Synthesis of Arylbis[(triorganophosphine)gold(I)]oxonium Tetrafluoroborates $[RO(AuPR'_3)_2]^+BF_4^-$. Crystal Structure of (8-Quinolinyl)bis[(triphenylphosphine)gold(I)]oxonium Tetrafluoroborate

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Potassium phenolate, PhO^-K^+, was reacted with 2 equiv of a (triorganophosphine)gold(I) tetrafluoroborate, $[R_3PAu]^+BF_4^-$, in THF to give novel oxonium salts of the type $[PhO(AuPR_3)_2]^+BF_4^-$ [R = Ph (**2a**), 2-MeC_6H_4 (**2b**), Et (**2c**)]. The compounds were obtained in good yields and have been characterized by NMR spectroscopy as well as mass spectrometry and elemental analysis. Treatment of potassium quinolin-8-olate with 2 equiv of (triphenylphosphine)gold(I) tetrafluoroborate also yields a dinuclear complex, $[(C_9H_6N)O(AuPPh_3)_2]^+BF_4^-$ (**3**). The cation of compound **3** appears to be fluxional in haloalkane solution at room temperature, with the quinolyl group interacting alternatingly with both gold atoms, but at low temperature the compound shows two inequivalent gold atoms. The unsymmetrical ground-state structure could be confirmed by a single-crystal X-ray diffraction study. Crystal data: $3{\cdot}2C_4H_8O$, triclinic $P\bar{1}$ (No. 2), a = 12.721(1) Å, b = 14.381(1) Å, c = 14.730(1) Å, α = 92.69(1)°, β = 93.50(1)°, γ = 100.83(1)°, Z = 2, R (R_w) = 0.040 (0.045).

Introduction

The number of compounds with direct bonding between gold(I) and oxygen is rather limited,[1] indicating that gold(I) quite generally has little affinity for oxygen donors. Characterization of binary gold oxides is still unsatisfactory, and the only simple ternary oxide complex of gold(I) is $CsAuO$.[2] However, tertiary phosphine ligands have been shown to greatly stabilize Au(I)–O bonds, and a long list of mononuclear complexes of formula $XAuPR_3$ with ligands X = $MeCO_2$,[3] $PhSO_3$,[4] NO_3,[5] or Me_3SiO[6] have been prepared. Aryloxy derivatives $ROAuPPh_3$ are known for several phenols,[7] including 8-hydroxyquinoline.[8]

The tendency of monovalent gold to become engaged in secondary Au···Au bonding ("auriophilicity")[9] strongly favours the formation of trinuclear oxonium salts $[O(AuL)_3]^+X^-$. The first example to be examined was $[O(AuPPh_3)_3]^+BF_4^-$, which was found to crystallize with dimeric cationic units.[10] More recent work has led to the discovery of other salts of this type, some of which have monomeric, pyramidal cations $[O(AuL)_3]^+$ in the crystal lattice.[11] These complexes are useful reagents for the synthesis of many novel, highly aurated complexes.[1,12]

The same type of complexes are known as derived from H_2S and thiols. Complexes of the types $RSAuL$,[1,13] $[S(AuL)_3]^+$,[11c,14] and $[RS(AuL)_2]^+$ [15] have become readily available. In this paper we describe the synthesis of the first aryloxonium complexes $[RO(AuL)_2]^+BF_4^-$.

Experimental Section

General Methods. All reactions were carried out under a nitrogen atmosphere. All solvents were dried, saturated with nitrogen, and distilled before use. Exposure to direct daylight was avoided if possible.

Equipment. A Jeol GX 400 NMR spectrometer (deuterated solvents as internal standards, converted to TMS, for ^1H; external aqueous H_3PO_4 for ^{31}P) and a MAT 90 mass spectrometer (field desorption) were used. Elemental analyses were performed in the microanalytical laboratory of this Institute.

Reagents. The (phosphine)gold(I) chlorides[16] Ph_3PAuCl (**1a**), $(2\text{-}MeC_6H_4)_3PAuCl$ (**1b**), and Et_3PAuCl (**1c**) and the potassium phenolates[17] PhO^+K^- and $C_9H_6NO^+K^-$ were prepared according to the literature.

