

Phosphoniodithioformate gold derivatives. Synthesis of tricationic gold(II) complexes

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Abstract

The reaction of $[\text{Au}_2\{\mu\text{-(CH}_2)_2\text{PPh}_2\}_2]$ with $[\text{Au}_2(\mu\text{-S}_2\text{CPCy}_3)_2](\text{ClO}_4)_2$ leads to the heterobridged gold(I) complex $[\text{Au}_2\{\mu\text{-(CH}_2)_2\text{PPh}_2\}(\mu\text{-S}_2\text{CPCy}_3)](\text{ClO}_4)$ **1**. Complex **1** reacts with halogens via oxidative addition to give monocationic gold(II) derivatives $[\text{Au}_2\{\mu\text{-(CH}_2)_2\text{PPh}_2\}(\mu\text{-S}_2\text{CPCy}_3)\text{X}_2](\text{ClO}_4)$ (X = Cl **2**, Br **3**, or I **4**) which undergo substitution reactions with silver salts to afford the first tricationic gold(II) complexes $[\text{Au}_2\{\mu\text{-(CH}_2)_2\text{PPh}_2\}(\mu\text{-S}_2\text{CPCy}_3)(\text{PR}_3)_2](\text{ClO}_4)_3$ (R = Ph **5** or 4-MeOC₆H₄ **6**).

Keywords: Gold(II); Tricationic, dinuclear complexes; Preparation; Ylide

1. Introduction

In recent years, the synthesis of dinuclear gold(II) complexes has attracted special attention because of the short metal–metal bonds. Most of these derivatives are neutral complexes, mainly of bis(ylide) ligands, obtained by oxidative addition reactions [1]. Only a few mono- or dicationic gold(II) complexes have been synthesized by oxidative addition [2] or substitution reactions [3] and no cationic derivatives with higher charge have been reported so far.

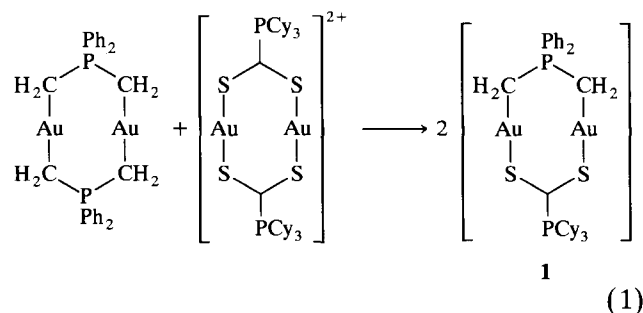
We have recently described the synthesis of heterobridged dinuclear gold(I) complexes which allow us, by choosing the right combination of ligands, to obtain good precursors to gold(II) compounds [4]. We have succeeded in stabilising the gold(II) derivatives $[\text{Au}_2\{\mu\text{-(CH}_2)_2\text{PPh}_2\}(\mu\text{-L-L})\text{X}_2]^{n+}$ (X = halide) which are neutral when L–L is dithiocarbamate or xanthate, and monocationic when L–L is a diphosphine. Their complexes all contain the bis(ylide) $\text{CH}_2\text{PPh}_2\text{CH}_2$. Substitution in these complexes of X^- by neutral ligands did not take place, rather mixed-valence gold(I)–gold(III) or gold(I) derivatives were obtained.

To approach the synthesis of tricationic gold(II) derivatives we selected the zwitterion phosphoniodithioformate $\text{Cy}_3\text{P}^+\text{-CS}_2^-$ (Cy = cyclohexyl) as a ligand,

which can behave with mononegative character in the proximity of gold atoms but is neutral overall. In the present paper we report the preparation not only of monocationic gold(II) complexes, $[\text{Au}_2\{\mu\text{-(CH}_2)_2\text{PPh}_2\}(\mu\text{-S}_2\text{CPCy}_3)\text{X}_2]^+$ (X = Cl, Br or I) via oxidative addition reactions but also of tricationic gold(II) derivatives $[\text{Au}_2\{\mu\text{-(CH}_2)_2\text{PPh}_2\}(\mu\text{-S}_2\text{CPCy}_3)(\text{PR}_3)_2]^{3+}$ (R = Ph or 4-MeOC₆H₄) by substitution reactions.

