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TRIS(TRIPHENYLPHOSPHINEGOLD)OXONIUM SALTS *

A.N. NESMEYANOV, E.G. PEREVALOVA *, Yu.T. STRUCHKOV, M.Yu. ANTIPIN,
K.I. GRANDBERG and V.P. DYADCHENKO
Chemistry Department, Moscow State University, Moscow B-234 (U.S.S.R.)

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Summary

The oxonium salts $(Ph_3PAu)_3O^+X^-$ where $X^- = BF_4^-$, CF_3COO^-, MnO_4^- have been prepared. These salts are formed from coordinatively unsaturated Ph_3PAu^+ cations in alkaline or acid media. An X-ray study of $(Ph_3PAu)_3O^+BF_4^-$ indicates that the oxonium ions are dimeric in the crystalline form. The fragment $(Ph_3PAu)_3O$ has a pyramidal structure: the oxygen atom is outside the Au_3 plane.

The chemistry of univalent gold has been well developed, various compounds of different structure being obtained. However up to this moment, such common gold (I) derivatives as oxides, hydroxides, alkoxides and phenoxides have not been prepared. Salts of some oxygen containing acids and siloxy-derivatives of type $R_3PAuOSiR_3$ represent a rather rare set of compounds incorporating a gold(I)—oxygen bond. The LAu^+ moiety, the structural unit of many complexes of gold, is a "soft" Lewis acid. It does not usually combine with "rigid" oxygen containing anions. The most vivid example demonstrating this tendency of gold is acetylacetonato(triphenylphosphine)gold(I). In this complex the gold atom is bound to the carbon atom [1] whereas transition metals, in particular copper and silver, are usually bound to oxygen atoms in β-diketonates. Another example is presented by a reaction of a gold(I) chloride complex with sodium methoxide [2] yielding a trinuclear cluster, not gold methoxide. So, it is clear that syntheses of new types of compounds containing gold(I)—oxygen bonds and investigation of their properties are of interest.

In this paper we report syntheses of gold compounds of a new type, salts of gold containing the oxonium cation $(Ph_3PAu)_3O^+$. The analogous salts are known for some transition and non-transition metals but their reaction ability is scarcely investigated.

In the course of our work we have found that tris(triphenylphosphinegold)-

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* Dedicated to Prof. G.A. Razuvaev on the occasion of his 85th birthday on August 23rd, 1980.

oxonium salts can be easily prepared and that they are highly reactive. This makes the above salts very useful precursors for the synthesis of gold(I) complexes and particularly of organogold(I) compounds.

Gold containing oxonium salts are produced in high yields when water interacts with coordinatively unsaturated Ph_3PAu^+ cations in an alkaline or acid medium. The Ph_3PAu^+ ions in solution are obtained readily in the reaction of chloro(triphenylphosphine)gold with silver tetrafluoroborate. When alkali being added to this solution, tris(triphenylphosphinegold)oxonium tetrafluoroborate is formed.

$$\mathrm{Ph_3PAuCl \xrightarrow{AgBF_4} Ph_3PAu^+BF_4^- \xrightarrow{OH^-} \underset{84\%}{(Ph_3PAu)_3O^+BF_4^-}}$$

The same oxonium salt is also obtained by the action of tetrafluoroboric acid and water on acetato(triphenylphosphine)gold in ether solution.

$$\mathrm{CH_3COOAuPPh_3 \xrightarrow{H_2O,\ HBF_4} \underset{74\%}{(Ph_3PAu)_3O^+BF_4^-}}$$

Tris(triphenylphosphinegold)oxonium trifluoroacetate results from the reaction of water with trifluoroacetato(triphenylphosphine)gold.

$$\mathrm{CF_3COOAuPPh_3 \xrightarrow[CHCl_3]{H_2O} \underset{46\%}{(Ph_3PAu)_3O^+CF_3COO^-}}$$

A convenient method of the synthesis of tris(triphenylphosphinegold)oxonium tetrafluoroborate and permanganate consists in the interaction of chloro- or bromo(triphenylphosphine)gold with Ag_2O and $NaBF_4$ or $KMnO_4$, respectively.

