 408870 (3).

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