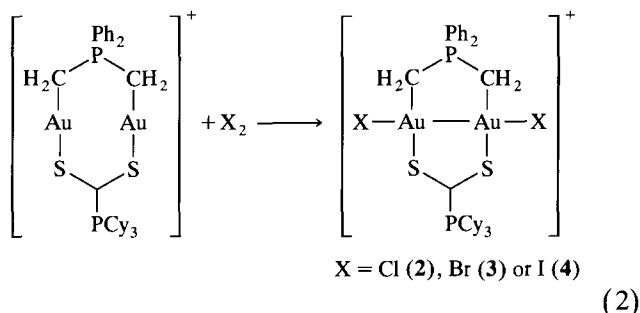
2. Results and discussion

The reaction of $[\text{Au}_2\{\mu\text{-(CH}_2)_2\text{PPh}_2\}_2]$ with $[\text{Au}_2(\mu\text{-S}_2\text{CPCy}_3)_2](\text{ClO}_4)_2$ in dichloromethane (1:1 molar ratio) leads to a green solution from which the heterobridged complex **1** can be isolated according to Eq. (1).

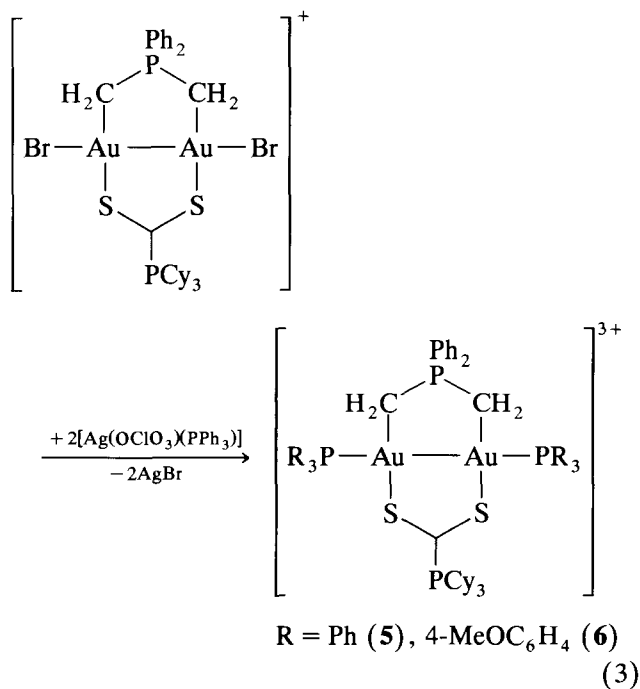


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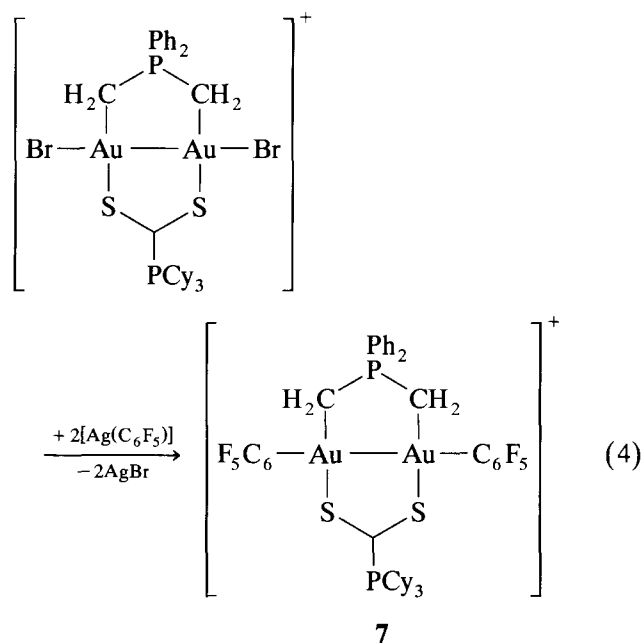
Complex **1** is a potential precursor to cationic gold(II) compounds by oxidative addition of halogen, and reactions according to Eq. (2) are indeed observed. To the best of our knowledge, they represent the first examples of gold(II) complexes containing phosphoniodithioformate.



