Isolation of an Intermediate during the Decomposition of a Tetragold-Phosphane Complex

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Reaction of the diphosphanylamine 2,6-$\{(Ph_2P)_2N\}_2C_5H_3N$ with four equivalents of Au(tht)Cl (tht = tetrahydrothiophene) affords the tetragold complex 2,6-$\{(ClAuPh_2P)_2N\}_2C_5H_3N$ in high yield. Decomposition of the tetragold compound results in the formation of the digold complex 2,6-$\{(ClAuPh_2P)HN\}_2C_5H_3N$ and colloidal gold. A trigold intermediate, which contains a Au–Au interaction [2.9886(5) Å] has been isolated, and while ultimately unstable, it is thought to be partially stabilised by virtue of the aurophilic nature of gold.

Introduction

Gold(I)-phosphane complexes and clusters have been extensively studied over the years.[1] Apart from fundamental interest in these types of compounds, they exhibit a number of interesting properties which gives rise to a wide range of different applications. Gold(I) complexes display anticancer activity and are employed in clinics for the treatment of rheumatoid arthritis.[2] In addition, they exhibit interesting photophysical[3] and catalytic properties.[4] From the plethora of studies involving gold(I) complexes, interactions between linearly coordinated gold(I) centres have been found to be extremely common, leading to self-assembled suprastructures through Au−Au intermolecular contacts.[5] In many cases these suprastructures exhibit strong photo-luminescence.[6] The term used to describe the affinity of gold to form Au−Au interactions is "aurophilicity",[7] which was introduced in 1989, and theoretical studies have since placed the effect on a solid foundation.[8]

Many different phosphane ligands have been used to form complexes with gold, in particular heterodentate phosphanes, which tend to afford multi-nuclear complexes containing Au−Au interactions.[9] Such interactions have been shown to persist in solution.[10] Aurophilicity is especially favoured where several phosphorus centres are in close proximity, enabling intramolecular auration, for example, in calix[3]arene and calix[4]arene based phosphane systems.[11] Complexes with diphosphanylamine ligands are also known.[12] Diphosphanylamines comprise a P−N−P backbone and some of their gold(I) complexes are light/moisture sensitive,[13] presumably due to the instability of both the P−N and Au−P bonds, resulting in the formation of colloidal gold particles. Formation of gold colloids, typically denoted by the precipitation of a purple/black powder, is frequently observed in gold(I) chemistry, however, the intermediate species formed during the decomposition process and decomposition mechanism remain essentially unknown. In this paper we describe the synthesis of a tetragold-diphosphanylamine complex and its decomposition to a digold species in which an intermediate trigold compound is isolated and characterised, providing insight into the decomposition mechanism.

Results and Discussion

The diphosphanylamine ligand 2,6-$\{(Ph_2P)_2N\}_2C_5H_3N$ (**L₁**) has previously been shown to undergo a remarkable reaction with H^+ to form the iminobiphosphane 2,6-$(Ph_2P{-}Ph_2P{=}N)_2C_5H_3NH^+$.[14] Since H^+ and certain gold fragments are isolobal[15] we thought that it would be interesting to explore the reactivity of **L₁** towards gold. Thus, under an inert atmosphere, **L₁** was treated with four equivalents of Au(tht)Cl (tht = tetrahydrothiophene) in dichloromethane at room temperature yielding 2,6-$\{(ClAuPh_2P)_2N\}_2C_5H_3N$ (**1**) as the only product (Scheme 1). The ^{31}P NMR spectrum of the reaction solution exhibits a sharp singlet at δ = 84.0 ppm indicating that all of the phosphorus atoms are equivalent. In addition, the electrospray ionisation mass spectrum of **1** in dichloromethane exhibits a parent peak at m/z = 1775 which corresponds to the protonated intact parent ion $[M + H]^+$. After removal of the solvent under reduced pressure **1** was obtained as a white powder.

