Gold(I) Complexes of Organic Nitrogen Compounds: Synthesis and Structures of (Phthalimido)(triphenylphosphine)gold(I) in Crystals $C_6H_4(CO)_2N(AuPPh_3)$ and $C_6H_4(CO)_2N(AuPPh_3)\cdot CHCl_3$

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$[O(AuPPh_3)_3]^+BF_4^-$ has been found to be a powerful aurating reagent for phthalimide, to give (phthalimido)(triphenylphosphine)gold(I) (**1**) in high yield. Two different crystal systems, with or without $CHCl_3$ molecules in the unit cell, have been obtained. In both cases the monoaurated diacylamido complex $C_6H_4(CO)_2N(AuPPh_3)$ (**1**) is present as a monomer with linear two-coordinate gold atoms. The N–Au(I) bond lengths (2.028(4), 2.040(4) Å) are similar to those found in other monoaurated complexes of the type $R^1R^2N(AuPPh_3)$ with strongly electron-withdrawing organic substituents R^1, R^2. Crystal data: **1,** monoclinic, $P2_1/c$, a = 9.948(1), b = 15.712(1), c = 14.651(1) Å, β = 103.40(1)°, V = 2227.7 Å^3, Z = 4; **1**·$CHCl_3$, orthorhombic, $P2_12_12_1$, a = 8.889(1), b = 10.349(1), c = 29.198(2) Å, V = 2686.0 Å^3, Z = 4.

Introduction

The number of compounds containing a bond between gold(I) and nitrogen is rather limited [1]. In the majority of "classical" cases the linear two-coordinate gold atom, a soft coordination center [2], carries a tertiary phosphine as a stabilizing π-acceptor ligand, and the "hard" N-donor ligand is "softened" by integration of the nitrogen atom into an aromatic system ($[LAuPR_3]^{n+}$: *e.g.* L = pyridine, n = 1 [3]; imidazole, n = 0 [4]; adenine, n = 0 [5]).

In more recent work it has been shown that strongly aurating agents such as $[O(AuPR_3)_3]^+X^-$ or $[R_3PAu]^+X^-$ (with X^- representing non-coordinating counter ions) can "gild" the nitrogen atom of organic substrates more effectively to give N-polyaurated compounds. In the extreme case of ammonia not only quaternary ammonium salts of the type $[N(AuPR_3)_4]^+X^-$ [6–9], but also novel hypercoordinate dications $[N(AuPR_3)_5]^{2+}2X^-$ [10] could be obtained. The solid-state structures of these compounds feature tetrahedral and trigonal-bipyramidal geometries, respectively, with short Au···Au contacts near 3.0 Å that bear witness to attractive forces between the linear two-coordinate gold(I) centers ("auriophilicity") [11].

Primary, secondary and tertiary organic nitrogen compounds, *i.e.* amines, amides and imides, were subsequently found to undergo similar reactions. Depending on the nature of the organic substituents R, the N–H protons of primary amines or related ammonium salts can be replaced stepwise by an isolobal $[AuPR_3]^+$ fragment to form amido and imido complexes of the type $[R-NH_{2-x}(AuPR_3)_x]$ (x = 1, 2; [12, 13]), or amino complexes of the type $[R-NH_{3-x}(AuPR_3)_x]^+$ (x = 1 [14–16], 2 [12, 17], 3 [18–23]).

If through the steric or electronic influence of R^1, R^2 and R^3 the donor qualities of nitrogen are sufficiently increased, the direct addition of $[R_3PAu]^+X^-$ to secondary and tertiary amines to give ammonium derivates of the type $[R^1R^2NH(AuPR_3)]^+$ and $[R^1R^2R^3N(AuPR_3)]^+$ [24–26] is possible. With the $[O(AuPR_3)_3]^+X^-$ reagents the driving force of the process is the formation of water, leaving non-protonated amido complexes of the type $[R^1R^2N(AuPR_3)]$ as the sole products [13, 27].

Only very few examples are known, however, where N–H protons could be substituted in this way, and they are limited largely to cases with the strongly electron-withdrawing p-nitrophenyl substituent (R^1 = p-$O_2N-C_6H_4$–; R^2 = –CO–). The majority of $[R^1R^2N(AuPR_3)]$ complexes were prepared by the reaction of alkali imides $R^1R^2N^-M^+$

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($R^1 = R^2 = -CO-$; *e.g.* potassium phthalimide) with triorganophosphinegold(I) chlorides R_3PAuCl [28–30].

It was the purpose of this study to demonstrate that phthalimide as an example of an amine with two carbonyl substituents activating the N–H proton allows the use of $[O(AuPR_3)_3]^+X^-$ compounds as aurating agents to give a gold amide species.