Phenylbis[(triphenylphosphine)gold(I)]oxonium Tetrafluoroborate (2a) and Phenylbis[(tri(2-methylphenyl)phosphine)gold(I)]oxonium Tetrafluoroborate (2b). Typically, a solution of 1.05 mmol of (phosphine)gold(I) chloride (**1a**, 0.52 g; **1b**, 0.56 g) in THF (15 mL) was added to a solution of $AgBF_4$ (0.21 g, 1.07 mmol) in THF (10 mL), and the reaction mixture was stirred for 10 min. The AgCl precipitate was removed and the clear, colorless filtrate added dropwise over a period of 10 min to a suspension of potassium phenolate (70 mg, 0.53 mmol) and $NaBF_4$ (0.5 g, 4.55 mmol) in THF (10 mL). After being stirred for 1 h at room temperature the suspension was evaporated to dryness. The residue was extracted with CH_2Cl_2 (20 mL) and filtered over cellulose to remove

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Table I. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters for $3 \cdot 2C_4H_8O$

atom	x/a	y/b	z/c	U(eq), Å^2
Au1	0.25514(2)	0.14245(2)	0.00638(2)	0.051
Au2	0.20940(3)	0.14082(2)	0.27597(2)	0.054
P1	0.3550(2)	0.2864(1)	0.0086(2)	0.049
P2	0.2858(2)	0.1866(2)	0.4134(2)	0.055
N	0.1683(5)	0.0033(4)	–0.0191(5)	0.054
O	0.1539(4)	0.0905(4)	0.1473(4)	0.057
B	0.088(1)	0.6684(9)	0.695(1)	0.075
F1	0.1760(6)	0.6799(6)	0.7532(6)	0.130
F2	0.0827(8)	0.7485(6)	0.6567(7)	0.156
F3	0.0044(7)	0.654(1)	0.7392(7)	0.164
F4	0.086(1)	0.6007(8)	0.6361(8)	0.179
C1	0.0995(6)	0.0017(6)	0.1300(6)	0.055
C2	0.0357(7)	–0.0492(7)	0.1911(7)	0.068
C3	–0.0210(8)	–0.1408(8)	0.1681(8)	0.073
C4	–0.0181(7)	–0.1832(6)	0.0856(9)	0.067
C5	0.0452(6)	–0.1358(5)	0.0203(7)	0.055
C6	0.0531(7)	–0.1764(6)	–0.0670(8)	0.061
C7	0.1157(8)	–0.1289(7)	–0.1259(7)	0.070
C8	0.1734(7)	–0.0386(6)	–0.1010(6)	0.064
C9	0.1051(6)	–0.0434(5)	0.0426(6)	0.048
C111	0.3120(6)	0.3545(5)	–0.0820(5)	0.048
C112	0.3010(7)	0.4474(6)	–0.0682(6)	0.057
C113	0.2651(8)	0.4960(6)	–0.1394(7)	0.068
C114	0.2403(8)	0.4524(8)	–0.2242(7)	0.072
C115	0.2527(9)	0.3599(8)	–0.2394(6)	0.078
C116	0.2877(8)	0.3102(6)	–0.1692(7)	0.070
C121	0.4955(6)	0.2859(5)	–0.0051(6)	0.053
C122	0.5500(7)	0.3289(7)	–0.0728(7)	0.069
C123	0.6586(8)	0.3251(8)	–0.0793(9)	0.082
C124	0.7106(9)	0.2792(9)	–0.020(1)	0.089
C125	0.6582(9)	0.2386(9)	0.053(1)	0.089
C126	0.5486(8)	0.2402(8)	0.0603(8)	0.081
C131	0.3520(6)	0.3558(5)	0.1131(5)	0.049
C132	0.4414(7)	0.4190(6)	0.1516(6)	0.061
C133	0.4349(9)	0.4733(7)	0.2315(7)	0.074
C134	0.33891)	0.4639(8)	0.2714(7)	0.077
C135	0.2490(8)	0.4008(8)	0.2334(7)	0.075
C136	0.2559(7)	0.3472(6)	0.1560(6)	0.062
C211	0.2329(7)	0.1059(6)	0.4980(6)	0.058
C212	0.1789(9)	0.0169(8)	0.4712(7)	0.079
C213	0.137(1)	–0.0451(8)	0.5356(9)	0.094
C214	0.150(1)	–0.0171(9)	0.6241(9)	0.089
C215	0.205(2)	0.069(1)	0.6516(8)	0.110
C216	0.247(1)	0.1319(8)	0.5893(7)	0.088
C221	0.2745(7)	0.3033(6)	0.4594(5)	0.058
C222	0.3636(8)	0.3665(7)	0.5033(6)	0.072
C223	0.349(1)	0.4548(8)	0.5377(7)	0.082
C224	0.252(1)	0.4809(8)	0.5297(8)	0.087
C225	0.168(1)	0.4204(9)	0.4850(8)	0.085
C226	0.1751(8)	0.3309(7)	0.4496(7)	0.074
C231	0.4283(7)	0.1879(6)	0.4131(6)	0.061
C232	0.4845(8)	0.2421(8)	0.3494(7)	0.075
C233	0.5936(9)	0.2473(9)	0.3462(9)	0.095
C234	0.6463(9)	0.198(1)	0.403(1)	0.102
C235	0.592(1)	0.144(1)	0.465(1)	0.109
C236	0.4819(9)	0.1387(9)	0.4715(8)	0.085
O10	0.43405	0.06719	0.80391	0.249
C10	0.47138	0.01175	0.86746	0.210
C20	0.85592	0.1317	0.84784	0.203
C30	0.60237	0.04375	0.76183	0.239
C40	0.51505	0.08775	0.73608	0.252
O20	0.16253	0.77513	0.35095	0.362
C21	0.21880	0.70510	0.29629	0.322
C22	0.16125	0.64222	0.34359	0.328
C23	0.05029	0.63504	0.33619	0.309
C24	0.04892	0.72515	0.37782	0.295