Compound **1** is stable in the solid state, but decomposes slowly in solution on exposure to air/moisture. The decomposition reaction can be monitored by ^{31}P NMR spectroscopy. The ^{31}P NMR spectrum in dichloromethane exhi-

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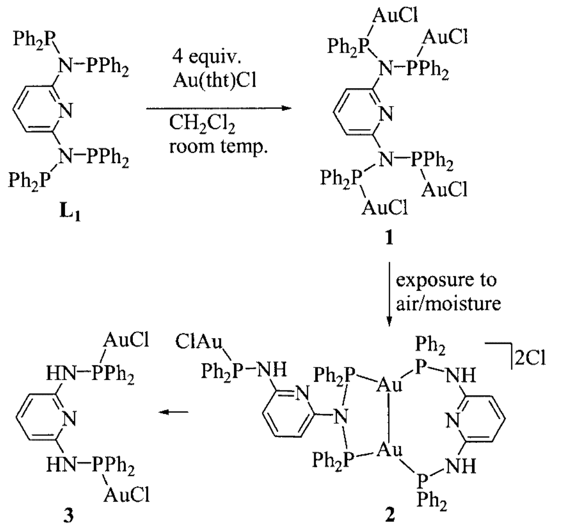


Scheme 1. Degradation of **1** and its decomposition to **3** via **2**, following exposure to air/light

bits, in the first instance, the signal at δ = 84.0 ppm corresponding to **1**, which decreases in intensity until it has completely disappeared after six hours. In its place three broad signals at 97.0, 68.9, 52.2 ppm (for which the P−P coupling could not be resolved) together with signals at δ = 35.6 ppm and −20.6 ppm ($J_{\text{P-P}}$ = 229.0 Hz) which are readily attributed to $Ph_2P(O)PPh_2$,[16] are observed. Simultaneously, the reaction mixture turns from colourless to purple, a characteristic colloid colouration, due to the formation of elemental gold. The three unidentified signals correspond to a new complex **2**, which by virtue of being a salt, precipitates from solution, on addition of diethyl ether. After filtration and removal of the solvent, the solid was washed with diethyl ether and obtained in its pure form and recrystallised from chloroform to afford crystals suitable for analysis by X-ray diffraction. The structure of the dication in **2** is shown in Figure 1 and key bond parameters are listed in the caption. Crystal data and details of the structure determination are listed in Table 1 and further details are given in the Experimental Section.

Compound **2** contains three gold centres and two different ligands, 2-{$(Ph_2P)_2N$}-6-{$(Ph_2P)HN$}-C_5H_3N (**L$_2$**) and 2,6-{$(Ph_2P)HN$}$_2C_5H_3N$ (**L$_3$**) (see Figure 2), both derived from the diphosphanylamine ligand **L$_1$** by substitution of one and two Ph_2P units by a proton, respectively. The Au−P and Au−Cl distances in **2** are similar to those observed in structurally related compounds;[17] whereas the Au−Au distance is 2.9886(5) Å, which is somewhat longer than those usually found in complexes containing Au−Au bonds within an "A"-frame structure involving a five-membered ring.[18] However, this distance is not long when compared to those observed in complexes where the gold centres are not orientated in such close proximity. The Au(1)−P(1) [2.301(2) Å], Au(1)−P(3) [2.312(2) Å], Au(2)−P(2) [2.303(2) Å] and Au(2)−P(4) [2.299(2) Å] distances are all similar, being slightly longer than the Au(3)−P(5) [2.219(3) Å] distance which involves the P−Au−Cl system. While the P(5)−Au(3)−Cl(1) fragment is nearly linear with an angle of 177.33(9)°, the P(1)−Au(1)−P(3) and P(2)−Au(2)−P(4) units form angles

