Gold Coordination by 2-(Diphenylphosphanyl)aniline

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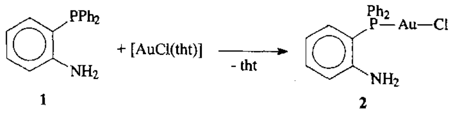
The reaction of 2-(diphenylphosphanyl)aniline (**1**) with (*te*tra*h*ydro*t*hiophene)gold(I) chloride in the molar ratio 1:1 gives a stable molecular complex **2**, in which the gold atom is bonded to the phosphorus atom. Reaction of two equivalents of ligand **1** with one equivalent of the salt $[(tht)_2Au]ClO_4$ results in the displacement of both thioether ligands, affording the ionic complex $\{[(2\text{-}NH_2C_6H_4)PPh_2]_2Au\}^+$ ClO_4^- (**3a**), in which the metal center is exclusively P-coordinated. Treatment of $[(tht)_2Au]ClO_4$ with ligand **1** (1:1) affords the mixed P/S-coordinated complex **4**, the structure of which has been confirmed by single-crystal X-ray diffraction. The reaction of ligand **1** with $[(Ph_3P)Au]^+$ BF_4^- leads to a mixture of products which are components of an equilibrium between the unsymmetrical salt $\{[(2\text{-}NH_2C_6H_4)PPh_2]Au(PPh_3)\}^+$ BF_4^- with the two symmetrical species **3b** (the BF_4^- analogue of **3a**) and $[(Ph_3P)_2Au]^+$ BF_4^-. With $\{[(Ph_3P)Au]_3O\}^+$ BF_4^- as the aurating agent, the ligand **1** (molar ratio 1:1) is converted into a polynuclear complex **7**, which is tentatively assigned a structure with intimate aggregation of six gold atoms.

Introduction

Polyfunctional ligands with P-, S-, or N-donor centers are instrumental in the preparation of a variety of polynuclear gold complexes which may be used for a number of applications including chemotherapy, diagnostics, electron microscopy, catalysis and surface technology[1-4]. After a series of investigations with ligands containing P/S and P/O functionalities, we have now also studied the new ligand 2-(diphenylphosphanyl)aniline, recently prepared by Stelzer et al.[5]. With this P,N-difunctional donor it should be possible to build both trinuclear NAu_3 and mononuclear Ph_2PAu units in close proximity, allowing self-assembly into polynuclear aggregates.

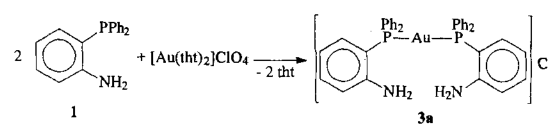
Results

2-(Diphenylphosphanyl)aniline (**1**) reacts rapidly with (*t*etra*h*ydro*t*hiophene)gold(I) chloride in the molar ratio 1:1 in dichloromethane at ambient temperature with liberation of the tht ligand to give a colourless crystalline product **2** in high yield [Eq. (1)]. The composition of the compound was readily confirmed by elemental analysis and mass spectroscopy. The $^{31}P\{^1H\}$-NMR spectrum shows a single resonance which is shifted more than 25 ppm downfield compared to that of ligand **1**, indicative of Au–P coordination.



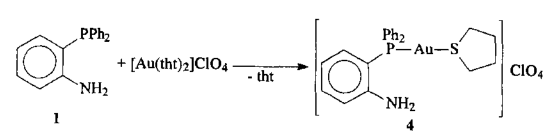
(1)

Treatment of $[(tht)_2Au]ClO_4$ with two equivalents of ligand **1** leads to a displacement of both thioethers by the phosphane, to give a colourless crystalline product **3a**. The cation of this salt has been identified by FAB mass spectrometry (m/z = 751.6 [M^+]), the anion by its IR absorptions [Eq. (2)].

