Tetramethylguanidine and Benzophenoneimine as Ligands in Gold Chemistry

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(Tetramethylguanidine)gold(I) chloride (**1**) and bromide (**2**) are readily prepared in high yield from $(Me_2N)_2C{=}NH$ and $[AuCl(Me_2S)]$ or $[AuBr(tht)]$ (tht = tetrahydrothiophene), respectively. NMR spectra of chloroform solutions of the two products indicate equilibria of the type $2\ LAuX \rightleftharpoons L_2Au^+AuX_2^-$. The cationic complex $[Au\{NH{=}C(NMe_2)_2\}(PPh_3)]^+$ is obtained as the triflate salt **3** from tetramethylguanidine and $[Au(PPh_3)]^+O_3SCF_3^-$. In solution at low temperature (−60 °C), this compound adopts a rigid structure whereby the NMe_2 groups are rendered non-equivalent, but at ambient temperature there is coalescence of the NMe_2 signals in the ^1H- and ^{13}C-NMR spectra. The related benzophenoneimine complex $[Au\{NH{=}CPh_2\}(PPh_3)]^+BF_4^-$ (**4**), which was synthesized as a reference compound, exhibits similar behaviour. In solution at low temperature (−60 °C) the two phenyl rings of the ligand are diastereotopic. In contrast, the triisopropylphosphane derivative $[Au\{NH{=}CPh_2\}(PiPr_3)]^+BF_4^-$ (**5**) is rigid on the NMR time scale, even at 25 °C. The solid-state structures of **2**, **3**, **4**, and **5** have been determined by single-crystal X-ray diffraction. Compound **2** crystallizes in the ionic form with discrete Au···Au bonded ion pairs $[Au\{NH{=}C(NMe_2)_2\}_2]^+\ [AuBr_2]^-$ [Au···Au 3.1413(8) Å]. The cations of **3**, **4**, and **5** show the $[Au(PPh_3)]^+$ units *N*-coordinated to the imino groups, with the nitrogen atoms in a trigonal-planar configuration.

Introduction

The successful introduction of guanidine-functionalized resins[1] for the extraction of gold from cyanide leaching brines has prompted considerable interest in the coordination chemistry of gold with guanidine ligands. The efficiency and selectivity of these resins is comparable to that of conventional active carbon used in the carbon-in-pulp/resin process[1]. Complexation of gold by guanidine is also relevant to the uptake, transport and action of gold drugs in biological systems, where guanidines are widely distributed natural ligands[2].

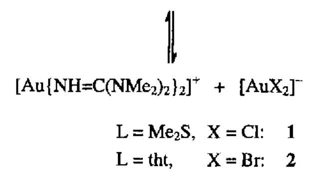
Furthermore, and quite generally, in recent years there has been a greater incentive to study the coordination chemistry of gold with nitrogen ligands since the discovery that hard nitrogen donors such as primary[3][5], secondary[4][5], and tertiary amines[4b][5], and even ammonia[6] can form surprisingly stable complexes with gold(I). In contrast, hard oxygen donor ligands such as dialkyl ethers, alcohols or water are known to induce rapid and irreversible disproportionation of Au^I to give gold metal and Au^{III}, and this is also true of aqueous ammonia. Clearly, for too long the coordination chemistry with simple nitrogen ligands has been dismissed as a "difficult field", not least because of the adverse thermodynamics of the explosive binary Au/N compounds.

After investigations into the coordination chemistry of several representative amines[4b][7] and imines[8], we have now extended our studies to tetramethylguanidine as a prototype of the class of polyfunctional amine/imine ligands.

Results

The reactions of stoichiometric amounts of tetramethylguanidine with $[AuCl(Me_2S)]$ or $[AuBr(tht)]$ (tht = tetrahydrothiophene) give high yields of (tetramethylguanidine)gold(I) chloride, **1**, and (tetramethylguanidine)gold(I) bromide, **2**, respectively. Both halides are thermally less stable than the corresponding benzophenoneimine complexes reported recently[8a] as indicated by their low decomposition temperatures [**1**: 145 °C; **2**: 129 °C]. Their limited stability is also apparent in solution, where both compounds decompose at room temperature within a few hours with precipitation of gold metal. However, analytically pure samples can be obtained by precipitation of the complexes from the reaction mixtures with pentane. The solid materials can be stored indefinitely below −10 °C.