We have carried out substitution reactions of these gold(II) derivatives with silver salts, which produce new cationic gold(II) complexes. For example, complex **3** reacts with $[\text{Ag}(\text{OCIO}_3)(\text{PR}_3)]$ (R = Ph or 4-MeOC₆H₄) in 1 : 2 molar ratio leading to the first tricationic gold(II) derivatives (**5** or **6**, Eq. (3)), in which one positive charge is mainly located on the PCy₃ moiety because of the zwitterionic nature of the ligand. When $[\text{Ag}(\text{OCIO}_3)(\text{tht})]$ (tht = tetrahydrothiophene) was used, a mixture of products was obtained, of which only the ³¹P{¹H} NMR resonance due to $[\text{Au}_2\{\mu-(\text{CH}_2)_2\text{-PPh}_2\}_2(\text{tht})_2](\text{ClO}_4)_2$ [3c] could be assigned. The combination of bis(ylide) and phosphoniodithioformate as ligands is able to stabilise cationic gold(II) complexes, whereas bis(ylide) and dithiocarbamate or xanthate do not [4b].



In a similar way, starting from the same gold(II) complex, reaction with $[\text{Ag}(\text{C}_6\text{F}_5)]$ in 1 : 2 molar ratio gives complex **7** (Eq. (4)).



The complexes **1–7** are air- and moisture-stable, dark green (**1**), yellow (**2**), orange (**3**, **7**), garnet (**4**) or brown (**5–6**) solids. They are conducting in acetone solution and behave as 1 : 1 (**1–4**, **7**) or 3 : 1 (**5–6**) electrolytes (see Section 3). Their IR spectra show medium intensity absorptions at ca. 560 cm⁻¹ assignable to $\nu(\text{Au}-\text{C}_{\text{ylide}})$ [5] and bands at 1100 (s, br) and 623 (m) cm⁻¹ which are characteristic of the perchlorate anion [6]. The IR spectrum of complex **2** shows a band at 267 (m) cm⁻¹ due to $\nu(\text{Au(II)}-\text{Cl})$ [2a] and the spectrum of **7** show only a single absorption in the 800 cm⁻¹ region (at 790 cm⁻¹) for the pentafluorophenyl groups which indicates their equivalence [7]. The mass spectra (FAB⁺, nitrobenzyl alcohol as matrix) show the parent ion $[\text{M}-\text{ClO}_4]^+$ at *m/z* (abundance, complex): 963 (100, **1**), 1033 (5, **2**), 1123 (17, **3**), 1217 (48, **4**), 1297 (100, **7**). The mass spectra of gold(II) derivatives **2–4** and **7** show a peak at *m/z* 963 due to $[\text{M}-2\text{X}-\text{ClO}_4]^+$.

Their ³¹P{¹H} NMR spectra show signals between 38.0 and 57.5 ppm (Table 1) from the phosphorus atom of the bis(ylide) group and from 54.1 to 60.2 ppm for the phosphoniodithioformate. These are singlets, except in the case of **5–6** because of the coupling with phosphine ligands. Spectra of **5–6** show a triplet for the phosphorus of the bis(ylide), a doublet for the phosphine groups and a singlet for the phosphoniodithioformate. This pattern is to be expected for the gold(II) derivatives which do not isomerize to the corresponding gold(I)–gold(III) complexes. This is also supported by the values of the coupling constants (ca. 30 Hz) which are characteristic of gold(II) complexes. The ¹H NMR spectra in the ylide methylene region show a doublet in