Experimental

General methods

The experiments were carried out with exclusion of light in an atmosphere of purified nitrogen, employing standard Schlenk techniques. The solvents were dried, saturated with nitrogen, and distilled before use.

Reagents and equipment

Phthalimide is commercially available. μ_3-Oxotris[(triphenylphosphine)gold(I)] tetrafluoroborate was prepared by the published method [31]. A Jeol-GX 400 NMR spectrometer (deuterated solvents as internal standards, converted to TMS, for ^1H and ^{13}C; external aqueous H_3PO_4 for ^{31}P) and a Finnigan MAT 90 mass spectrometer (FAB source; matrix material 4-nitrobenzyl alcohol) were used. Melting points (sealed capillaries in a Büchi apparatus) are uncorrected. The elemental analysis was performed in the microanalytical laboratory of this institute.

(Phthalimido)(triphenylphosphine)gold(I) (**1**)

To a solution of phthalimide (0.15 g, 1.02 mmol) in tetrahydrofuran (10 ml) was added a suspension of $[O(AuPPh_3)_3]^+BF_4^-$ (0.50 g, 0.34 mmol) in the same solvent (10 ml). The reaction mixture was stirred for 2 h at room temperature. The resulting solution was then filtered over cellulose to remove impurities of colloidal gold. After reducing the filtrate to a small volume, precipitation of the product by addition of pentane gave a colourless solid, which was washed with water and dried *in vacuo*. Yield: 0.44 g, 71%; m.p. 200 °C (m.p. 92–96 °C for **1**·$CHCl_3$ after slow crystallization from chloroform).

Analysis for **1** ($C_{26}H_{19}AuNO_2P$, 605.39)
Calcd C 51.58 H 3.16 N 2.31 P 5.12%,
Found C 51.99 H 3.12 N 2.74 P 5.37%.

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ = 122.0 [s, C3/6]; 128.7 [d, ^1J(CP) = 62, Ph–C_{ipso}]; 129.3 [d, ^3J(CP) = 12, Ph–C_{meta}]; 131.8 [d, ^4J(CP) = 3, Ph–C_{para}]; 132.5 [s, C2/7]; 134.0 [d, ^2J(CP) = 14, Ph–C_{ortho}]; 136.1 [s, C4/5]; 178.4 [s, C1/8]. ^1H NMR ($CDCl_3$, 20 °C): δ = 7.25–7.31 [m, 6H, *m*-$C_6\underline{H}_5$]; 7.43–7.49 [m, 9H, *o/p*-$C_6\underline{H}_5$]; 7.67 [m, 4H, $C_6\underline{H}_4$]. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ = 33.2 [s]. FAB-MS *(m/z):* 606.5 (23%, M^+); 459.1 (100%, $AuPPh_3^{1+}$).

Crystal structure determination

Details of the X-ray structure determinations of compounds **1** and **1**·$CHCl_3$ are summarized in Tables I–III. Selected bond distances and angles are presented in Table IV. Further information on the structure determinations may be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen,

Table I. Details of the X-ray structure determinations of compounds **1** and **1**·$CHCl_3$.

	1	**1**·$CHCl_3$
Formula	$C_{26}H_{19}NO_2PAu$	$C_{27}H_{20}NO_2PAuCl_3$
M_r	605.39	724.77
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	$P2_12_12_1$
a [Å]	9.948(1)	8.889(1)
b [Å]	15.712(1)	10.349(1)
c [Å]	14.651(1)	29.198(2)
α [°]	90	90
β [°]	103.40(1)	90
γ [°]	90	90
V [Å^3]	2227.7	2686.0
$\varrho_{calc.}$ [g cm^{-3}]	1.805	1.792
Z	4	4
F(000) [e]	1168	1400
μ(Mo–K_α) [cm^{-1}]	66.75	58.44
Absorption correction		
T_{min}/T_{max} [%]	78.15/99.89	55.29/99.88
T [°C]	+23	+23
Diffractometer	Enraf-Nonius CAD4	
Radiation	Mo–K_α	Mo–K_α
	graphite monochromator	
Scan	ω	ω
Scan width [°, in ω]	1.00	0.80
hkl range	±12/+20/+17	±11/+13/+32
$\sin(\theta/\lambda)_{max}$ [Å^{-1}]	0.66	0.66
Measured reflections	5736	6776
Unique reflections	4822	6530
R_{int}	0.044	0.045
Observed reflections	4085	6081
$F_o \geq$	$4\sigma(F_o)$	$4\sigma(F_o)$
Refined parameters	337	376
H atoms (found/calcd.)	19/0	19/1
R	0.0227	0.0219/0.0503*
R_w	0.0243	0.0233/0.0578*
$(\text{shift/error})_{max}$	0.002	0.001
ϱ_{fin} (max./min.) [eÅ^{-3}]	+1.10/–0.64	+1.89/–0.88
	(located at Au)	

$R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$, $w = 1/\sigma^2(F_o) + k(F_o)^2$; k = 0.000000; * inverse model.