The ^1H-NMR spectra of chloroform solutions of both compounds show two signals for the NH protons in the temperature range investigated (−60 to +25 °C), which indicate an equilibrium of ligand redistribution involving molecular and ionic species.



$$\begin{tikzcd}
2\,(Me_2N)_2C{=}NH + 2\,[AuXL] \arrow[r] & 2\,[AuX\{NH{=}C(NMe_2)_2\}] + 2\,L \arrow[d, shift left] \\
 & {[Au\{NH{=}C(NMe_2)_2\}_2]^+ + [AuX_2]^-} \arrow[u, shift left]
\end{tikzcd}$$

$L = Me_2S,\ X = Cl$: **1**
$L = tht,\ X = Br$: **2**

The crystalline precipitates of **1** and **2** are uniform products, as is evident from the single ν(NH) and ν(C=N) absorption bands in their IR spectra. The crystals of **2** have been identified as being of the ionic form by X-ray crystallography (see below).

With one equivalent of (triphenylphosphane)gold(I) triflate, tetramethylguanidine is quantitatively converted into a more stable monoaurated imine complex $[Au\{NH{=}C(NMe_2)_2\}(PPh_3)]^+CF_3SO_3^-$, **3**, m.p. 203 °C. This complex does not undergo ligand redistribution in solution, as is apparent from its variable temperature NMR spectra. Only a single NH proton and a single Ph_3P phosphorus resonance are observed over the whole temperature range investigated (−60 to +25 °C). It should be noted that the NMR data of the cation $[Au(PPh_3)_2]^+$ are well-known and that its signals would be easily recognized in the spectra if such cations were present.

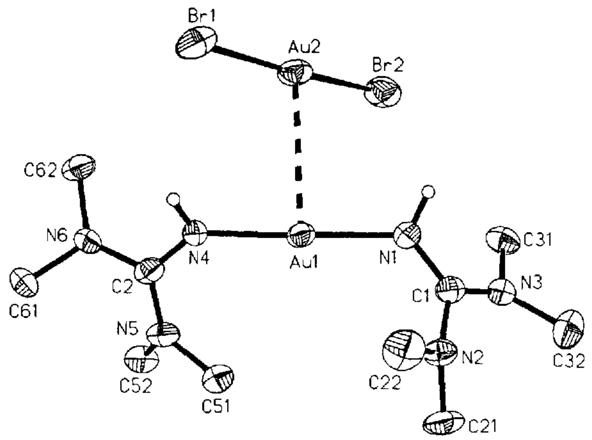
A splitting of the ^1H and ^{13}C resonances of the two Me_2N groups occurs as the temperature is lowered to −60 °C. The process is reversible and is ascribed to a site exchange of imino protons and $[Au(PPh_3)]^+$ units (a virtual rotation about the C=N bond), which renders the two amino groups non-equivalent on the NMR time scale. Free rotation about the $C-NMe_2$ bonds is not inhibited, leading to NMR equivalence of the methyl groups at each amino nitrogen atom.

For comparison purposes we also synthesized the corresponding benzophenoneimine complex $[Au\{NH{=}CPh_2\}(PPh_3)]BF_4$, **4**. The $^{13}C\{^1H\}$-NMR spectra of its $CHCl_3$ solutions show two sets of phenyl resonances for the Ph_2CNH group at −60 °C, which are partly obscured by the resonances of the Ph_3P ligands (only six of the eight requisite resonances were found, see Experimental Section). In order to avoid such overlap of signals, the triisopropyl phosphane analogue **5** was also synthesized, where the phosphane has similar steric bulk as that in complex **4**. This complex shows two complete sets of phenyl resonances even at room temperature, which can be ascribed to the *cis* and *trans* positions of the two phenyl rings relative to the gold (or hydrogen) atom at a fixed imino C=N double bond.