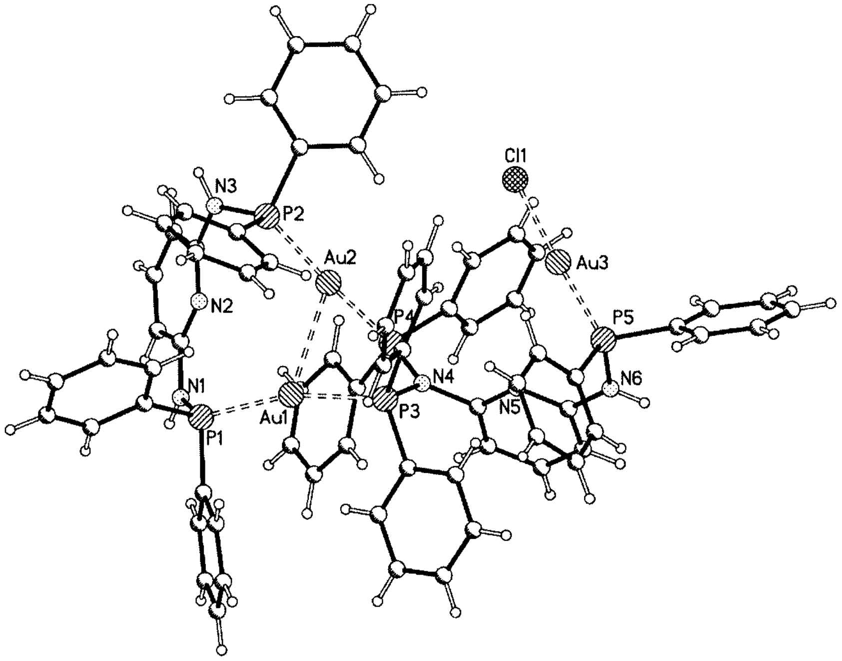


Figure 1. Molecular structure of **2** in the solid state (ball-and-stick representation showing just the cation with a partial labelling scheme, the Cl anions and all the solvent molecules have been omitted for clarity); key bond lengths (Å) and angles (°) include: Au(1)−P(1) 2.301(2), Au(1)−P(3) 2.312(2), Au(1)−Au(2) 2.9886(5), Au(2)−P(4) 2.299(2), Au(2)−P(2) 2.303(2), Au(3)−P(5) 2.219(3), Au(3)−Cl(1) 2.305(3), P(1)−N(1) 1.670(7), P(2)−N(3) 1.673(8), P(3)−N(4) 1.694(7), P(4)−N(4) 1.702(8), P(5)−N(6) 1.676(8), P(1)−Au(1)−P(3) 163.94(8), P(1)−Au(1)−Au(2) 112.58(6), P(3)−Au(1)−Au(2) 80.68(6), P(4)−Au(2)−P(2) 174.23(8), P(4)−Au(2)−Au(1) 78.00(6), P(2)−Au(2)−Au(1) 107.24(6), P(5)−Au(3)−Cl(1) 177.33(9)

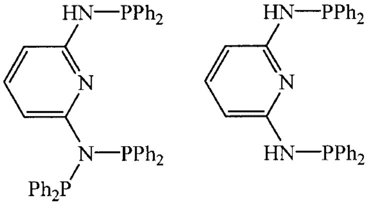
Table 1. Crystal data and details of the structure determination for **2** and **3**

	2	**3**
Empirical formula	$C_{78}H_{67}Au_3Cl_{27}N_6P_5$	$C_{30.5}H_{28}Au_2Cl_5N_3P_2$
Molecular mass	2791.28	1069.68
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	15.8163(11)	10.0883(7)
b (Å)	16.2804(8)	12.4008(9)
c (Å)	22.6502(12)	15.1675(10)
a (°)	83.714(4)	112.597(7)
b (°)	73.581(5)	95.294(5)
g (°)	65.340(6)	99.932(6)
V (Å^3)	5084.1(5)	1699.1(2)
Z	2	2
$D_{calcd.}$ (g cm^{-3})	1.823	2.091
$F(000)$	2696	1010
m (mm^{-1})	5.150	9.138
Temp. (K)	140(2)	140(2)
Wavelength (Å)	0.71073	0.71073
Measured reflections	29979	9959
Unique reflections	15710	5244
Unique reflections with $I > 2\sigma(I)$	12810	4698
Data/parameters	15710/1075	5244/388
R[a] [$I > 2\sigma(I)$]	0.0563	0.0280
$wR2$[a] (all data)	0.1602	0.0745
GoF	1.051	1.070

