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

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The reaction of $[(Ph_3As)AuCl]$ with Ag_2O in the presence of $NaBF_4$ in tetrahydrofuran affords three products, identified as $[(Ph_3As)_4Au]BF_4$ (40.3%), $[(Ph_3As)_2Au]BF_4$ (16.4%) and $\{[(Ph_3As)Au]_3O\}BF_4$ (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 Ph_3P 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 $[(LAu)_nE]^+$, 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 arsine ligand to the gold center was much more labile, and that redistribution of ligands is a major complication not observed with the phosphine 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 [tetrakis(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].

$$\begin{array}{l} (Ph_3As)AuCl + Ag_2O + NaBF_4\\ \rightarrow [(Ph_3As)_4Au]^+BF_4^-\\ 1\\ [(Ph_3As)_2Au]^+BF_4^-\\ 2\\ \{[(Ph_3As)Au]_3O\}^+BF_4^-\\ 3\end{array}$$

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	2	3	Table I. Crystal data, data collec- tion, and structure refinement for
Crystal data			compounds 2 and 3 .
Formula M_r Crystal system Space group a (Å) b (Å) c (Å) β (°) V (Å ³) ρ_{calc} (gcm ⁻³) Z	$\begin{array}{c} C_{36}H_{30}As_{2}AuBF_{4}\\ 896.22\\ monoclinic\\ C2/c\;[No.\;15]\\ 21.743(2)\\ 12.493(1)\\ 24.391(3)\\ 92.74(1)\\ 6617.9(11)\\ 1.799\\ 8\end{array}$	$\begin{array}{c} C_{54}H_{45}As_{3}Au_{3}BF_{4}O\\ 1612.37\\ monoclinic\\ P2_{1}/c\\ 12.731(2)\\ 24.853(4)\\ 16.018(2)\\ 98.90(1)\\ 5007.1(13)\\ 2.139\\ 4\end{array}$	^[a] $R = \Sigma(F_0 - F_c / \Sigma F_0 ;$ ^[b] $wR2= \{[\Sigma w(F_0^2 - F_c^2)^2] / \Sigma[w(F_0^2)^2]\}^{1/2}; w = 1/[\sigma^2(F_0^2) + (ap)^2 + bp]; p = (F_0^2 + 2F_c^2)/3;$ a = 0.0188 (2), 0.0652 (3); b = 36.30 (2), 51.10 (3).
F(000)	3456	3016	
$\mu(MOK\alpha)$ (cm) Data collection	04.78	107.89	
T (°C) Scan mode hkl range $\sin(\theta/\lambda)_{max}$ (Å ⁻¹) Measured reflections Refls. used for refinement Absorption correction T_{min}/T_{max} Refinement	$ \begin{array}{l} -52 \\ \omega \\ -27 \rightarrow 27, 0 \rightarrow 15, 0 \rightarrow 31 \\ 0.64 \\ 7325 \\ 7160 \left[R_{\text{int}} = 0.0201 \right] \\ \text{psi-scans} \\ 0.654/0.999 \\ \end{array} $	$-74 \\ \omega \\ -15 \rightarrow 15, 0 \rightarrow 29, 0 \rightarrow 19 \\ 0.64 \\ 8056 \\ 7778 [R_{int} = 0.0278] \\ psi-scans \\ 0.920/1.000$	
Refined parameters H atoms (found/calcd) Final R values $[I > 2\sigma(I)]$ $R1^{[a]}$ $wR2^{[b]}$ (shift/error) _{max} $\rho_{fin}(max/min)$ (eÅ ⁻³)	433 0/30 0.0423 0.0732 < 0.001 1.044/-1.083	192 0/45 0.0484 0.1096 < 0.001 1.730/-0.928	

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⁺BF₄⁻ 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 $[166.07(2)^{\circ}]$, 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 Ph₃P and Ph₃As 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



Fig. 1. Molecular structure of compound **2** (ORTEP drawing with 50% probability ellipsoids. Only one position of the disordered BF_4^- is shown, H-atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Au-As1 2.3988(6), Au-As2 2.3957(6), Au···F1 3.382(1); As1-Au-As2 166.07(2).

the cation dimers are related by a crystallographically imposed center of inversion in the center of the square of gold atoms Au1Au3-Au1'-Au3'. The core of the dication is an aggregate of two OAu₃ pyramids facing edges (Au1-Au3 versus Au1'-Au3'). The gold atoms thus form a six-membered ring in a chair conformation with Au--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 O-Au-As bonding. However, the angles at the oxygen atoms are all smaller than the tetrahedral standard and reflect very nicely the influence of Au-Au bonding at the basis of the OAu₃ pyramids.

These observations are all very similar to those reported for the corresponding triphenylphosphine complex [3]. Again, major differences are only found for the Au-P/Au-As and P-C/As-C 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



Fig. 2. Molecular structure of compound **3** (ORTEP drawing with 50% probability ellipsoids, H-atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Au1-O 2.050(8), Au2-O 2.035(8), Au3-O 2.026(8), Au1-Au2 3.0208(7), Au1-Au3 3.0295(8), Au2-Au3 3.1553(8), Au1-Au3' 3.0506(8), Au1-As1 2.2204(14), Au2-As2 2.3176(14), Au3-As3 2.3227(14); Au1-O-Au2 95.4(3), Au1-O-Au3 96.0(3), Au2-O-Au3 102.0(3), As1-Au1-O 176.2(2), As2-Au2-O 178.3(2) As3-Au3-O 176.6(2).

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 [(Ph₃As)₄Au]BF₄ is an energy sink and draws arsine 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 Au/As versus 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. (Ph₃As)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.

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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)₄Au]BF₄ [8].

b) Pale yellow plates (**2**), 0.41 g (16.4 %), m. p. 211 - 212 °C.

Elemental analysis for C₃₆H₃₀As₂AuBF₄ (896.22).

Calcd C 48.25 H 3.34 Au 21.98%,

Found C 48.10 H 3.33 Au 22.16%.

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 = 809.3 (100%, [M⁺]).

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

Elemental anlysis for C₅₄H₄₅As₃Au₃BF₄O (1612.37)

Calcd C 40.23 H 3.33 Au 36.66 F 4.71%,

Found C 40.10 H 3.10 Au 36.90 F 4.62%.

¹H NMR (CDCl₃): δ 7.56 (t, 9H, *J* = 6.95 Hz, Ph-p), 7.32 (t, 18H, *J* = 7.32 Hz, Ph-m), 7.47 (d, 18H, J = 7.32 Hz, Ph-o). ¹³C{¹H} NMR (CDCl₃): δ 133.24, 131.74, 130.97, 130.06 (s, Ph for o, p, ipso, and m, respectively). MS (FAB): *m/z* = 1525.5 (15% [{[(Ph₃As)Au]₃O}]⁺).

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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 $BF_4^$ 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 $U_{iso(fix)} = 1.5 U_{eq}$ (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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