Crystal and Molecular Structures of Complexes 2, 3, 4, and 5

Colourless crystals of **2** are obtained by cautiously layering a solution in dichloromethane with pentane at −30 °C (rapid decomposition occurs above −10 °C). The orthorhombic crystals, space group $P2_12_12_1$, contain 4 formula units in the unit cell. The lattice is composed of $Au\{NH{=}C(NMe_2)_2\}_2^+$ cations and $AuBr_2^-$ anions, which form ion pairs via Au···Au contacts [3.1413(8) Å]. The axes N4−Au−N1 and Br1−Au2−Br2 are virtually linear and enclose a dihedral angle (average) of 41.5°. These structural parameters preclude hydrogen bonding between the NH and Br units. The Au−N and Au−Br bond lengths are similar to those found in the recently reported bis(benzophenoneimine)gold(I) dibromoaurate(I)[8a]. The central carbon atoms of the tetramethylguanidine ligands (C1 and C2) are in a planar configuration (sum of angles 359.9 and 360.0°, respectively). The overall geometry is similar to that of hexamethylguanidinium cations described in the literature with various other counterions[9]. This structure shows that the imine group of the ligand is the favoured coordination site for gold(I). The two NMe_2 groups are not engaged in coordinative bonding.

Figure 1. Cation-anion pair of compound **2** in the solid state (ORTEP, 50% probability ellipsoids; methyl hydrogen atoms omitted for clarity)[a]



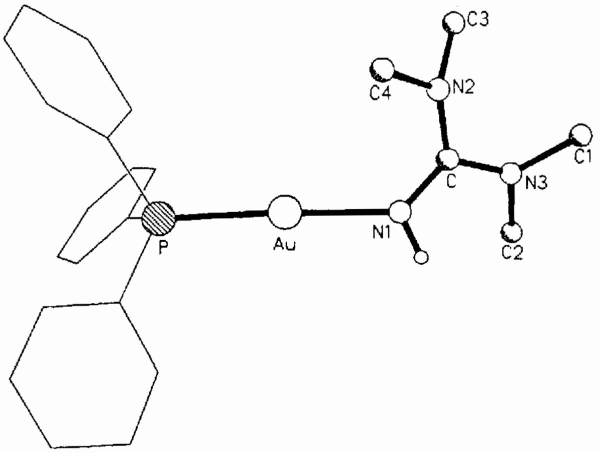
[a] Selected bond lengths [Å] and angles [°]: Au1−Au2 3.1413(8), Au2−Br1 2.396(2), Au2−Br2 2.389(2), Au1−N1 2.006(9), Au1−N4 1.993(9), C1−N1/C2−N4 1.30(2)/1.34(2), C1−N2/C2−N5 1.39(2)/1.33(2), C1−N3/2−N6 1.33(2)/1.38(2); N4−Au1−N1 178.8(5), Br2−Au2−Br1 176.89(6), N1−Au1−Au2 92.3(3), N4−Au1−Au2 86.6(3), C1−N1−Au1 128.5(9), C2−N4−Au1 132.8(8), N1−C1−N2 120(1), N1−C1−N3 124(1), N2−C1−N3 116(1).

Crystals of compound **3** are monoclinic, space group $P2_1/c$, with 4 formula units in the unit cell. The lattice consists of crystallographically independent (triphenylphosphane)gold(I) tetramethylguanidinium cations and triflate anions. The P−Au−N1 group is nearly linear [177.1(3)°] and the Au−N1 bond length [2.044(9) Å] is not unusual compared to other (imine)gold(I) complexes, in which the corresponding bonds range from 2.04 to 2.20 Å[10]. The central carbon atom of the tetramethylguanidine unit is in a planar configuration (360°). The N−C distance of the HN=C group is significantly shorter than the two $C-NMe_2$ bonds, but all three bond lengths are intermediate between the ranges of N−C single and N=C double bonds, suggesting extensive delocalization of the π-electron density in what may be described as a guanidinium resonance.

Compound **4** crystallizes from a dichloromethane/pentane mixture as a dichloromethane solvate in the orthorhombic space group *Pbca* with 8 formula units in the unit cell. The lattice contains (benzophenoneimine)(triphenylphosphane)gold(I) cations, tetrafluoroborate anions and solvent molecules (dichloromethane), which are readily released through evaporation. In the cation, the P−Au−N angle is almost linear [172.0(2)°] and the Au−N distance [2.036(7) Å] is comparable to the Au−N bond lengths found in **3** and other (imine)gold(I) complexes. The benzophenoneimine unit has the standard ketimine geometry.