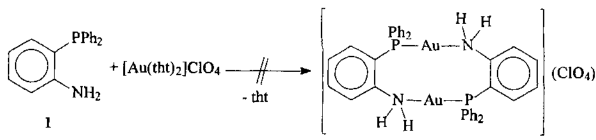


(2)

The reaction of the two components in a 1:1 molar ratio affords the mono-substitution product **4**, which thus has a cation with mixed P–Au–S coordination [Eq. (3a)]. This cation has been observed in the mass spectrum (m/z = 561.8 [M^+]), and has also been structurally characterized in a single-crystal X-ray diffraction study (see below). It should be noted that the second tht ligand is *not* displaced by the amino group of a phosphane **1** in a condensation reaction between two cations which should give a cyclic dication [Eq. (3b)].

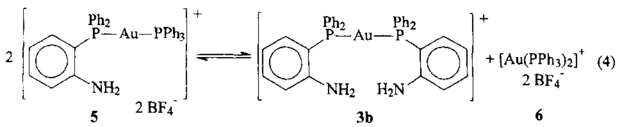


(3a)



(3b)

The reaction of ligand **1** with freshly prepared $[(Ph_3P)Au]BF_4$ in tetrahydrofuran at 0 °C leads to a product, the analytical data of which are consistent with the formula of the mixed 1:1 complex $[(Ph_3P)Au(Ph_2PC_6H_4NH_2\text{-}2)]BF_4$ (**5**). However, the ^{31}P-NMR spectrum in $CDCl_3$ solution shows that the product is in fact a mixture of three salts (**3b**, **5**, **6**), the remaining two having the symmetrical cations $[(Ph_3P)_2Au]^+$ (in **6**) and $[(\mathbf{1})_2Au]^+]$ (in **3b**). The chemical shifts δP of these cations are known from the literature (**6**) and compound **3a**, above, respectively [Eq. (4)].

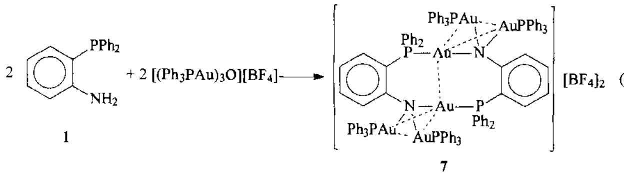


(4)

The three components are in equilibrium with one another, and thus the symmetrical cations are always present in solutions of the mixed species and vice versa. At low temperature, the AB pattern of the mixed species is clearly resolved [−60 °C: $\delta P_A = 44.1$; $\delta P_B = 34.1$, $J(P_AP_B) = 329.2$ Hz]. At 20 °C, the signals are broad owing to rapid ligand exchange on the NMR time scale. Because of this fast site exchange of the ligands, the pertinent equilibrium is reached instantaneously when the compounds are dissolved in $CDCl_3$.

Treatment of the ligand **1** with an equimolar quantity of tris[(triphenylphosphane)gold(I)]oxonium tetrafluoroborate in dichloromethane gives a colourless, microcrystalline product **7**, which is readily soluble in dichloromethane or chloroform. Its IR spectrum shows no NH_2 stretching vibrations, suggesting that the amino group of the ligand has been fully aurated by the oxonium reagent. This type of reaction is well-established and has been probed for many aliphatic and aromatic primary amines[6]. Analytical data, however, show that not all three triphenylphosphane ligands are retained in the auration reaction. The $^{31}P\{^1H\}$-NMR spectrum of **7** in $CDCl_3$ solution exhibits two singlet resonances in the intensity ratio 2:1, which show no further splitting when the temperature is lowered to −50 °C.

From these data, the product can be tentatively assigned a structure with a cyclic dication containing six gold atoms, four Ph_3P molecules and two fully deprotonated ligands **1**, associated with two BF_4^- anions [Eq. (5)]. In such a structure, two NAu_3 pyramids are linked through the two ligands **1**, but are also associated through intimate Au–Au contacts typical for polygold units of this type. Unfortunately, no single crystals could be grown to verify this assumption.