Table 1
Analytical and $^{31}\text{P}\{^1\text{H}\}$ NMR data of the complexes

Complex	Yield (%)	Analyses (%) ^a		$^{31}\text{P}\{^1\text{H}\}$ NMR ^b			M.p. ^c (°)
		C	H	δ (S ₂ C–P)	δ (PPh ₂)	δ (Au–PR ₃)	
1 [Au ₂ { μ -(CH ₂) ₂ PPh ₂ }(μ -S ₂ CPCy ₃)]ClO ₄	78	37.1 (37.3)	4.55 (4.45)	54.1(s)	38.0(s)	–	156
2 [Au ₂ { μ -(CH ₂) ₂ PPh ₂ }(μ -S ₂ CPCy ₃)Cl ₂]ClO ₄	82	34.6 (34.95)	4.2 (4.2)	56.9(s)	46.2(s)	–	154
3 [Au ₂ { μ -(CH ₂) ₂ PPh ₂ }(μ -S ₂ CPCy ₃)Br ₂]ClO ₄	84	32.45 (32.4)	3.7 (3.85)	58.5(s)	50.7(s)	–	150
4 [Au ₂ { μ -(CH ₂) ₂ PPh ₂ }(μ -S ₂ CPCy ₃)I ₂]ClO ₄	85	29.85 (30.1)	3.8 (3.6)	58.8(s)	57.5(s)	–	136
5 [Au ₂ { μ -(CH ₂) ₂ PPh ₂ }(μ -S ₂ CPCy ₃)(PPh ₃) ₂](ClO ₄) ₃	87	46.4 (46.4)	4.4 (4.35)	60.2(s)	53.7(t) (27.5)	51.3(d)	105
6 [Au ₂ { μ -(CH ₂) ₂ PPh ₂ }(μ -S ₂ CPCy ₃)(P(4-MeOC ₆ H ₄) ₃) ₂](ClO ₄) ₃	74	46.25 (45.8)	4.65 (4.55)	60.0(s)	52.4(t) (28.9)	50.1(d)	100
7 [Au ₂ { μ -(CH ₂) ₂ PPh ₂ }(μ -S ₂ CPCy ₃)(C ₆ F ₅) ₂]ClO ₄	50	38.35 (38.7)	3.4 (3.4)	56.9(s)	38.1(s)	–	144

^a Calculated values in parentheses. ^b Recorded in CDCl₃ referenced to external H₃PO₄. Coupling constants (Hz) are given in parentheses; s = singlet, d = doublet, t = triplet. ^c Decomposition.

the range 2.10–3.10 ppm (see Section 3) for complexes 1–4. Such an assignment is not possible for 5–7 because of overlap with the phosphoniodithioformate resonances. The ¹⁹F NMR spectrum of 7 confirms the presence of two equivalent pentafluorophenyl groups with multiplets at –116.6 (*o*-F), –156.1 (*p*-F) and –160.8 (*m*-F).

3. Experimental details

3.1. General

IR spectra were recorded on a Perkin Elmer 883 spectrophotometer, over the range 4000–200 cm⁻¹, using Nujol mulls between polyethylene sheets. ¹H, ¹⁹F and ³¹P NMR spectra were recorded on a Varian UNITY 300 in CDCl₃ solutions; chemical shifts are quoted relative to SiMe₄ (external, ¹H), CFCl₃ (external, ¹⁹F) and H₃PO₄ (external, ³¹P). C, H and N analyses were performed with a Perkin Elmer 2400 microanalyser. Conductivities were measured in acetone solution with a Philips PW 9509 apparatus. Melting points were measured on a Büchi apparatus and are uncorrected. Mass spectra were recorded on a VG Autospec using FAB⁺ techniques.

Yields, melting points, C and H analyses and ³¹P{¹H} NMR data are listed in Table 1.

3.2. Preparation of complexes

3.2.1. [Au₂{ μ -(CH₂)₂PPh₂}(μ -S₂CPCy₃)]ClO₄ (1)

To a solution of [Au₂{ μ -(CH₂)₂PPh₂}] [1e] (0.082 g, 0.1 mmol) in dichloromethane (40 ml) was added [Au₂(μ -S₂CPCy₃)₂](ClO₄)₂ [8] (0.13 g, 0.1 mmol).