$$\mathrm{Ph_3PAuX + Ag_2O} \begin{cases} \xrightarrow{\mathrm{NaBF_4}} \mathrm{(Ph_3PAu)_3O^+BF_4^-} \\ \qquad 90\% \\ \\ \xrightarrow{\mathrm{KMnO_4}} \mathrm{(Ph_3PAu)_3O^+MnO_4^-} \\ \qquad 70\% \end{cases}$$

The tendency of Ph_3Au^+ cations to form oxonium species in the reactions that would be expected to lead to the hydrate $Ph_3PAuOH_2^+$, hydroxide Ph_3PAuOH or oxide $(Ph_3PAu)_2O$ suggests the existence of structural factors enhancing the stability of the $(Ph_3PAu)_3O^+$ ion as compared with the above complexes that are not known in the individual state. Such a factor may be represented, for example, by the intramolecular interaction of gold atoms.

The molecular structure of tris(triphenylphosphinegold)oxonium tetrafluoroborate was determined by X-ray diffraction.

The crystals of $(Ph_3PAu)_3O^+BF_4^-$ are monoclinic: a = 12.616(8), b =

24.796(15), $c = 16.151(10)$ Å, $Z = 4$, $\beta = 97.37(5)°$, $V = 5011(4)$ Å^3, $D_{calc} = 1.94$ g cm^{-1}, $D_{exp} = 1.93$ g cm^{-1}, space group $P2_1/c$.

A total of 4377 independent reflections (3804 reflections with $I \geqslant 2\sigma$) were obtained on an automatic Syntex-P2$_1$ diffractometer (λMo-K_α) equipped with a graphite monochromator using $\theta/2\theta$ scans ($2\theta \leqslant 40.5°$, absorption correction not applied). Since the determination of the positions of heavy atoms by the Patterson method failed, three gold atoms were located by a direct method using the programme MULTAN. The coordinates of other atoms were obtained from the series of successive difference syntheses of an electron density. A least squares refinement was carried out only for Au, P (anisotropic) and O (isotropic) atoms. When the whole structure was refined, thermal parameters of several carbon atoms became negative. That probably arose from uncorrected absorption errors. That is why the coordinates of carbon atoms and of BF_4^- determined from the difference synthesis of an electron density were fixed with $B_{iso} = 6$ Å^2. The final R-factor is 0.079. The atomic coordinates are listed in Table 1. The structure of the cation (excluding the C_6H_5 groups) and the most important angles and interatomic distances are shown in Fig. 1. The calculations were carried out on Eclipse S/200 computer using the programme EXTL.

In the crystal the $(Ph_3PAu)_3O$ moieties are combined into centrosymmetric $(1 - x, -y, 1 - z)$ dimers. The Au(1)...Au(3)′ "intermolecular" distance is close to the Au...Au distances inside the $(Ph_3PAu)_3O$ fragment. The gold atoms of the dimer form a 6-membered circle in a chair conformation. Both oxygen atoms are slightly out of the Au_3 planes (0.30 Å). This non-planarity is close to that observed for tris(chloromercury)oxonium chloride [3] but Au—O—Au angles are nearer to pyramidal in comparison with $(ClHg)_3O^+Cl^-$ (118.9°) and $(CH_3Hg)_3O^+X^-$ where $X^- = ClO_4^-, NO_2^-$ (the average value is 116°) [4].

Au—O bond lengths coincide with each other within the limits of 2σ and the average distance (1.97 Å) is just slightly shorter than the sum of singly-bound Au and O covalent radii (2.10 Å).