$NaBF_4$ and impurities of colloidal gold. On addition of hexane (30 mL), a precipitate was obtained, which was filtered, washed with hexane, and dried in a vacuum.

2a: yellow solid, yield 270 mg (48%). ^{1}H NMR (CD_2Cl_2, 20 °C): δ = 6.88 (m, 3 H, o/p-OC_6H_5), 7.22 (t, N = 15.1 Hz, 2 H, m-OC_6H_5), 7.37–7.55 (m, 30 H, C_6H_5). {^{1}H}^{31}P NMR (CD_2Cl_2, 20 °C): δ = 25.4 (s). MS (FD, CH_2Cl_2): m/z = 1011.3 [M^+] (17%), 459.2 [Ph_3PAu^+] (100%). Anal. Calcd for $C_{42}H_{35}Au_2BF_4OP_2$ (1098.43): C, 45.93; H, 3.21. Found: C, 45.58; H, 3.26.

Table II. Selected Bond Distances (Å) and Angles (deg) for 3

Au1–N	2.101(6)	Au1···Au2	4.049(1)
Au2–O	2.033(6)	Au1···O	2.575(6)
Au1–P1	2.213(2)		
Au2–P2	2.209(2)		
O–Au2–P2	173.14(16)	Au2–O–C1	121.5(5)
N–Au1–P1	170.0(2)	Au1–O–C1	108.5(5)
Au2–O–C1–C2	29.7(10)	Au1–O–Au2	122.5(2)

2b: colorless solid, yield 260 mg (42%). ^{1}H NMR (CD_2Cl_2, 20 °C): δ = 2.36 (s, 18 H, CH_3), 6.85 (m, 3 H, o/p-OC_6H_5), 6.91 (dd, ^3J(HH) = 7.6 Hz, ^3J(PH) = 13.9 Hz, 6 H, o-C_6H_4); 7.17 (m, 2 H, m-OC_6H_5); 7.24 (t, N = 14.2 Hz, 12 H, m-C_6H_4); 7.56 (t, N = 15.1 Hz, 6 H, p-C_6H_4). {^{1}H}^{31}P NMR (CD_2Cl_2, 20 °C): δ = –1.20 (s). MS (FD, CH_2Cl_2): m/z = 1095.7 [M^+] (18%), 501.4 [Ar_3PAu^+] (100%). Anal. Calcd for $C_{48}H_{47}Au_2BF_4OP_2$ (1182.59): C, 48.75; H, 4.00. Found: C, 49.03; H, 4.28.

Phenylbis[(triethylphosphine)gold(I)]oxonium Tetrafluoroborate (2c). The procedure followed that described for compound **2b**, but at 0 °C, using (triethylphosphine)gold(I) chloride (**1c**) (0.7 g, 2.0 mmol), $AgBF_4$ (0.39 g, 2.0 mmol), potassium phenolate (130 mg, 0.98 mmol), and $NaBF_4$ (0.5 g, 4.55 mmol).