After stirring for 2 h, the solution was concentrated to ca. 5 ml. Addition of diethyl ether (20 ml) led to precipitation of 1 which was washed with diethyl ether (2 × 5 ml). 1, $\Lambda_M = 118 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. ¹H NMR: δ 7.79–7.50 (m, Ph), 2.98 (m, CH of Cy), 2.12 (d, CH₂–Au, *J* = 12.6 Hz), 1.99–1.41 (m, CH₂ of Cy).

3.2.2. [Au₂{ μ -(CH₂)₂PPh₂}(μ -S₂CPCy₃)X₂]ClO₄ [X = Cl (2), Br (3) or I (4)]

To a solution of 1 (0.08 g, 0.075 mmol) in dichloromethane (25 ml) was added a slight excess of halogen X₂ (0.079 mmol; X₂ = Cl₂ or Br₂, in CCl₄ solution, or I₂, 0.02 g). After stirring for about 15 min, the solution was concentrated to ca. 5 ml. Addition of diethyl ether (20 ml) afforded complexes 2–4 which were washed with diethyl ether (2 × 5 ml). 2, $\Lambda_M = 131 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$; ¹H NMR: δ 7.77–7.65 (m, Ph), 3.00 (m, CH of Cy), 2.94 (d, CH₂–Au, *J* = 8.0 Hz), 1.99–1.41 (m, CH₂ of Cy). 3, $\Lambda_M = 118 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$; ¹H NMR: δ 7.74–7.60 (m, Ph), 3.00 (m, CH of Cy), 2.97 (d, CH₂–Au, *J* = 8.2 Hz), 1.97–1.42 (m, CH₂ of Cy). 4, $\Lambda_M = 120 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. ¹H NMR: δ 7.74–7.65 (m, Ph), 3.07 (d, CH₂–Au, *J* = 8.5 Hz), 3.00 (m, CH of Cy), 2.00–1.42 (m, CH₂ of Cy).

3.2.3. [Au₂{ μ -(CH₂)₂PPh₂}(μ -S₂CPCy₃)(PR₃)₂](ClO₄)₃ [R = Ph (5), 4-MeOC₆H₄ (6)]

To a solution of 3 (0.061 g, 0.05 mmol) in dichloromethane (25 ml) was added [Ag(OClO₃)(PR₃)] [9] (0.1 mmol; R = Ph 0.047 g, 4-MeOC₆H₄ 0.056 g) and the mixture was stirred at 0°C in the dark for 15 min. The precipitated AgBr was filtered off and the filtrate concentrated to ca. 5 ml. Addition of diethyl ether (20 ml) led to the precipitation of complexes 5–6. The solids were washed with diethyl ether (2 × 5 ml). 5,

$\Lambda_M = 296 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. $^1\text{H NMR}$: δ 7.80–7.30 (m, Ph), 2.45–1.20 (m, Cy and $\text{CH}_2\text{-Au}$). **6**, $\Lambda_M = 281 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. $^1\text{H NMR}$: δ 7.70–7.00 (m, Ph), 3.85 (s, Me–O), 2.40–1.20 (m, Cy and $\text{CH}_2\text{-Au}$).

3.2.4. $[\text{Au}_2\{\mu\text{-(CH}_2)_2\text{PPh}_2\}(\mu\text{-S}_2\text{CPCy}_3)(\text{C}_6\text{F}_5)_2]\text{ClO}_4$ (**7**)

To a solution of $[\text{AgC}_6\text{F}_5]$ [**10**] (0.11 mmol) in anhydrous diethyl ether (30 ml) was added an anhydrous dichloromethane solution (10 ml) of complex **3** (0.061 g, 0.05 mmol). After stirring the mixture for 5 min at room temperature and in the dark, the AgBr was removed and the solution evaporated to ca. 5 ml. Addition of hexane (15 ml) led to precipitation of complex **7**, which was washed with hexane (2×5 ml). **7**, $\Lambda_M = 121 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. $^1\text{H NMR}$: δ 7.80–7.40 (m, Ph), 3.00 (m, CH of Cy), 2.05–1.20 (m, CH_2 of Cy and $\text{CH}_2\text{-Au}$).

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