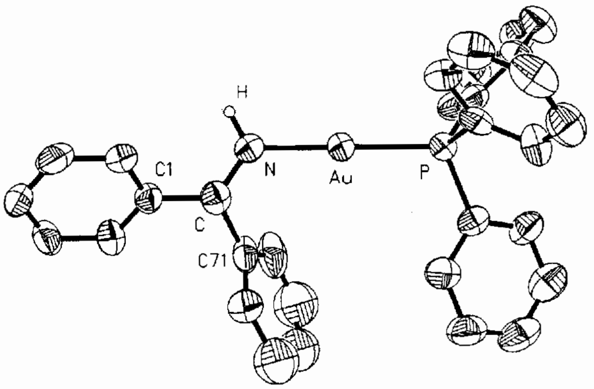
Complex **5** crystallizes from a dichloromethane/pentane mixture in the triclinic space group $P\bar{1}$ with 2 formula units in the unit cell. The lattice is free from solvent molecules

Figure 2. Solid-state structure of the cation of compound **3**[a]



[a] Selected bond lengths [Å] and angles [°]: Au−N1 2.044(9), Au−P 2.229(2), N1−C 1.27(1), N2−C 1.32(1), N3−C 1.38(1); N1−Au−P 177.1(3), C−N1−Au 132.0(7), N1−C−N2 123(1), N1−C−N3 120(1), N2−C−N3 117(1).

Figure 3. Solid-state structure of the cation of compound **4** (ORTEP, 50% probability ellipsoids; phenyl hydrogen atoms omitted for clarity)[a]

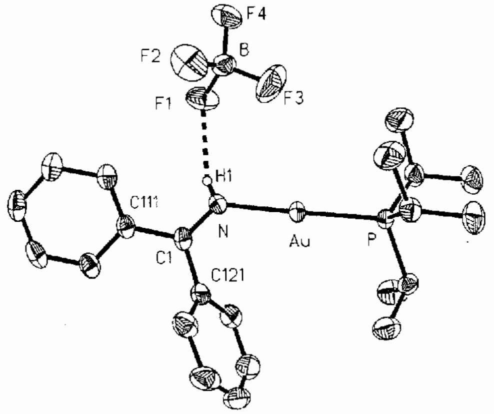


[a] Selected bond lengths [Å] and angles [°]: Au−N 2.036(7), Au−P 2.234(2), N−C 1.30(1), C−C1 1.49(1), C−C71 1.47(1); N−Au−P 172.0(2), C−N−Au 124.6(6), N−C−C71 118.0(8), N−C−C1 122.4(8), C71−C−C1 119.5(7).

and consists of (triisopropylphosphane)gold(I) cations and tetrafluoroborate anions. The N−P−Au angle is virtually linear [176.23(9)°] and the Au−N distance [2.069(3) Å] is slightly longer than in complex **4** (see above), presumably due to the larger *trans* influence of the triisopropylphosphane ligand. The C=N bond length [1.281(5) Å] is shorter than in complex **4** [1.30(1) Å]. The standard deviation of the C=N distance in complex **4** is, however, rather high, and therefore there is some uncertainty as to the significance of this result.

Owing to the better crystal quality of compound **5** (see Table 2) the data for this structure are more reliable. There is hydrogen bonding between one fluorine atom of the tetrafluoroborate anion and the N−H proton of the imine group [F···H1 2.254 Å, N−H1 0.71(5) Å; N−H1···F 158.1°] and a weak contact between the fluorine atom F3 of the anion and the gold atom in the cation (3.38 Å) (Figure 4).

Figure 4. Solid-state structure of one formula unit of compound **5** (ORTEP, 50% probability ellipsoids; phenyl hydrogen atoms omitted for clarity)[a]



[a] Selected bond lengths [Å] and angles [°]: Au−N 2.069(3), Au−P 2.2465(8), N−C1 1.281(5), C1−C111 1.480(4), C1−C121 1.479(5), N−H1 0.71(5), F1···H1 2.254; N−Au−P 176.23(9), C1−N−Au 126.4(3), N−C1−C121 118.4(3), N−C1−C111 122.6(3), C121−C1−C111 119.0(3), N−H1···F1 158.1.

