Tris[(triphenylphosphine)gold(I)]oxonium Dihydrogentrifluoride as the Product of an Attempted Preparation of [(Triphenylphosphine)gold(I)] Fluoride

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Herrn Prof. Dr. D. Sellmann zum 60. Geburtstag gewidmet
Z. Naturforsch. 55 b, 1000–1004 (2000); received August 31, 2000
Gold Fluoride, Trigoldoxonium Salts, Dihydrogentrifluoride

The reaction of equivalent quantities of (triphenylphosphine)gold chloride and silver fluoride in CHCl3/MeOH gives tris(triphenylphosphine)gold(I)oxonium trifluoride in good yield. This product is formed through the action of water in the reaction medium. Crystals of [(Ph3P)Au]2+·[H2F3]− (monoclinic, space group P21/c, Z = 4) contain the cations as hexanuclear dimers with short intra- and intermolecular Au-Au contacts. The structural details are similar to those of related salts with different anions. The [H2F3]− anion is V-shaped with one symmetrical and one unsymmetrical F-H-F hydrogen bond and is best described as an addition compound of an HF molecule and a [F-H-F]− anion. The results indicate a high affinity of H2O/OH− for (phosphine)gold fluorides and – by the same token – prove that tri(gold)oxonium cations are stable to anhydrous HF and F− anions. By contrast, hydrochloric acid is known to degrade [(R3P)Au]2O affording (R3P)AuCl and water.

Introduction

(Triorganophosphine)gold halides [(R3P)AuX] with the heavier halogens (X = Cl, Br or I) are among the most important groups of gold(I) coordination compounds. Virtually irrespective of the nature of the R3P (or R3As) ligands, compounds of this stoichiometry are readily prepared, are stable to air and moisture and have therefore been the convenient base chemicals for most endeavours in gold chemistry [1]. The complexes feature linear two-coordinate gold centers and are monomers in solution and in the gas phase, but are associated into oligomers through aurophilic bonding in the crystalline state if the steric requirements of the ligand leave a sufficiently open coordination sphere at the metal atom [2].

It has intrigued several generations of precious metal chemists that none of the corresponding complexes of gold(I) fluoride [(R3P)AuF] are available [3] and that the ligand-free gold(I) fluoride [AuF] could never be prepared in the condensed phase. Although there is now convincing evidence for the existence of AuF molecules in the gas phase with a detailed knowledge of their physical characteristics [4], all attempts to prepare solid AuF have been unsuccessful. This is surprising because solid silver(I) fluoride AgF is readily prepared and there is a whole host of binary and complex gold fluorides with the metal in higher valence states (AuF2, AuF3, AuF5; [AuF4]−, [AuF5]−, etc.) [5].

These observations have parallels in the chemistry of gold oxides, where complexes of simple gold(I) oxide of the type [(R3P)Au]2O were found to be inaccessible. While the corresponding sulfides can be prepared by simple substitution reactions (from the corresponding chloride with sulfide or hydrogen sulfide anions) the analogous reactions with oxide or hydride anions do not give access to related complexes of [Au2O] [6]. In this case, however, the corresponding tri(gold)oxonium complexes of the type {[(R3P)Au]2O}+ are obtained, which are very robust species of high thermal stability [7]. In fact, these tri(gold)oxonium salts are encountered as components in virtually all reaction mixtures containing [(R3P)Au][X] compounds and oxide or hydride anions. If X represents a good leaving group, even traces of water are captured

0932-0776/00/1100-1000 $ 06.00 © 2000 Verlag der Zeitschrift für Naturforschung, Tübingen • www.znaturforsch.com K
by the [(R₃P)Au]⁺ units to generate the oxonium cations [8]. With strongly aurating reagents the oxonium center will accept even a fourth [(R₃P)Au]⁺ unit to give tetrahedral \{[(R₃P)Au]₄O\}²⁺ dications [9].

The cations [(R₃P)Au]₃O⁺ have remarkable structures in that the Au₃O core units are compact trigonal pyramidal clusters with small Au-O-Au angles and short Au–Au contacts [7]. Moreover, the cations are found to be associated into hexanuclear dimers in the crystal lattices with short Au–Au contacts between pairs of gold atoms of the two components. Two edges of the trigonal pyramids are aligned either parallel or perpendicular to form, respectively, a square (A) or a tetrahedron (B) of gold atoms [8]. Bulky ligands R₃P may impede this association [10] and may also cause a widening of the Au-O-Au angles in the components, but in the absence of steric crowding the association is a recurrent phenomenon which is also common with the analogous sulfonium, selenonium and telluronium compounds [7].