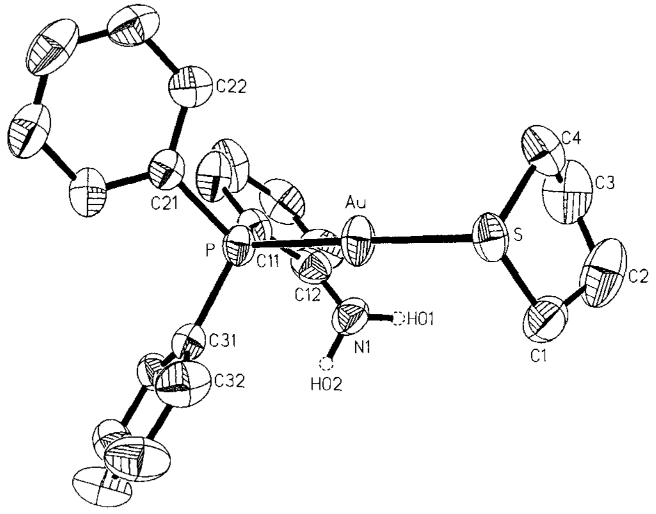


(5)

The Crystal and Molecular Structure of Complex 4

Crystals of compound **4** are monoclinic, space group *C2/c*, with 8 molecules in the unit cell. The lattice is composed of mononuclear cations and perchlorate anions. The cation has no crystallographically imposed symmetry and shows geometric disorder of the amino groups over one *ortho* position at each phenyl ring. In Figure 1, only one of these three positions is shown. There is also rotational disorder of the perchlorate anion, which has ill-defined hydrogen bonding contacts with the amino group(s).

Figure 1. Molecular structure of the cation of compound **4** with atomic numbering (ORTEP plot with 50% probability ellipsoids, H atoms omitted for clarity, only one of the three positions of the amino group is shown); selected bond lengths [Å] and angles [°]: Au–P 2.261(2), Au–S 2.321(2), P–C11 1.814(7), P–C21 1.804(7), P–C31 1.809(8), S–C1 1.834(9), S–C4 1.823(9); P–Au–S 179.19(7), C11–P–C21 107.4(3), C11–P–C31 107.7(3), C11–P–Au 112.0(2), C21–P–C31 105.8(3), C21–P–Au 112.0(2), C31–P–Au 111.6(2), C1–S–C4 93.3(5), C1–S–Au 103.6(3), C4–S–Au 104.2(3)



The coordination at the gold atom is linear [P–Au–S 179.19(7)°] with standard Au–S and Au–P bond lengths. The three aryl groups have a propeller conformation with a tetrahedral phosphorus center. The disordered amino group(s) are thus oriented towards the metal atom, but all N···Au distances are longer than the sums of the van der Waals radii. The sulfur atom is in a steep pyramidal configuration, and the tetrahydrothiophene ring has a distorted envelope conformation. The situation resembles that of the (dimethyl sulfide)(triphenylphosphane)gold(I) cation in the tetrafluoroborate salt[7].

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Experimental Section

All experiments were carried out routinely under dry, pure nitrogen. Standard equipment was used throughout. $[AuPPh_3]^+[BF_4]^-$ was prepared in situ by reaction of $AgBF_4$ and $AuClPPh_3$ in THF according to a standard procedure; $1,2\text{-}Ph_2PC_6H_4NH_2$[5], [AuCl(tht)], $[Au(tht)_2]ClO_4$[8] and $[O(AuPPh_3)_3][BF_4]$[9] were prepared according to literature procedures. The NMR spectra were recorded in $CDCl_3$ with TMS as internal standard for ^1H, and H_3PO_4 (85%) as external standard for $^{31}P\{H\}$ on a JEOL GX 400 spectrometer. Mass spectra were obtained with a Varian MAT 311A spectrometer.