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Experimental Section

All experiments were carried out under dry, purified nitrogen. Glassware was dried and filled with nitrogen, solvents were distilled and kept under nitrogen. − NMR: Jeol GX 400, TMS as internal standard (^{1}H and ^{13}C{^{1}H}) and H_3PO_4 as external standard (^{31}P{^{1}H}). − IR: Perkin-Elmer 1600, FT-IR. − MS: Finnigan MAT 90. − Microanalyses: In-house analyzers (by combustion and atomic absorption spectroscopy). − Starting materials were either commercially available or were prepared following literature procedures: $[AuCl(Me_2S)]$[11], [AuBr(tht)][12], $[AuCl(PPh_3)]$[13] and $[AuCl(P\mathit{i}Pr_3)]$.[14]

(Tetramethylguanidine)gold(I) Chloride (**1**): A solution of $[AuCl(Me_2S)]$ (187 mg, 0.68 mmol) in dichloromethane (10 ml) was slowly added to a solution of tetramethylguanidine (86 µl, 0.69 mmol) in the same solvent (5 ml) at 0 °C. After 1 h, the product (186 mg, 78% yield) was precipitated by the addition of pentane (30 ml) as a colourless solid (m.p. 145 °C with decomposition). The compound decomposes completely within 24 h if kept in solution above 0 °C. − ^{1}H NMR ($CDCl_3$, room temp.): δ = 5.05 and 5.30 (br. s, N−H, intensity ratio 3:1), 2.78−3.08 [br., $N(CH_3)_2$]; (−60 °C): δ = 5.36 and 5.34 (br. s, N−H, intensity ratio 1:4), 2.97, 2.84 and 2.96, 2.85 [each br. s, $N(CH_3)_2$; the pairs of resonances are assigned to the bis(tetramethylguanidine)gold(I) cation and (tetramethylguanidine)gold(I) chloride, respectively, intensity ratio 4:1]. − ^{13}C{^{1}H} NMR ($CDCl_3$, room temp.): δ = 167.4 and 167.3 [s, C=N, intensity ratio 3:1], 39.4−40.1 [br., $N(CH_3)_2$]; (−60 °C): δ = 166.2 and 166.1 [s, C=N, intensity ratio 4:1], 39.8, 39.1 and 39.8, 39.2 [each s, $N(CH_3)_2$, intensity ratio 4:1 (see above)]. − IR (KBr): $\tilde{\nu}$ = 3329 [s, ν(NH)], 1555 cm^{-1} [s, ν(C=N)]. − $C_5H_{13}AuClN_3$ (347.59): calcd. C 17.28, H 3.77, N 12.09; found C 17.38, H 3.79, N 12.38.

(Tetramethylguanidine)gold(I) Bromide (**2**): To a solution of tetramethylguanidine (68 µl, 0.54 mmol) in dichloromethane (5 ml), a solution of [AuBr(tht)] (198 mg, 0.54 mmol) in the same solvent (10 ml) was slowly added at 0 °C. After 30 min, the solution was concentrated to a volume of 5 ml and then cautiously layered with pentane. The mixture was cooled to −30 °C to give, after several days, colourless needles (148 mg, 68% yield) with a melting point of 129 °C (with decomposition). In solution at room temperature, the compound decomposes within a few hours. – ^{1}H NMR ($CDCl_3$, room temp.): δ = 5.09 and 4.87 (br. s, N–H, intensity ratio 2:1), 2.75–3.10 [br., $N(CH_3)_2$]; (−60 °C): δ = 5.19 and 4.98 (s, N–H, intensity ratio 2:3), 3.00, 2.88 and 2.99, 2.89 [each s, $N(CH_3)_2$; the pairs of resonances are assigned to bis(tetramethylguanidine)gold(I) dibromoaurate(I) and (tetramethylguanidine)gold(I) bromide, respectively, intensity ratio 3:2]. – $^{13}C\{^1H\}$ NMR ($CDCl_3$, room temp.): no spectrum could be recorded due to decomposition of the compound; (−60 °C): δ = 166.35 and 166.3 (s, C=N, intensity ratio 1:2), 40.1, 39.4 and 39.8, 39.2 [each s, $N(CH_3)_2$, intensity ratio 2:1 (see above)]. – IR (KBr): $\tilde{\nu}$ = 3340.5 [s, ν(N–H)], 1577 cm^{-1} [s, ν(C=N)]. – $C_5H_{13}AuBrN_3$ (392.05): calcd. C 15.32, H 3.34, N 10.72; found C 15.35, H 3.21, N 10.75.