The Au...Au distances in the gold oxonium ion are significantly longer than the distances in Au metal (2.884 Å) [5] and in a number of investigated polynuclei gold complexes incorporating metal-to-metal bonds: $\{Au_9[P(C_6H_4CH_3\text{-}p)_3]_8\}[PF_6]$ 2.71 Å [6], $Au_{11}(SCN)_3(PPh_3)_7$ 2.67 Å [7], $Au_{11}I_3[P(C_6H_4Cl\text{-}p)_3]_7$ and $Au_{11}I_3[P(C_6H_4F\text{-}p)_3]_7$ 2.68 Å [8,9], $[(\pi\text{-}C_5H_5)Fe(\pi\text{-}C_5H_4)Au_2(PPh_3)_2][BF_4]$ 2.77 Å [10]. However the Au...Au distances in $(Ph_3PAu)_3O^+BF_4^-$ are shorter then the sum of Au Van der Vaals radii (3.32 Å) [11] and can correspond to a gold-to-gold interaction. The ability of gold compounds to form chains and clusters with Au...Au distances exceeding the covalent bond value is well known. Our results for the Au...Au distances (3.03—3.215 Å) are close to the values established for the chain structures $(C_3H_7NH_2)AuC{\equiv}CPh$ 3.274 Å [12], $AuCl(PCl_3)$ 3.14 Å [13] and for the clusters Au_6P_6 (the average value 3.02 Å) [14] and $[PyAuCl]_4$. The linear molecules of the latter compound are combined in tetramers, the Au...Au distances being 3.301 Å [15].

The Au—P bond lengths in the gold oxonium salt (2.25—2.27 Å) are shorter then the sum of Au and P covalent radii. It is common for phosphine complexes of gold(I) and arises probably from a contribution of a dative Au → P interaction. The phosphorus coordination is close to tetrahedral.

TABLE 1

ATOMIC COORDINATES (Au and P × 10^4 and others × 10^3) FOR $(Ph_3PAu)_3O^+BF_4^-$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Au(1)	6532(4)	170(2)	4632(3)	C(16)	634	190	679	C(38)	201	−31	236
Au(2)	4074(4)	4273(2)	1794(3)	C(17)	748	176	706	C(39)	122	−55	175
Au(3)	4298(4)	83(2)	3654(3)	C(18)	810	143	644	C(40)	50	−21	125
P(1)	7663(25)	861(10)	4993(20)	C(19)	237	348	273	C(41)	53	26	112
P(2)	3578(30)	3893(15)	2956(20)	C(20)	149	344	317	C(42)	148	55	168
P(3)	3131(25)	659(15)	2933(20)	C(21)	62	316	283	C(43)	252	115	352
O	543(6)	−39(3)	410(5)	C(22)	61	279	223	C(44)	151	141	336
C(1)	903	59	539	C(23)	158	281	178	C(45)	100	180	380
C(2)	915	485	900	C(24)	245	316	208	C(46)	192	194	455
C(3)	1009	−2	633	C(25)	469	350	349	C(47)	288	164	464
C(4)	1100	35	633	C(26)	456	301	378	C(48)	315	127	423
C(5)	1112	81	599	C(27)	536	266	412	C(49)	360	102	220
C(6)	1000	90	540	C(28)	632	289	427	C(50)	472	85	189
C(7)	783	125	411	C(29)	646	346	417	C(51)	519	114	139
C(8)	819	181	425	C(30)	553	371	379	C(52)	489	165	114
C(9)	846	209	350	C(31)	333	440	370	C(53)	404	183	134
C(10)	819	184	273	C(32)	325	425	450	C(54)	337	157	202
C(11)	771	136	264	C(33)	305	463	509	B	953	324	526
C(12)	761	103	335	C(34)	284	512	483	F(1)	1080	322	528
C(13)	729	131	579	C(35)	271	522	404	F(2)	901	369	569
C(14)	602	142	562	C(36)	290	483	346	F(3)	899	338	456
C(15)	568	176	619	C(37)	209	22	223	F(4)	915	338	456