Caution: Perchlorates can be explosive!

Chloro[2-(diphenylphosphanyl)aniline]gold(I) (**2**): To a solution of 2-(diphenylphosphanyl)aniline (0.08 g, 0.30 mmol) in 20 ml of dichloromethane was added chloro(tetrahydrothiophene)gold(I) (0.09 g, 0.30 mmol) and the mixture was stirred for 1 h. The solvent was then evaporated until a volume of ca. 5 ml remained. Addition of diethyl ether afforded complex **2** as a white solid (yield 0.09 g, 60%). – $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25°C): δ = 20.3 (s, PPh_2). – ^1H NMR ($CDCl_3$, 25°C): δ = 4.25 (br., NH_2), 6.6–7.6 (m, Ph). – FAB MS; *m/z* (%): 508.8 (13) $[M^+]$. – $C_{18}H_{16}AuClNP$ (509.73): calcd. C 42.7, H 4.07, N 2.27; found C 42.8, H 4.33, N 2.55.

Bis[2-(diphenylphosphanyl)aniline]gold(I) Perchlorate (**3a**): To a solution of 2-(diphenylphosphanyl)aniline (0.08 g, 0.30 mmol) in 20 ml of dichloromethane was added bis(tetrahydrothiophene)gold(I) perchlorate (0.07 g, 0.15 mmol). After 30 min, the solvent was evaporated to leave a volume of ca. 5 ml. Addition of diethyl ether gave complex **3a** as a white solid (yield 0.07 g, 67%). – $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25°C): δ = 33.4 (s, PPh_2).– ^1H NMR ($CDCl_3$, 25°C): δ = 4.64 (br., NH_2), 6.56–7.62 (m, Ph). – FAB MS; *m/z* (%): 751.6 (100) $[M^+]$. – $C_{36}H_{32}AuClN_2O_4P_2$ (851.04): calcd. C 50.8, H 3.8, N 3.3; found C 50.2, H 4.46, N 2.9.

[2-(Diphenylphosphanyl)aniline](tetrahydrothiophene)gold(I) Perchlorate (**4**): To a solution of bis(tetrahydrothiophene)gold(I) perchlorate (0.14 g, 0.30 mmol) in 20 ml of dichloromethane was added 2-(diphenylphosphanyl)aniline (0.08 g, 0.30 mmol) and the mixture was stirred for 1 h. Concentration of the solution in vacuo and addition of diethyl ether afforded complex **4** as a white solid (yield 0.14 g, 70%). – $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25°C): δ = 22.8 (s, PPh_2). – ^1H NMR ($CDCl_3$, 25°C): δ = 4.7 (br., NH_2), 2.12 (m, CH_2), 3.38 (m, CH_2S), 6.6–7.8 (m, Ph). – FAB MS; *m/z* (%): 561.8 (59.6) $[M^+]$. – $C_{22}H_{24}AuClNO_4PS$ (661.87): calcd. C 40.0, H 3.75, N 2.1; found C 39.9, H 3.65, N 2.2.

Reaction of 2-(Diphenylphosphanyl)aniline with $[AuPPh_3]^+[BF_4]^-$: To a freshly prepared solution of $[AuPPh_3]^+[BF_4]^-$ (0.16 g, 0.30 mmol) in 20 ml of THF at 0°C was added 2-(diphenylphosphanyl)aniline (0.08 g, 0.30 mmol) and the mixture was stirred for 1 h. Concentration of the solution in vacuo and addition of diethyl ether afforded a white solid (yield 0.15 g, 63%). – $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25°C): δ = 33.37 (s, PPh_2, **3b**), 45.4 (s, PPh_2, **6**), 44.1 (d, δ_A, J_{AB} = 329.2 Hz), 34.1 (d, δ_B, J_{AB} = 329.2 Hz) (**5**). – ^1H NMR ($CDCl_3$, 25°C): δ = 4.65 (br., NH_2), 6.54–7.62 (m, Ph).