2c: colorless oil, yield 265 mg (49%).

^{1}H NMR (CD_2Cl_2, 20 °C): δ = 1.21 (dt, ^3J(HH) = 7.7 Hz, ^3J(PH) = 19.1 Hz, 18 H, CH_3), 1.93 (dq, ^3J(HH) = 7.7 Hz, ^2J(PH) = 10.8 Hz, 12 H, CH_2), 6.83 (d, J = 8.7, 2 H, o-OC_6H_5), 6.88 (t, J = 14.8 Hz, 1 H, p-OC_6H_5), 7.22 (t, J = 16.0 Hz, 2 H, m-OC_6H_5). {^{1}H}^{31}P NMR (CD_2Cl_2, 20 °C): δ = 28.2 (s). Anal. Calcd for $C_{18}H_{35}Au_2BF_4OP_2$ (810.17): C, 26.69; H, 4.35. Found: C, 25.82; H, 4.43.

8-Quinolinylbis[(triphenylphosphine)gold(I)]oxonium Tetrafluoroborate (3). The procedure followed that described for compound **2b**, using (triphenylphosphine)gold(I) chloride (0.55 g, 1.11 mmol), $AgBF_4$ (0.21 g, 1.10 mmol), potassium quinolin-8-olate (0.10 g, 0.55 mmol), and $NaBF_4$ (0.5 g, 4.55 mmol).

3: yellow solid, yield 340 mg (54%). ^{1}H NMR (CD_2Cl_2, 20 °C): δ = 7.35–7.53 (m, 31 H, H7 + C_6H_5), 7.59 (t, N = 15.3 Hz, 1 H, H6), 7.64 (dd, ^3J(HH) = 7.9 Hz, ^4J(HH) = 1.2 Hz, 1 H, H4), 7.71 (dd, ^3J(HH) = 7.9 Hz, ^3J(HH) = 4.9 Hz, 1 H, H3), 8.52 (dd, ^3J(HH) = 7.9 Hz, ^4J(HH) = 1.2 Hz, 1 H, H5), 8.94 (dd, ^3J(HH) = 4.9 Hz, ^4J(HH) = 1.2 Hz, 1 H, H2). {^{1}H}^{31}P NMR (CD_2Cl_2): at 20 °C, δ = 28.8 (s, br); at –60 °C, δ = 30.3 (s, 1 P), 27.1 (s, 1 P). MS (FD, CH_2Cl_2): m/z = 1062.1 [M^+] (100%), 459.1 [Ph_3PAu^+] (6%). Anal. Calcd for $C_{45}H_{36}Au_2BF_4NOP_2$ (1149.44) C, 47.02; H, 3.16; N, 1.21. Found: C, 46.67; H, 3.46; N, 1.07.

Crystal Structure Determination. A suitable crystal of compound **3** was sealed under argon at dry ice temperature into a glass capillary and examined directly on the diffractometer. Reduced cell calculations did not indicate any higher symmetry. 12040 reflections were measured and corrected for Lorentz, polarization and—empirically—for absorption effects (T_{min} = 0.722, T_{max} = 1.000). Of 12 039 unique reflections 8560 were considered as "observed" with $F_o \geq 4\sigma(F_o)$ and used for all calculations.

3 crystallizes in the triclinic space group $P\bar{1}$ (No. 2[23]) with one molecule of **3** and two molecules of tetrahydrofuran in the asymmetric unit: $C_{53}H_{52}Au_2BF_4NO_3P_2$, M_r = 1293.697, a = 12.721(1) Å, b = 14.381(1) Å, c = 14.730(1) Å, α = 92.69(1)°, β = 93.50(1)°, γ = 100.83(1)°, V = 2637.1 Å^3, Z = 2, ρ(calc) = 1.629 g cm^{-3}, μ(Mo Kα) = 56.5 cm^{-1}, T = 23 °C, sin (Θ/λ_{max}) = 0.661 Å^{-1}. The structure was solved by Patterson methods (SHELXS 86),[18] completed by difference Fourier syntheses, and refined using full-matrix techniques (SHELX 76).[19] All non-hydrogen atoms were refined with anisotropic thermal displacement parameters (except solvent molecules), while all hydrogen atoms were calculated in idealized positions, fixed, and included in the structure factor calculations with fixed atomic contributions (U_{iso} = 0.05 Å^2). The structure converged [R (R_w) = 0.040 (0.045); $w = 1/\sigma^2(F_0)$] for 505 refined parameters with a residual electron density of +1.82/–0.88 e Å^{-3}.