[LAu]⁺ units are also clustering at chloride and bromide anions to give \{[(R₃P)Au]₂X\}⁺ cations (X = Cl, Br) [11] with small Au-X-Au angles and hence short Au–Au contacts. Recent work by Seppelt et al. has shown that hexafluoroantimonate anions appear to be mono-coordinate to [(F₃As)Au]⁺ cations [12]. No other coordination compounds with fluorine atoms attached to gold (I) centers are known.

This literature background set the stage for some new attempts in this laboratory to prepare either [(R₃P)AuF] molecules or \{[(R₃P)Au]₂F\}⁺ cations. The initial experiments were not successful but produced the title compound in which a tri(gold)oxonium cation coexists with the dihydrogentrifluoride anion \(\text{H}_2\text{F}_3⁻\). The implications of this unexpected result are discussed.

**Results**

From the reaction of (triphenylphosphine)gold chloride and silver fluoride in CH₂Cl₂/MeOH at -78 °C a precipitate of white AgCl in a clear supernatant solution is obtained. After filtration, evaporation and recrystallisation of the solid residue from dichloromethane/pentane, colourless crystals were isolated in 68% yield. The product is soluble in dichloromethane, trichloromethane and tetrahydrofuran but insoluble in pentane and other non-polar solvents. The solutions in trichloromethane show only one signal in the ³¹P NMR spectrum and one set of phenyl resonances in both the ¹H and ¹³C NMR spectra indicating the equivalence of all P₃ ligands. In the mass spectrum, the parent cation is observed.

Single crystals grown upon careful layering of a dichloromethane solution with pentane are monoclinic, space group P2₁/c. The unit cell contains four formula units together with 6 molecules of dichloromethane: \{[(Ph₃P)Au]₃O]⁺ [H₂F₃]⁻ 1.5 CH₂Cl₂. The trinuclear cations are associated into dimers, the individual units of which are related by a center of inversion (Fig. 1). The hexanuclear dications, the anions and the solvent molecules are well separated in the lattice and show no sub-van der Waals contacts. One of the two CH₂Cl₂ molecules is disordered around a center of inversion.

**Cation:** The pseudo-trigonal pyramidal core unit Au₃O of the monomeric trinuclear cation has three different Au-O bond lengths of 2.049(4) Å (Au1), 2.042(4) Å (Au2) and 2.067(3) Å (Au3). The Au-O-Au angles are 102.8(1), 97.0(1) and 90.0(1)°, meaning significant deviations from ideal threefold symmetry. The average Au-O-Au angle of 96.6° and the
sum of these angles of 289.8° both indicate a steep pyramid with short base edges of 2.911(1) (Au1-Au3), 3.174(1) (Au1-Au2) and 3.077(1) Å (Au2-Au3) (average: 3.054 Å). The angles O-Au-P are all close to 180°, with individual values of 174.0(1) (Au1), 174.6(1) (Au2) and 173.7(1)° (Au3).

The hexanuclear Au6O2 clusters of the dimers (dication) are formed through a close alignment of two Au2-Au3 edges to give two short contacts Au2-Au3*/Au3-Au2* of 3.120(1) Å. These inter-ionic distances are thus only slightly longer than the intra-ionic distances (average 3.054 Å, above). With Au2-Au3/Au2*-Au3* at 3.0773(3) Å, the quadrangle Au2-Au3-Au2*-Au3* is an only slightly distorted square (Au3-Au2-Au3*/Au3-Au3 93.12°) (Fig. 1).

The overall geometry of the cations in the [H2F3]− salt is in good agreement with dimensions reported for salts with other counterions [7]. Crystallographic data are available for solvent-free [{(Ph3P)Au3O}BF4, (and its sesqui-dichloromethane solvate) [8], 13] as well as for a solvent-free 1,1,1-trifluoroacetylacetonate [14] and a 3,5-dinitro-4-pyridinolinate [15]. Because these salts contain the same phosphine ligand, the structures of the cationic components are particularly close to that of the title compound. However, the differences are also not great for the tri(gold)oxonium complexes with a) tri(p-anisyl)phosphine ligands, trifluoromethylsulfonate counterions and acetone as the solvate molecule [16], and b) diphenylmethylphosphine as the ligand, tetrafluoroborate anions and dichloromethane as the solvate molecule [13]. Clearly the steric bulk of these triarylpiphosphines is very similar and has comparable influence on the structure of the core unit.