Bis{2-[diphenylphosphanyl]-N,N-bis[(triphenylphosphane)gold(I)]anilinegold(I)} Bis(tetrafluoroborate) (**7**): To a solution of 2-(diphenylphosphanyl)aniline (0.04 g, 0.15 mmol) in 20 ml of dichloromethane was added tris[(triphenylphosphane)gold(I)]oxonium tetrafluoroborate (0.22 g, 0.15 mmol) and the mixture was stirred for 1 h. Concentration of the solution in vacuo and addition of diethyl ether afforded complex **7** as a yellow solid (yield 0.19 g, 85%). – $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25°C): δ = 27.0 (s, 2 P, PPh_3), 11.4 (s, 1 P, PPh_2). – ^1H NMR ($CDCl_3$, 25°C): δ = 6.17–7.53 (m, Ph). – FAB MS; *m/z* (%): 1390.1 (10.07 $[M^+]$. – $C_{108}H_{88}Au_6B_2F_8N_2P_6$ (2955.17): calcd. C 44.0, H 3.0; found C 45.3, H 3.18.

Table 1. Crystal data, data collection and structure refinement for compound **4**

Crystal data:	
Formula	$C_{22}H_{24}AuClNO_4PS$
M_r	661.87
Crystal system	monoclinic
Space group	*C2/c* [No. 15]
a [Å]	26.417(3)
b [Å]	9.507(1)
c [Å]	18.871(1)
β [°]	101.67(1)
V [Å^3]	4641.4(8)
$\rho_{calcd.}$ [gcm^{-3}]	1.894
Z	8
F(000) [e]	2576
μ (Mo-K_α) [cm^{-1}]	66.42
Data collection:	
Diffractometer	Enraf-Nonius CAD4
Radiation	Mo-K_α, λ = 0.71073 Å
T [°C]	−74
Scan mode	ω-Θ
hkl range	−32→+23/−11→0/−23→+23
Θ-Range for data collection [°]	3–26
Measured refl.	8112
Unique refl.	4452
Observed refl.	4429
$I \geqslant$	2 σ(*I*)
Absorption correction	ψ-scans
T_{min}/T_{max}	0.711/0.999
Refinement:	
Refined parameters	326
H atoms (found/calcd.)	0/24
*R*1[a]	0.0448
*wR*2[b]	0.0901
GOOF	1.298
(shift/error)$_{max}$	0.001
ρ_{fin}(max/min) [eÅ^{-3}]	+1.81/−1.36

[a] $R1 = \Sigma(\|F_o| - |F_c\|)/\Sigma|F_o|$. – [b] $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/2\sigma^2(F_o^2) + (ap)^2 + bp$; $p = (F_o^2 + F_c^2)/3$; $a = 0.0163$; $b = 48.22$.

Crystal-Structure Determination: A specimen of suitable quality was mounted in a glass capillary and used for measurements 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. Lp correction was applied and intensity data were corrected for decay (−12%) and absorption effects (ψ-scans). The structure was solved by Patterson methods and completed by full-matrix least-squares techniques against F^2. The oxygen atoms of the perchlorate ions were strongly disordered and were refined isotropically in split positions. All remaining non-H atoms were refined with anisotropic displacement parameters. The NH_2 group of the aniline ring was also disordered at C12, C22 and C32 (see text), and was refined in split positions with s.o.f. of 40, 40 and 20, respectively. All H atoms were placed in idealized calculated positions and allowed to ride on their carbon/nitrogen atoms with $U_{iso(fix)} = 1.5 \times U_{eq}$(C/N). The N*H* atoms were calculated on the assumption that the lone pair of N points towards the gold atom. Details of the crystal data, data collection and structure refinement are summarized in Table 1; selected bond lengths and angles are given in the figure caption. Further information on the X-ray structure determination can be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-406474, the names of the authors, and the journal citation.

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