Results

Synthesis of Phenylbis[(triorganophosphine)gold(I)]oxonium Tetrafluoroborates 2a–c. Treatment of potassium phenolate in tetrahydrofuran with 2 equiv of a freshly prepared solution of

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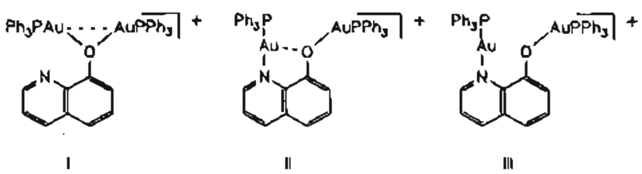
(18) Sheldrick, G. M. SHELXS 86, Program for Crystal Structure Determination. Göttingen, Germany, 1986.

(19) Sheldrick, G. M. SHELX 76, Program for Crystal Structure Determination, Cambridge, England, 1976.

Chart I



I II III

(triorganophosphine)gold(I) tetrafluoroborate in the presence of sodium tetrafluoroborate leads to cationic, dinuclear oxonium complexes **2a–c** (eq 1). The products are obtained in moderate

$$\underset{}{PhO^-K^+} + \underset{\mathbf{1}}{2[R_3PAu]^+BF_4^-} \xrightarrow{NaBF_4} \underset{\mathbf{2}}{[PhO(AuPR_3)_2]^+BF_4^-} + KBF_4 \quad (1)$$

$$(\mathbf{a})\ R = Ph,\ (\mathbf{b})\ R = 2\text{-}MeC_6H_4,\ (\mathbf{c})\ R = Et$$

yields as yellow (**2a**, 48%) or colorless (**2b**, 42%) solids or as a colorless oil (**2c**, 49%).

The compounds are soluble in methylene chloride and chloroform and are insoluble in tetrahydrofuran, benzene, and hexane. Protected against light, the air-stable compounds **2a** and **2b** can be stored at room temperature, while **2c** can only be kept at −78 °C for a longer time. Dissolution in methylene chloride or chloroform results in slow decomposition. The compounds have been identified by elemental analyses, mass spectrometry, and NMR spectroscopy.

Proton and $^{31}P\{^1H\}$ NMR spectra (CD_2Cl_2) confirm the equivalence of the two phosphinegold(I) groups in all cases. In the ^1H NMR spectrum of **2a** the phenolate signals appear upfield relative to the phenyl signals of Ph_3P (intensity ratio of 5:30). The ^1H NMR spectrum of **2b** shows only one set of signals for the *o*-tolyl groups indicating the equivalence of the two (phosphine)gold fragments. Two separate multiplets of the phenolate hydrogens are distinguishable, similar to those of **2a**. The ^1H-NMR spectrum of **2c** shows well-resolved multiplet signals, with a correct intensity ratio of aliphatic and aromatic protons.

In the proton-decoupled ^{31}P spectra (CD_2Cl_2) of **2a–c** only singlet signals are observed, which appear with upfield shifts of 5–10 ppm relative to those of the (phosphine)gold(I) chlorides **1a–c**.

In field desorption mass spectra the cations of the salts **2a** and **2b** could be observed only in low intensity. (**2a**, m/z = 1011.3 (17%); **2b**, m/z = 1095.7 (18%)). The base peaks of **2a** at m/z = 459.2 and of **2b** at m/z = 501.4 correspond to the (phosphine)gold cations R_3PAu^+.

In the FD mass spectra of **2c** there is no direct evidence for the parent ion, which appears to be too labile under the experimental conditions. The ionization leads to two smaller fragments, namely $[Et_3PAuPEt_3]^+$ and $[Et_3PAu]^+$.

Synthesis and Structure of 8-Quinolinylbis[(triphenylphosphine)gold(I)]oxonium Tetrafluoroborate (3). (8-Quinolinyl)-bis[(triphenylphosphine)gold(I)]oxonium tetrafluoroborate (**3**) was prepared according to eq 2. The product was obtained as

$$(C_9H_6N)O^-K^+ + \underset{\mathbf{1a}}{2[Ph_3PAu]^+BF_4^-} \xrightarrow{NaBF_4} \underset{\mathbf{3}}{[(C_9H_6N)O(AuPPh_3)_2]^+BF_4^-} + KBF_4 \quad (2)$$

a yellow, air-stable solid in moderate yield (54%). It is soluble in methylene chloride, chloroform and tetrahydrofuran, but insoluble in diethyl ether, benzene, or hexane.