[(Triphenylphosphane)gold(I)]tetramethylguanidinium Triflate (**3**): A solution of $[AuCl(PPh_3)]$ (207 mg, 0.43 mmol) in THF (20 ml) was stirred with $AgCF_3SO_3$ (110 mg, 0.43 mmol) at 0 °C for 30 min and then filtered. Tetramethylguanidine (54 µl, 0.43 mmol) was added and after 1 h the solvent was removed and the colourless residue was taken up in dichloromethane. By cautiously layering this solution with pentane, colourless crystals (303 mg, 98% yield) with a melting point of 203 °C were obtained. – ^{1}H NMR ($CDCl_3$, room temp.): δ = 2.8–3.1 [br., 12 H, $N(CH_3)_2$], 6.0 (br. s, 1 H, NH), 7.45–7.55 (m, 15 H, Ph–H); (−60 °C): δ = 2.92 and 3.03 [s, $N(CH_3)_2$], 5.95 [br. s, NH], 7.45–7.55 (m, Ph–H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, room temp.): δ = 168.5 (s, C=N), 134.1 [d, ^2J(CP) = 13.8 Hz, *ortho*-C], 132.3 (br. s, *para*-C), 129.7 [d, ^3J(CP) = 11.5 Hz, *meta*-C], 128.0 [d, ^1J(CP) = 62.9 Hz, *ipso*-C], 121.0 [q, ^1J(CF) = 321 Hz, CF_3], 39.0–40.8 [br., $N(CH_3)_2$]; (−60 °C): δ = 167.4 (s, C=N), 127.4 [d, ^1J(CP) = 63.4 Hz, *ipso*-C], 133.7 [d, ^2J(CP) = 12.9 Hz, *ortho*-C], 129.2 [d, ^3J(CP) = 12.2 Hz, *meta*-C], 132.0 (br. s, *para*-C), 120.0 [q, ^1J(CF) = 320 Hz, CF_3], 39.1 and 40.0 [s, $N(CH_3)_2$]. – $^{31}P\{^1H\}$ NMR ($CDCl_3$, room temp.): δ = 31.8 (s, P–Au). – $C_{24}H_{28}AuF_3N_3O_3PS$ (723.49): calcd. C 39.84, H 3.90, N 5.81; found C 39.74, H 3.96, N 5.90.

[(Triphenylphosphane)gold(I)]benzophenoneiminium Tetrafluoroborate (**4**): A solution of $[Au(PPh_3)]BF_4$ in THF (20 ml) [prepared in situ from $AgBF_4$ (0.59 mg, 0.30 mmol) and $[AuCl(PPh_3)]$ (150 mg, 0.30 mmol)] was added to a solution of benzophenoneimine (51 µl, 0.30 mmol) in the same solvent (10 ml) at −78 °C. After 30 min, the solvent was removed and the colourless product was crystallized from a dichloromethane/pentane mixture (77 mg, 35% yield). The crystals had a melting point of 105 °C and were found to contain solvent (dichloromethane), which was lost very easily. – ^{1}H NMR ($CDCl_3$, room temp.): δ = 10.20 (br. s, 1 H, N–H), 7.31–7.78 (m, 25 H, Ph–H]; (−60 °C): δ = 10.52 (br. s, 1 H, N–H), 7.31–7.80 (m, 25 H, Ph–H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, room temp.): δ = 184.9 (s, C=N), 134.1 [d, ^2J(CP) = 14.0 Hz, *ortho*-C (PPh_3)], 132.4 [br. s, *para*-C (Ph_3P)], 129.5 [d, ^3J(CP) = 11.9 Hz, *meta*-C (Ph_3P)], 127.5 [d, ^1J(CP) = 64.3 Hz, *ipso*-C (Ph_3P)], 129.8 and 129.1 [br. s, *ortho*- and *meta*-C ($Ph_2C=NH$)], *ipso*- and *para*-C of $Ph_2C=NH$ are not observed at room temperature; (−60 °C): δ = 184.8 (s, C=N), 134.2 [d, ^2J(CP) = 14.0 Hz,