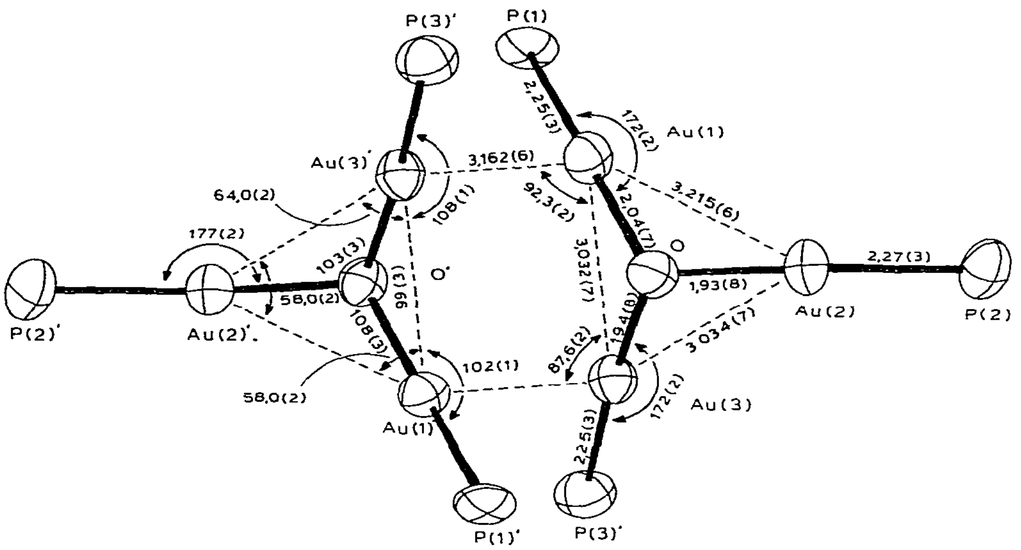

Fig. 1. Structure of the $(Ph_3PAu)_3O^+$ cation.

Tris(triphenylphosphinegold)oxonium salts are crystalline solids melting with decomposition. They are readily soluble in chloroform, methylene chloride, sparingly soluble in alcohols, ketones and organic nitro-compounds and insoluble in ethers and hydrocarbons. Gold oxonium tetrafluoroborate and trifluoroacetate are stable in the solid state and in solutions, whereas the permanganate salt is unstable in solution and gradually decomposes.

The gold—oxygen bonds in the oxonium salts $(Ph_3PAu)_3O^+X^-$ are labile. These salts break under the action of halide ions. Tris(triphenylphosphinegold)-oxonium salts are converted into Ph_3PAuCl when being treated with aqueous NaCl.

$$(Ph_3PAu)_3O^+X^- + 3\ NaCl + H_2O \xrightarrow{CHCl_3} 3\ Ph_3PAuCl + NaX + 2\ NaOH$$

$$X^- = BF_4^-, CF_3COO^-, MnO_4^-$$

Similarly, hydrogen chloride reacts with the gold oxonium salts producing Ph_3PAuCl. In contrast, $(Ph_3PAu)_3O^+X^-$ salts are resistant towards the action of acids with non-coordinating anions (HBF_4) or of alkalies in diluted solutions.

Tris(triphenylphosphinegold)oxonium salts react readily with aliphatic, aliphatic aromatic ketones, ferrocene and its derivatives and with vinyl ethers forming organogold(I) compounds. These reactions will be reported in a subsequent paper.

Experimental section

A solution of HBF_4 in ether was prepared from the aqueous acid by extraction with ether. Acetato- and trifluoroacetato(triphenylphosphine)gold were prepared from Ph_3PAuCl and CH_3COOAg or CF_3COOAg, respectively, in THF. Silver oxide prepared from $AgNO_3$ was washed successively with water, ethanol, acetone and methylethyl ketone by decantation and was not dried for further use.

IR-spectra were recorded as oil mulls on an UR-20 spectrometer.

Tris(triphenylphosphinegold)oxonium tetrafluoroborate

a) In alkaline medium. A solution of $AgBF_4$ (0.2 g, 1.03 mmol) in methanol (5 ml) was added to a solution of Ph_3PAuCl (0.5 g, 1.01 mmol) in THF (20 ml) and silver chloride precipitated was filtered off. A solution of KOH (0.1 g, 1.78 mmol) and $NaBF_4$ (0.5 g, 4.55 mmol) in methanol (100 ml) was added to the filtrate. After stirring for 1 h the solvent was removed under a reduced pressure. The residue was extracted by chloroform (30 ml in two portions). The combined chloroform extract was filtered and hexane (100 ml) was added to the filtrate to precipitate the oxonium salt. Tris(triphenylphosphinegold)-oxonium tetrafluoroborate (0.42 g, 84%), m.p. 220—221°C, decomp. (after a crystallization from a saturated solution in chloroform by adding a 1.5-fold volume of acetone) was obtained. C, 43.80; H, 3.08; Au, 39.17. $C_{54}H_{45}Au_3BF_4OP_3$, calcd.: C, 43.80; H, 3.06; Au, 39.91%. IR spectrum: 1050—1070(br) cm^{-1} (BF_4).