Table II. Fractional atomic coordinates and equivalent isotropic displacement parameters for compound **1** [$U_{eq} = (U_1 \cdot U_2 \cdot U_3)^{1/3}$, where U_1, U_2 and U_3 are the Eigenvalues of the U_{ij} matrix; E.s.d. values in parentheses].

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
AU	–0.00219(2)	0.21242(1)	0.12607(1)	0.040
P	0.1756(1)	0.20025(7)	0.05833(7)	0.036
N	–0.1443(3)	0.2366(2)	0.2024(2)	0.039
O1	–0.2359(4)	0.3629(2)	0.1343(2)	0.064
O2	–0.0908(4)	0.1260(2)	0.3081(2)	0.056
C11	0.2388(4)	0.3064(3)	0.0426(3)	0.036
C12	0.1456(5)	0.3646(4)	–0.0069(4)	0.060
C13	0.1869(6)	0.4462(4)	–0.0197(4)	0.067
C14	0.3198(6)	0.4718(3)	0.0175(4)	0.058
C15	0.4128(6)	0.4151(3)	0.0676(4)	0.057
C16	0.3738(5)	0.3321(3)	0.0794(3)	0.046
C21	0.3209(4)	0.1453(3)	0.1329(3)	0.038
C22	0.3306(5)	0.1408(3)	0.2286(3)	0.050
C23	0.4458(6)	0.1071(4)	0.2876(4)	0.062
C24	0.5534(5)	0.0768(3)	0.2524(4)	0.058
C25	0.5435(5)	0.0790(3)	0.1576(4)	0.057
C26	0.4285(5)	0.1132(3)	0.0981(4)	0.050
C31	0.1470(4)	0.1510(3)	–0.0559(3)	0.040
C32	0.2253(5)	0.1717(4)	–0.1190(3)	0.053
C33	0.2071(7)	0.1296(4)	–0.2044(4)	0.066
C34	0.1120(8)	0.0664(4)	–0.2259(4)	0.076
C35	0.0323(8)	0.0450(4)	–0.1660(5)	0.081
C36	0.0468(6)	0.0878(4)	–0.0798(4)	0.064
C1	–0.2195(4)	0.3112(3)	0.1973(3)	0.044
C2	–0.2732(4)	0.3164(3)	0.2844(3)	0.043
C3	–0.3472(6)	0.3793(4)	0.3163(4)	0.063
C4	–0.3771(6)	0.3665(4)	0.4038(4)	0.068
C5	–0.3340(6)	0.2947(4)	0.4555(4)	0.061
C6	–0.2587(5)	0.2319(3)	0.4238(3)	0.047
C7	–0.2296(4)	0.2451(3)	0.3372(3)	0.037
C8	–0.1471(4)	0.1930(3)	0.2843(3)	0.038

Table III. Fractional atomic coordinates and equivalent isotropic displacement parameters for compound **1**·$CHCl_3$ [$U_{eq} = (U_1 \cdot U_2 \cdot U_3)^{1/3}$, where U_1, U_2 and U_3 are the Eigenvalues of the U_{ij} matrix; E.s.d. values in parentheses].