With larger ligands like tri(i-propyl)phosphine [17], tri(o-tolyl)phosphine [13], tris(mesityl)phosphine [18], and tris(dimethylamino)phosphine [10], the Au6O pyramidal is widened to account for the steric pressure in the periphery, and the dimerization into dication (A) is no longer observed because the intimate approach of two cations is impeded. These salts were prepared either as tetrafluoroborates or as triflates and contain dichloromethane or hexane/water solvate molecules, which do not appear to play any role in determining the structure.

With the smallest tertiary phosphine, trimethylphosphine, dimers are also formed, but the mode of dimerization is different (B) [19]. The geometry of the monomers is more distorted in this more intimate cluster and difficult to compare with species of dimerization mode A.

**Anion:** Although the dihydrogentrifluoride anion [H2F3]− was formulated more than a century ago [20], to the best of our knowledge there are only three attempts to determine the crystal structure documented in the literature. In 1963, Forrester et al. [21] analyzed the crystal structure of K[H2F3] (m. p. 71.7 °C) at 24 °C and found a V-shaped geometry of the three fluorine atoms with F–F distances of 2.33 Å (average) and F–F–F angles of 130 and 139° (two independent molecules in the unit cell). The hydrogen atoms could not be localized, but strong F–H–F hydrogen bonds were proposed with the suggestion of an adduct between [HF2]− and HF.

In 1986, Mootz and Boenigk [22] studied (at −100 °C) the crystalline phase of (pyridine)(HF)3 (m. p. −17 °C). This was formulated as a pyridinium dihydrogentrifluoride [Pyrr][H2F3]− with the structure being characterized by hydrogen bonding between cations and anions. Disregarding the N–H⋯F contact, the structure of the anion may also be described as V-shaped with F⋯F distances of 2.344 Å (average) and an F⋯F⋯F angle of 118°. The hydrogen atoms are both shifted towards the outer fluorine atoms, such that the unit may be described as an adduct of two HF molecules with a fluoride anion, [F(HF)2]−.

In 1987, the same authors reported the structure of [Me3N][H2F3], in which the anion has a similar geometry [23]. The two F⋯F distances are shorter at 2.309 Å (average) and the F⋯F⋯F angle is wider at 123°, probably owing to the absence of the N–H⋯F contact (above).

In the title compound the V-shaped structure of the anion has been confirmed (Fig. 2). The F⋯F
distances are 2.273 Å for F1–F3 and 2.325 Å for F2–F3 with an angle F1–F3–F2 of 117.5°. The positions of the hydrogen atoms were found, but only H1 could be refined. It has an unsymmetrical position between F1 and F3, while H2 is approximately symmetrical between F2 and F3 with an angle F2–H2–F3 close to linear [179.7°], indicating an adduct of HF to [HF2]−.

Discussion

The reaction of (Ph3P)AuCl with AgF in CH2Cl2/MeOH does not produce the desired (Ph3P)AuF product. In good yield the corresponding tri(gold)oxonium salt was obtained instead which must originate from hydrolysis. Rigorous drying of the reaction components appears to suppress all reactivity in the system.

During the hydrolysis, hydrogen fluoride is (presumably) generated which is then trapped by the fluoride anions to give the anion [F(HF)2]−.

The stability of the resulting salt shows that the tri(gold)oxonium cation is inert towards HF. In this context it should be pointed out that the same tri(gold)oxonium cation is cleaved by HC1 or HBr presumably) generated which is then trapped by the fluoride anions (around the Au atoms). The function minimized was: $R(\text{obs}) = \frac{1}{n} \sum w(F_o^2 - F_c^2)\frac{1}{2}$; $w = 1/\sigma^2(F_o^2)$ + $(ap)^2 + bp$; $p = (F_o^2 + 2F_c^2)/3$; $a = 0.0322$. Important interatomic distances and angles are given in the figure captions. Anisotropic thermal parameters and complete lists of interatomic distances and angles have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk). The data are available on request on quoting CCDC 151050.

Acknowledgement

This work was supported by Deutsche Forschungsgemeinschaft, by Fonds der Chemischen Industrie and by the Alexander von Humboldt Stiftung (T.M.).