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [b] GoF $= \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$ where n is the number of data and p is the number of parameters refined.

of 163.94(8) and 174.23(8)°, respectively. The deviation from linearity is presumably due to the bulky ligands surrounding the Au−Au unit, which also results in the relatively long Au−Au contact.

Compound **2** is stable in the solid-state, but decomposes in solution on exposure to air/light. The decomposition reaction of complex **2** in dichloromethane was followed in situ by ^{31}P NMR spectroscopy. The peaks corresponding to **2** steadily disappear, with the concomitant formation of a new singlet resonance at $\delta = 55.1$ ppm. The peak at $\delta = 55.1$ ppm has been assigned to **3**, which has been isolated in its pure form following the decomposition of **2** in dichloromethane on a preparative scale. In addition, **3** can be prepared directly from the reaction of Au(tht)Cl with 2,6-$\{(Ph_2P)HN\}_2C_5H_3N$ (see below). The other components from the reaction, as denoted by ^{31}P NMR spectroscopy, have been tentatively assigned as $Ph_2P(O)PPh_2$ (see above), with lesser amounts of $Ph_2P(O)OH$ and Ph_2POH, as represented by signals of low relative intensity at $\delta = 35.5$ and 24.0 ppm. A dark purple precipitate is observed which presumably corresponds to gold colloid. The structure of **3** has been established in the solid-state by single-crystal X-ray diffraction on crystals grown from a dichloromethane/diethyl ether solution at room temperature. The molecular structure of **3** is shown in Figure 3 and key bond parameters are listed in the caption.



L₂ **L₃**

Figure 2. Ligands **L₂** and **L₃**

Compound **3** is based on a **L₃**-type ligand in which a Au−Cl fragment coordinates to each phosphorus(III) centre. The parameters in **3** are largely in accordance with the structurally similar compounds.[12,13] The Au(1)−P(1) [2.2377(14) Å] and Au(2)−P(2) [2.2359(15) Å] bond lengths are similar and somewhat longer than the related Au(3)−P(5) bond of 2.219(3) Å in **2**. The P(1)−Au(1)−Cl(1) and P(2)−Au(2)−Cl(2) units are essen-

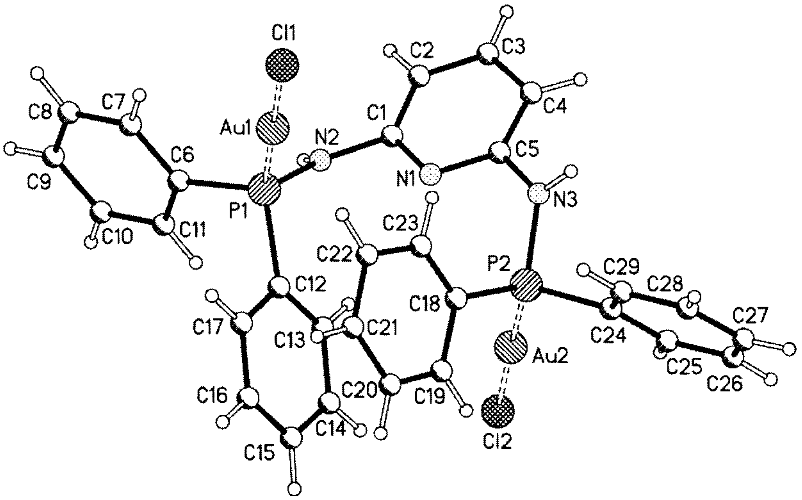


Figure 3. Molecular structure of **3** in the solid-state (ball-and-stick representation showing the labelling scheme, the solvent molecules have been omitted); key bond lengths (Å) and angles (°) include: Au(1)−P(1) 2.2377(14), Au(1)−Cl(1) 2.3229(13), Au(2)−P(2) 2.2359(15), Au(2)−Cl(2) 2.3063(14), P(1)−N(2) 1.698(5), P(2)−N(3) 1.710(5), P(1)−Au(1)−Cl(1) 179.59(5), P(2)−Au(2)−Cl(2) 178.69(6)