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
AU	0.68191(2)	–0.05435(1)	0.11385(1)	0.038
P	0.7879(1)	0.1353(1)	0.13156(4)	0.035
O1	0.6190(4)	–0.3592(3)	0.1538(1)	0.052
O2	0.4596(4)	–0.1278(4)	0.0310(1)	0.066
N	0.5672(4)	–0.2167(3)	0.0952(1)	0.039
C11	0.7106(4)	0.2037(4)	0.1835(1)	0.035
C12	0.6790(7)	0.1208(5)	0.2199(2)	0.050
C13	0.6231(7)	0.1693(7)	0.2603(2)	0.064
C14	0.5979(7)	0.2996(7)	0.2652(2)	0.067
C15	0.6306(7)	0.3823(6)	0.2297(2)	0.067
C16	0,6844(7)	0.3343(5)	0.1886(2)	0.051
C21	0.7554(5)	0.2517(4)	0.0863(1)	0.040
C22	0.6375(5)	0.2343(5)	0.0565(2)	0.048
C23	0.6095(7)	0.3244(7)	0.0227(2)	0.063
C24	0.6993(8)	0.4320(6)	0.0181(2)	0.065
C25	0.8167(7)	0.4515(6)	0.0481(2)	0.064
C26	0.8438(6)	0.3615(6)	0.0818(2)	0.054
C31	0.9906(5)	0.1306(4)	0.1399(2)	0.039
C32	1.0599(6)	0.1875(6)	0.1763(2)	0.057
C33	1.2139(6)	0.1777(8)	0.1820(2)	0.072
C34	1.2970(6)	0.1124(7)	0.1506(2)	0.071
C35	1.2314(5)	0.0591(7)	0.1137(3)	0.068
C36	1.0772(5)	0.0657(6)	0.1083(2)	0.055
C1	0.5523(4)	–0.3309(4)	0.1192(2)	0.039
C2	0.4388(4)	–0.4108(4)	0.0947(2)	0.040
C3	0.3794(6)	–0.5319(5)	0.1047(2)	0.060
C4	0.2719(6)	–0.5805(6)	0.0747(3)	0.073
C5	0.2292(7)	–0.5121(7)	0.0368(3)	0.077
C6	0.2867(6)	–0.3921(6)	0.0266(2)	0.063
C7	0.3934(5)	–0.3433(5)	0.0567(2)	0.045
C8	0.4738(5)	–0.2172(5)	0.0576(2)	0.044
C	0.9555(7)	0.6971(6)	0.1702(2)	0.070
Cl1	0.9910(3)	0.8320(2)	0.20432(7)	0.097
Cl2	1.0432(3)	0.7121(2)	0.1180(1)	0.129
Cl3	1.0086(3)	0.5554(2)	0.19751(9)	0.128

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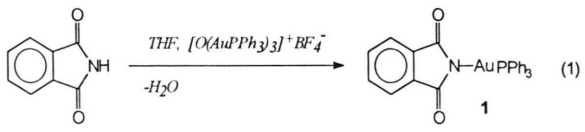
Results and Discussion

The reaction of phthalimide with the oxonium compound $[O(AuPPh_3)_3]^+BF_4^-$ in tetrahydrofuran results in a complete substitution of the N-bound hydrogen atom by a (triphenylphosphine)gold(I) group (eq. (1)).



1 (1)

(Phthalimido)(triphenylphosphine)gold(I) (**1**) is obtained in high yield (71%) as a solid stable to air, moisture and light, and soluble in most common organic solvents. The spectroscopic data obtained for the product confirm previous data where available (^1H, ^{31}P, ^{15}N NMR [28]). ^{197}Au-Mössbauer [32], FAB-MS and $^{13}C\{^1H\}$ NMR studies and single-crystal X-ray analyses of the solvent free product (**1**) and the $CHCl_3$ adduct (**1**·$CHCl_3$) have been carried out in the present work for further characterization.

The $^{13}C\{^1H\}$ resonances of the carbonyl carbon atoms in **1** are shifted downfield by about $\Delta\delta$ = +10 ppm upon auration with respect to the free ligand. The chemical shift values for the carbon atoms further away from the nitrogen function in

Table IV. Selected bond distances (Å) and angles (°) for compounds **1** and **1**·$CHCl_3$.

	1·$CHCl_3$	**1**		**1**·$CHCl_3$	**1**
Au–P	2.238(1)	2.224(1)	N–Au–P	174.2(1)	170.7(1)
Au–N	2.040(4)	2.028(4)	Au–N–C1	128.1(3)	124.4(3)
N–C1	1.381(5)	1.382(6)	Au–N–C8	121.2(3)	122.7(3)
N–C8	1.376(6)	1.385(6)	C1–N–C8	110.1(4)	110.7(4)
C1–C2	1.488(6)	1.493(7)	N–C1–O1	125.9(4)	125.8(5)
C2–C3	1.390(6)	1.375(8)	N–C1–C2	107.2(4)	107.2(4)
C3–C4	1.390(9)	1.395(9)	O1–C1–C2	126.9(4)	127.0(4)
C4–C5	1.37(1)	1.369(9)	C1–C2–C3	131.1(4)	130.8(4)
C5–C6	1.375(9)	1.380(8)	C1–C2–C7	107.8(4)	107.9(4)
C6–C7	1.387(7)	1.379(7)	C3–C2–C7	121.2(4)	121.2(4)
C7–C8	1.487(7)	1.494(6)	C3–C4–C5	120.8(6)	121.3(6)
C7–C2	1.376(6)	1.371(6)	C4–C5–C6	122.6(6)	121.8(5)
C1–O1	1.208(5)	1.210(6)	C5–C6–C7	116.5(6)	116.5(5)
C8–O2	1.215(6)	1.204(5)	C2–C7–C6	121.8(5)	122.3(4)
			C2–C7–C8	106.9(4)	107.1(4)
			C6–C7–C8	131.3(5)	130.6(4)
			N–C8–O2	124.7(4)	125.5(4)
			N–C8–C7	107.9(4)	107.5(3)
			O2–C8–C7	127.3(4)	127.0(4)