b) In acid medium. Tetrafluoroboric acid (2 mmol) in ether (10 ml) was added dropwise to a stirred solution of $CH_3COOAuPPh_3$ (0.5 g, 0.965 mmol) in THF-ether (20 and 30 ml, respectively). Tris(triphenylphosphinegold)oxonium tetrafluoroborate (0.35 g, 74%) was precipitated.

c) From chloro(triphenylphosphine)gold and silver oxide. Silver oxide, freshly prepared from $AgNO_3$ (5.0 g, 29.5 mmol), and a thin powder of $NaBF_4$ (5.0 g, 45.5 mmol) were added to a solution of Ph_3PAuCl (4.0 g, 8.08 mmol) in acetone (600 ml). After vigorous stirring for 1 h acetone was removed under reduced pressure. The residue was washed with benzene to remove unreacted Ph_3PAuCl and the oxonium salt was extracted with chloroform (120 ml in three portions). Tris(triphenylphosphinegold)oxonium tetrafluoroborate (3.6 g, 90%) was precipitated by adding hexane (400 ml) to the chloroform solution.

Tris(triphenylphosphinegold)oxonium trifluoroacetate

Water (10 ml) was added to a solution of $CF_3COOAuPPh_3$ (0.5 g, 0.87 mmol) in chloroform (15 ml). The mixture was stirred for 1 h. The organic layer was separated, dried over a small portion of K_2CO_3 and chloroform was removed under a reduced pressure. The residue was redissolved in a small portion of chloroform, the solution was filtered and mixed with an excess of ether. Tris(triphenylphospinegold)oxonium trifluoroacetate (0.2 g, 46%) was precipitated, m.p. 209.5—210°C (decomp.) (after a crystallization from chloroform solution by adding benzene), C, 44.20; H, 2.97; Au, 39.00. $C_{56}H_{45}Au_3F_3O_3P_3$, calcd.: C, 44.61; H, 3.01; Au, 39.24%. IR spectrum: 1700s cm^{-1} ν(COO).

Tris(triphenylphosphinegold)oxonium permanganate

Silver oxide freshly prepared from $AgNO_3$ (5.0 g, 29.5 mmol) and a thin powder of $KMnO_4$ (5.0 g, 31.6 mmol) were added to a solution of Ph_3PAuCl (4.0 g, 8.08 mmol) in acetone (600 ml). After vigorous stirring for 1 h a precipitate was filtered off and the oxonium salt was extracted from the precipitate with chloroform (120 ml in three portions). Hexane (400 ml) was added to the dark-purple chloroform solution to precipitate tris(triphenylphosphinegold)oxonium permanganate (2.86 g, 70%), m.p. 131—131.5°C (decomp), C, 42.92; H, 2.97; Au, 38.37. $C_{54}H_{45}Au_3MnO_5P_3$, calcd.: C, 42.88; H, 3.00; Au, 39.06%. IR spectrum: 905s cm^{-1} (MnO_4).

Reaction of gold oxonium salts and sodium chloride

Tris(triphenylphosphinegold)oxonium tetrafluoroborate (0.1254 g, 0.085 mmol) was dissolved in chloroform (5 ml). This solution was shaken with a solution of NaCl (0.02 g, 0.33 mmol) in water (10 ml). The resulting alkaline solution was titrated with HCl (0.01 *M*), with phenolphthalein indicator (95% yield of NaOH). Chloro(triphenylphosphine)gold (0.1250 g, 100%) was obtained from chloroform solution, m.p. 240—241°C (after crystallization from chloroform solution with hexane), lit. [16]: m.p. 243—244°C.

The reactions with gold oxonium trifluoroacetate and permanganate were carried out in the same manner.

Reaction of tris(triphenylphosphinegold)oxonium tetrafluoroborate with hydrogen chloride

Dry hydrogen chloride was bubbled through a solution of tris(triphenylphosphinegold)oxonium tetrafluoroborate (0.30 g, 0.202 mmol) in chloroform (20 ml) for 2 min. An excess of heptane was added to the resulting solution to precipitate chloro(triphenylphosphine)gold (0.30 g, 100%), m.p. 240—241°C (after recrystallization from chloroform solution with heptane).

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