tially linear with bond angles of 179.59(5) and 178.69(6)°, respectively.

The decomposition process **1** → **2** → **3** is worth some further comment since **2** cannot be prepared by a rational route. Complex **2** contains two different aminophosphane ligands, $\mathbf{L_2}$ and 2,6-$\{(Ph_2P)HN\}_2C_5H_3N$ ($\mathbf{L_3}$) which are derived from $\mathbf{L_1}$ by substitution of one and two Ph_2P units by a proton, respectively. Ligand $\mathbf{L_3}$ has been reported before,[19] and attempts to prepare $\mathbf{L_2}$ using a rational route, viz. reaction of one equivalent of 2,6-diaminopyridine with three equivalents of Ph_2PCl, are only partially successful. The main product from this reaction is $\mathbf{L_1}$ based on ^{31}P NMR spectroscopy and electrospray ionisation mass spectrometry. The formation of $\mathbf{L_2}$ was identified in the reaction mixture by electrospray ionisation mass spectrometry which contained peaks corresponding to $\mathbf{L_1}$ and $\mathbf{L_2}$, the peak at $m/z = 662$ corresponds to $[\mathbf{L_2}+H]^+$, but it has, as yet, not been possible to isolate $\mathbf{L_2}$ from the mixture, although attempts are ongoing.

Reaction of $\mathbf{L_3}$ with Au(tht)Cl in a 1:2 molar ratio gave complex **3** in quantitative yield, however, all attempts to prepare **2** from different combinations of $\mathbf{L_1}$ and $\mathbf{L_3}$ and Au(tht)Cl were unsuccessful. The reason that **2** is isolated at all is probably due to the lower solubility of **2** relative to **1** and **3** since it is a salt which facilitates precipitation from the reaction solution. However, this property alone does not fully explain the stability of **2** and we propose that the aurophilicity of gold, resulting in the Au−Au interaction, further stabilises the intermediate and facilitates its isolation. This property frequently results in structural diversity in gold(I) complexes.[20] However, we believe that compound **2** is especially pleasing as all researchers preparing novel gold complexes are frequently frustrated by decomposition to (or formation of) gold colloids, and in our system, we were fortunate enough to isolate a decomposition intermediate.

Experimental Section

The ligands 2,6-$\{(Ph_2P)_2N\}_2C_5H_3N$ ($\mathbf{L_1}$)[21] and 2,6-$\{(Ph_2P)HN\}_2C_5H_3N$ ($\mathbf{L_3}$)[19] and the complex Au(tht)Cl (tht = tetrahydrothiophene)[22] were prepared according to literature methods. Solvents were dried using appropriate reagents and distilled prior to use. NMR spectra were recorded in $CDCl_3$ at 20 °C with a Bruker DMX 200 instrument using $SiMe_4$ as the external standard for the ^1H NMR spectroscopy and 85% H_3PO_4 for the ^{31}P NMR spectroscopy. ESI-MS spectra were recorded on a ThermoFinnigan LCQ† Deca XP Plus quadrupole ion trap instrument using a literature method.[23] Samples were infused directly into the source at 5 µL min^{-1} using a syringe pump. The spray voltage was set at 5 kV and the capillary temperature at 50 °C. The MS detector was tuned automatically on the base peak, which optimised the remaining parameters. Elemental analyses was carried out at the Institute of Molecular and Biological Chemistry at the EPFL.