Table 1. Crystallographic data for **2** and **3**

Compound	**2**	**3**
empirical formula	$C_{10}H_{26}Au_2Br_2N_6$	$C_{24}H_{28}AuF_3N_3O_3PS$
formula weight	784.12	723.49
crystal system	orthorhombic	monoclinic
space group (No.)	$P2_12_12_1$ (19)	$P2_1/c$ (14)
a [Å]	7.698(1)	10.373(1)
b [Å]	15.678(1)	18.877(2)
c [Å]	15.842(2)	14.280(1)
α [°]	90	90
β [°]	90	99.41(1)
γ [°]	90	90
V [Å^3]	1912.0(4)	2758.6(4)
$\rho_{calcd.}$ [gcm^{-3}]	2.724	1.742
Z	4	4
F(000) [e]	1424	1416
λ(Mo-K_α) [Å]	0.71073	0.71073
T [°C]	−74	20
diffractometer	Enraf Nonius CAD4	Enraf Nonius CAD4
scan	ω	ω
hkl range	$-9 \leq h \leq 9, 0 \leq k \leq 19, 0 \leq l \leq 20$	$-12 \leq h \leq 7, 0 \leq k \leq 23, -17 \leq l \leq 17$
measured reflections	4120	7944
unique reflections	3878	4952
used reflections	3878	4938
R_{int}	0.0281	0.0217
refined parameters	182	261
H atoms (found/calcd.)	0/26	0/28
absorption corr.	semi-empirical	semi-empirical
T_{min}/T_{max}	0.42/0.99	0.84/0.99
$R1$[a] [$I > 2\sigma(I)$]	0.0391	0.0586
$wR2$[a] (used refl.)	0.0894	0.1628
weighting scheme[a]	a = 0.0497, b = 18.61	a = 0.1052, b = 13.14
ρ_{fin}(max/min) [eÅ^{-3}]	2.545/−2.055[b]	2.899/−1.489[b]

[a] $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$ $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/2\sigma^2(F_o^2) + (ap)^2 + bp$, $p = (F_o^2 + 2F_c^2)/3$. – [b] Residual electron densities are located at the gold atoms (**2**) and at the triflate anion (**3**).

Table 2. Crystallographic data for **4** and **5**

Compound	**4**	**5**
empirical formula	$C_{32}H_{28}AuBCl_2F_4NP$	$C_{22}H_{32}AuBF_4NP$
formula weight	812.20	625.23
crystal system	orthorhombic	triclinic
space group (No.)	*Pbca* (61)	$P\bar{1}$ (2)
a [Å]	22.022(2)	10.074(1)
b [Å]	12.298(2)	11.079(1)
c [Å]	23.514(3)	11.179(1)
α [°]	90	85.25(1)
β [°]	90	80.90(1)
γ [°]	90	78.81(1)
V[Å^3]	6368.2(14)	1206.8(2)
$\rho_{calcd.}$ [gcm^{-3}]	1.694	1.721
Z	8	2
F(000) [e]	3168	612
λ(Mo-K_α) [Å]	0.71073	0.71073
T [°C]	−62	−74
diffractometer	Enraf Nonius CAD4	Enraf Nonius CAD4
scan	ω	ω
hkl range	$-26 \le h \le 0, -15 \le k \le 0, 0 \le l \le 28$	$-12 \le h \le 12, -13 \le k \le 13, -13 \le l \le 12$
measured reflections	5120	5400
unique reflections	5114	4594
used reflections	5112	4581
R_{int}	0.000	0.0193
refined parameters	369	275
H atoms (found/calcd.)	0/28	1/21
absorption corr.	semi-empirical	semi-empirical
T_{min}/T_{max}	0.69/0.99	0.38/0.99
$R1$[a] [$I > 2\sigma(I)$]	0.0485	0.0211
$wR2$[a] (used refl.)	0.1091	0.0526
weighting scheme[a]	$a = 0.0572$, $b = 22.21$	$a = 0.0348$, $b = 1.14$
ρ_{fin}(max/min) [eÅ^{-3}]	1.055/−1.074[b]	0.942/−1.016[b]