The 8-quinolinate ligand was chosen in order to probe the influence of the donor capacity of the quinoline nitrogen atom on the aggregation of gold atoms, for which three modes of coordination of the two (phosphine)gold groups have to be considered (Chart I).

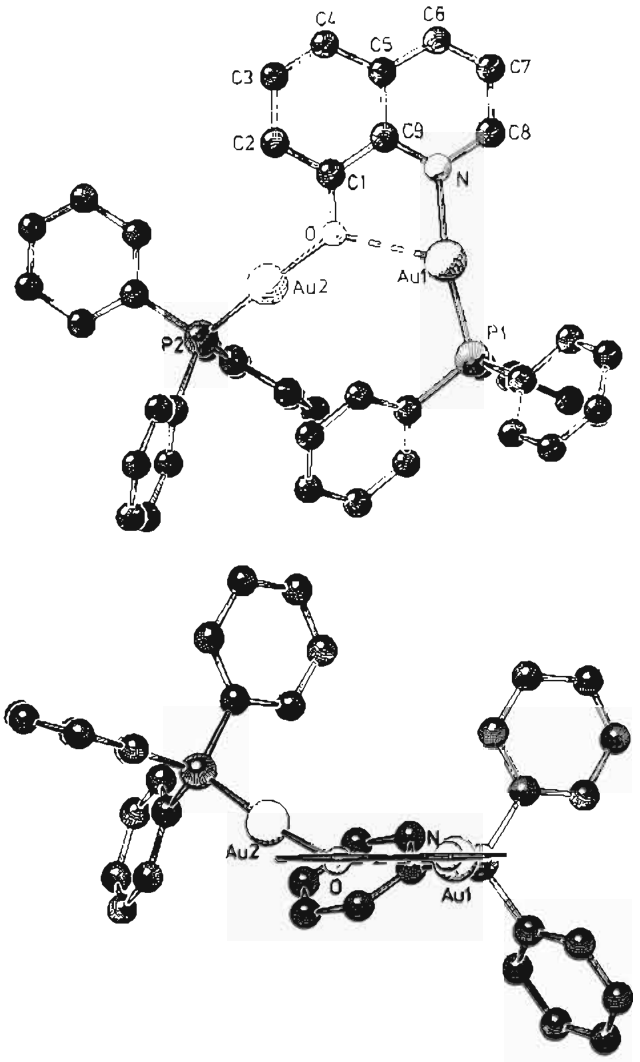


Figure 1. Structure of the cation in compound **3**, with atomic numbering (Schakal): (top, a) side projection; (bottom, b) projection parallel to the plane of the quinoline ring.

The compound was readily identified by its elemental analysis, by mass spectrometry, and by NMR spectroscopy. In field desorption mass spectra (from CH_2Cl_2), the complete cation is observed at m/z = 1062.1 as the parent peak (100%), accompanied only by a peak at m/z = 459.1 (6%, $[Ph_3PAu^+]$).

In the proton NMR spectrum (in CD_2Cl_2) the quinoline hydrogen signals are clearly resolved, while the phenyl hydrogen signals appear as a broad multiplet. In the proton-decoupled ^{31}P spectrum (CD_2Cl_2, room temperature) a broad resonance is also obtained, but this splits at −40 °C into two broad signals and finally at −60 °C into two sharp peaks. The signal at δ = 30.3 ppm is tentatively assigned to a Ph_3PAu group primarily attached to the nitrogen atom; the signal at 27.1 ppm, to a Ph_3PAu group attached to the oxygen atom. The temperature dependence of the signal pattern is indicative of site exchange of the donor in solution at ambient temperature.

Referring to the proposed structures **I–III**, for the solution state at low temperature only the structures **II** or **III** are in agreement with the spectroscopic data. In order to distinguish between the two alternatives, which differ mainly in their details of oxygen coordination, a single crystal structure analysis was carried out.