Synthesis of 1: Au(tht)Cl (256 mg, 0.80 mmol) was added to a solution of 2,6-$\{(Ph_2P)_2N\}_2C_5H_3N$ (170 mg, 0.20 mmol) in dichloromethane (10 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 15 minutes. The solvent was removed under vacuum and the resulting white solid was washed with diethyl ether (2 × 2 mL) to give the product **1** as a white powder. Yield: 330 mg, 94%. ^1H NMR: δ = 6.5−8.20 (m, aromatic H) ppm. ^{31}P NMR: δ = 84.0 (s) ppm. ESI-MS$^+$ m/z: 1775 $[M + H]^+$. $C_{53}H_{43}Au_4Cl_4N_3P_4$ (1775.52): H 2.44, C 35.85, N 2.37; found H 2.47, C 35.89, N 2.34.

Synthesis of 2: A solution of **1** (300 mg, 0.17 mmol) in dichloromethane (10 mL) was stirred in air for 6 h at room temperature, after which time the ^{31}P NMR spectra showed the absence of the starting material **1**. The solvent was removed under reduced pressure and the remaining solid was washed with diethyl ether (3 × 10 mL) to give **2** as a white powder. Colourless crystals were obtained by slow evaporation of a solution in $CDCl_3$ at room temperature. Yield: 105 mg, 22%. M.p. 147 °C. ^1H NMR: δ = 6.5−8.20 (m, aromatic H); 6.30 (broad signal, NH) ppm. ^{31}P NMR: δ = 97.0 (broad signal), 68.9 (broad signal), 52.2 (broad signal) ppm. ESI-MS$^+$ m/z: 1765 $[cation]^+$. $C_{70}H_{59}Au_3Cl_3N_6P_5$ (1836.40): H 3.24, C 45.78, N 4.58; found H 3.31, C 45.89, N 4.60.

Synthesis of 3. Method A: A solution of **2** (190 mg, 0.10 mmol) in dichloromethane (10 mL) was stirred in air in for 24 hours at room temperature. The solvent was removed under reduced pressure and the remaining solid was washed with diethyl ether (3 × 10 mL). Colourless crystals were obtained by slow evaporation of a solution in dichloromethane at room temperature in two days. Yield: 40 mg, 41%.

Method B: Au(tht)Cl (64 mg, 0.20 mmol) was added to a solution of $\mathbf{L_3}$ (47 mg, 0.10 mmol) in dichloromethane (10 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 30 minutes. The solvent was removed under vacuum and the resulting white solid was washed with diethyl ether (2 × 2 mL) to give the product **3** as a white powder. Yield: 90 mg, 95%. M.p. 163 °C (decmp.). ^1H NMR: δ = 6.5−8.20 (m, aromatic H); 6.50 (br., NH) ppm. ^{31}P NMR: δ = 55.1 (s) ppm. ESI-MS$^+$ m/z: 942 $[M + H]^+$. $C_{29}H_{25}Au_2Cl_2N_3P_2$ (942.32): H 2.67, C 36.96, N 4.46; found H 2.71, C 37.04, N 4.39.

X-ray Sructure Determination: Details about the crystals and their structure refinement are listed in Table 1, whereas relevant geometrical parameters, including bond lengths and angles are included in the figure captions. Data collections for both compounds were performed at 140 K on a 4-circle goniometer having kappa geometry and equipped with an Oxford Diffraction KM4 Sapphire CCD. Data reduction was carried out with CrysAlis RED, release 1.7.0.[24] Absorption corrections[25] have been applied to both data sets. Structure solution and refinement as well as molecular graphics and geometrical calculations were performed for both structures with the SHELXTL software package, release 5.1.[26] The structures were refined using the full-matrix least-squares on F^2 with all of the non-H atoms defined anisotropically. H atoms were placed in calculated positions using the "riding model".

CCDC-242559 (for **2**) and -242560 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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