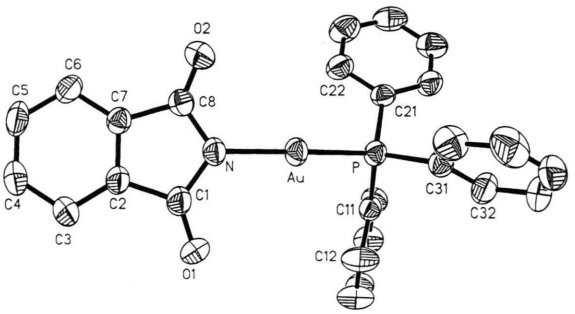


Fig. 1. Structure of compounds **1** and **1**·$CHCl_3$ in the crystal with atomic numbering scheme for both.

the phthalimide group show only minor effects. The resonances of the triphenylphosphinegold(I) unit feature the known pattern of doublets for the phenyl carbon atoms, originating from J(PC) couplings, frequently encountered for $AuPPh_3$ compounds. The fast atom bombardment mass spectrum shows the parent ion of **1** (m/z = 606.5, 23%, M^+). The base peak at m/z = 459.1 corresponds to the $AuPPh_3^{13}$ fragment.

In contrast to (phthalimido)(triethylphosphine)-gold(I) [28], for which only few related PEt_3 complexes are available, compound **1** with triphenylphosphine PPh_3 as the co-ligand can be compared with a wide range of LN–$AuPPh_3$ compounds. This is fortunately also true for structural data.

Colourless plates obtained by slow crystallization of **1** from acetone at 20 °C are monoclinic, space group $P2_1/c$, containing only the complex. Slow crystallization from chloroform leads to orthorhombic crystals, space group $P2_12_12_1$, containing one equivalent of solvent (**1**·$CHCl_3$), which has an influence neither on the interatomic distances and angles nor on the conformation of the complex species in the solid state (Tab. IV). The individual molecules, which have no crystallographic symmetry, show no unusual intermolecular contacts in both forms (Fig. 1).

The gold atom is coordinated to the nitrogen atom of the deprotonated phthalimide ligand and to the phosphorus atom of the triphenylphosphine ligand. The N–Au bond lengths (2.028(4) and 2.040(4) Å, respectively) agree well with those found in other monoaurated complexes of the type $R^1R^2N(AuPPh_3)$ (R^1R^2NH = *p*-nitroacetanilide: 2.050(6) Å [13]; cyclopropanecarboxylic acid *p*-nitroanilide: 2.039(5) Å [27]; 1,3-dihydro-7-nitro-5-phenyl-2 H-1,4-benzodiazepin-2-one (= NITRAZEPAM): 2.071(3) Å [29]; 5,5-diethyl-barbituric acid: 2.02(1) Å [30]).

The cationic complex formed by $AuPPh_3^{1+}$ with quinuclidine ($[R^1R^2R^3N(AuPPh_3)]^+$; $R^1R^2R^3N$ = quinuclidine) has a significantly longer bond between gold(I) and nitrogen (d(N–Au) = 2.11(1) Å) [25]. In triaurated ammonium ions $[RN(AuPPh_3)_3]^+$ the intramolecular Au···Au contacts lead to shorter gold(I)-nitrogen bonds (d(N–Au) = 1.99–2.07 Å) [18–23].

The phthalimide and phosphine ligands show no structural irregularities. The N–Au–P angles of 170.7(1) (**1**)/174.2(1)° (**1**·$CHCl_3$) are close to the standard value of 180° for two-coordinate d^{10} metal centers. Viewed along the N–Au–P axes, both ligands adopt a staggered conformation.

Conclusions

In this work it could be demonstrated that tris[(triphenylphosphine)aurio(I)]oxonium tetrafluoroborate can be used as a powerful aurating agent for diacylamine nitrogen atoms. It has thus become possible to convert imides like phthalimide into the gold(I) complexes without employing ionic alkali imides or auxiliary bases. This synthetic potential is important, since many gold

amido complexes show biological activity as anti-inflammatory or antitumor agents, with rheumatoid arthritis and leukemia as the most relevant target diseases [28, 33–35].

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