The compound crystallizes from THF/hexane mixtures with two molecules of crystal tetrahydrofuran. Crystals of $\mathbf{3}\cdot 2C_4H_8O$

are triclinic, space group $P\bar{1}$, with $Z = 2$ formula units in the unit cell. The structure is built from independent cations, tetrafluoroborate anions, and solvent molecules. The configuration of the cation is shown in Figure 1. The cation shows two nonequivalent Ph_3PAu^+ units, one being solely attached to the oxygen atom and the second mainly to the nitrogen atom, but with a significant contact also to the oxygen atom. The distances Au2–O [2.033(6) Å] and Au1–N [2.101(6) Å] are as expected for standard Au–O/N single bonds, while the distance Au1–O [2.575(6) Å] indicates a relatively weak donor/acceptor interaction. This interpretation is supported by the deviation of the P1–Au1–N angle [170.0(2)°] from linearity. The compound then possesses only weak "oxonium character" as judged from the geometrical details. The coordination geometry of the oxygen atom is distorted trigonal pyramidal with angles of 121.5(5)° [Au2–O–C1], 122.5(2)° [Au2–O–Au1], and 108.5(5)° [Au1–O–C1]. The Au1–N bond is found to lie in the plane of the quinoline ring system, but the Au2–O bond is twisted out of that plane, as illustrated by the dihedral angle C2–C1–O–Au2 [29.7(10)°].

Probably for steric reasons the compound shows no short inter- or intramolecular Au–Au contacts. Such contacts are a very common feature of gold complexes and clusters.[9,12,20] In complex 3 the intramolecular Au1···Au2 distance is 4.049(1) Å; the shortest intermolecular Au···Au distance well beyond 7 Å.

In the solid state the two (triphenylphosphine)gold units are clearly inequivalent. The virtual NMR equivalence of the phosphine ligands observed for solutions of the compound at room temperature therefore has to be ascribed to a dynamic phenomenon. For the site exchange we favor a model where the $[Ph_3PAu]^+$ units, and not only the Ph_3P ligands, are subject to a scrambling on the NMR time scale. The most likely mechanism is a dissociation of Au1 from the pyridine donor and a shift of the Ph_3PAu unit towards the oxygen atom to give a true oxonium intermediate (structure **I**). After rotation of the quinoline ring about the C–O axis the pyridine donor atom can be attached to the second gold atom Au2, which moves away from the oxygen atom in this process to give a new ground state as again represented by structure **II**.

Discussion

The present study has shown that phenolate and quinolin-8-olate anions can be converted into dinuclear oxonium cations $[RO(AuPR'_3)_2]^+$, through addition of two (triorganophosphine)gold(I) cations. With LAu^+ units isolobal with the proton H^+, this process resembles the protonation of the phenolate anion (or phenol) to give the corresponding phenyloxonium cation $PhOH_2^+$. A pyramidal structure at oxygen is to be proposed for both the $PhOH_2^+$ and $[PhO(AuL)_2^+]$ species.

Compounds of this new type of oxonium salts are not nearly as stable as the trinuclear oxonium salts $[O(AuPR_3)_3]^+BF_4^-$,[10,11] the cations of which are characterized by strong inter- and intramolecular Au···Au interactions. This suggests that the stability of the gold(I)–oxonium cations is crucially dependent of the number of metal–metal contacts that can be established in a given structure.

The increased stability of the quinolinolate complex originates from the donor capacity of the quinoline nitrogen atom assisting in the bonding of the second gold atom. This influence has become obvious both in the crystal structure and in the solution studies. Compound 3 is a direct analogue of the related triply aurated 8-*amino*quinoline complex,[21] $[(C_9H_6N)N(AuPPh_3)_3]^+BF_4^-$, which is also distinguished from analogous trinuclear organoammonium complexes through its stability and through the ability to accommodate a fourth $[Ph_3PAu]^+$ unit to form even a tetranuclear dication complex $[(C_9H_6N)N(AuPPh_3)_4]^{2+}[BF_4^-]_2$ with a square of gold atoms.[21] Attempts to prepare a similar dication, $[(C_9H_6N)O(AuPPh_3)_3]^{2+}$, by addition of $[Ph_3PAu]^+$ to compound 3 have not been successful. The results of experiments aiming at the synthesis of tetrakis[(phosphine)gold(I)]oxonium salts $[(R_3PAu)_4O]^{2+}[X^-]_2$ were inconclusive.[22]

Supplementary Material Available: Tables of crystallographic data, atomic coordinates and thermal parameters, hydrogen atom parameters, bond distances and angles, and hydrogen atom bond distances and angles (17 pages). Ordering information is given on any current masthead page.

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