[a] $R1 = \Sigma(\|F_o| - |F_c\|)/\Sigma|F_o|$ $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/2\sigma^2(F_o^2) + (ap)^2 + bp, p = (F_o^2 + 2F_c^2)/3$. – [b] Residual electron densities are located at the gold atoms (**4**, **5**) and at one phenyl ring (**4**).

ortho-C (PPh_3)], 132.6 [br. s, *para*-C (Ph_3P)], 129.6 [d, ^3J(CP) = 11.9 Hz, *meta*-C (Ph_3P)], 127.2 [d, ^1J(CP) = 64.3 Hz, *ipso*-C (Ph_3P)]; only the following six of a total of eight possible resonances of the two benzophenoneimine phenyl rings are observed (see above): 137.9 and 135.3 [br. s, *ipso*-C ($Ph_2C{=}NH$)], 133.0 [br. s, *para*-C ($Ph_2C{=}NH$)], 130.5, 129.5 and 129.1 [each br. s, *ortho*- and *meta*-C ($Ph_2C{=}NH$)]. – $^{31}P\{^1H\}$ NMR ($CDCl_3$, room temp.): δ = 30.6 (s, PPh_3). – MS (FAB); *m/z* (%): 639.8 (100) [M^+], 456.5 (72) [$(Ph_3P)Au^+$], 182.6 (33) [$Ph_2C{=}NH_2^+$]. – $C_{31}H_{26}AuBF_4NP$ (727.30): calcd. C 51.19, H 3.60, N 1.93; found C 51.29, H 3.72, N 1.83.

(Triisopropylphosphane)gold(I)benzophenoneiminium Tetrafluoroborate (**5**): The preparation was carried out similarly to that of complex **4**. From 320 mg [$AuCl(PiPr_3)$] (0.82 mmol), 159 mg $AgBF_4$ (0.81 mmol) and 137 µl $Ph_2C{=}NH$ (0.82 mmol), 470 mg (92% yield) of a colourless solid was obtained. The product could be purified by crystallization from a dichloromethane/pentane mixture. The crystals obtained were free of solvent (m.p. 198 °C). – ^1H NMR (CD_2Cl_2, room temp.): δ = 10.05 (br. s, 1 H, N–H), 7.48–7.74 (m, 10 H, Ph–H), 2.24 (m, 3 H, CH), 1.19 [dd, ^3J(HH) = 10.6 Hz, ^2J(HP) = 24.6 Hz, 18 H, CH_3]. – $^{13}C\{^1H\}$ NMR (CD_2Cl_2, room temp.): δ = 185.1 (s, C=N), 137.8 and 135.6 (s, *ipso*-C), 134.0 and 132.6 (s, *para*-C), 129.9, 129.4, 129.2 and 128.7 (s, *ortho*- and *meta*-C), 23.6 [d, ^1J(CP) = 33 Hz, CH], 19.9 (br. s, CH_3). – $^{31}P\{^1H\}$ NMR (CD_2Cl_2, room temp.): δ = 62.6 (s, iPr_3P). – $C_{22}H_{32}AuBF_4NP$ (625.23): calcd. C 42.24, H 5.12, N 2.24; found C 42.20, H 5.01, N 2.21.

Crystal Structure Determination: Suitable crystals of compounds **2**, **3**, **4**, and **5** were sealed into glass capillaries and used for measurement 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 any of the four compounds. Diffraction intensities were corrected for Lp and absorption effects. The structures were solved by direct methods and refined by full-matrix least-squares calculations against F^2[15]. The thermal motion of all non-hydrogen atoms was treated anisotropically. All hydrogen atoms of compounds **2**, **3**, and **4** were calculated in idealized positions and allowed to ride on their corresponding carbon or nitrogen atom, whereas the N–H atom of **5** was found and refined isotropically. Their isotropic thermal parameters were tied to that of the adjacent atom by a factor of 1.5. Important interatomic distances and angles are given in the figure captions. Crystal and structure solution data are summarized in Tables 1 and 2. Further information may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository numbers CSD-407082 (**2**), -407081 (**3**), -407083 (**4**), and -407080 (**5**), the names of the authors, and the journal citation.

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