

Tris(pentachlorophenyl) Gold(III) complexes

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Abstract

By reaction of $\text{Ti}(\text{C}_6\text{Cl}_5)_2\text{Cl}$ with $\text{Au}(\text{C}_6\text{Cl}_5)(\text{tht})$ (tht = tetrahydrothiophen) or $[\text{N}(\text{PPh}_3)_2][\text{Au}(\text{C}_6\text{Cl}_5)\text{Cl}]$ the gold(III) complexes $[\text{Au}(\text{C}_6\text{Cl}_5)_3(\text{tht})]$ or $[\text{N}(\text{PPh}_3)_2][\text{Au}(\text{C}_6\text{Cl}_5)_3\text{Cl}]$ respectively, can be prepared. They are the first tris(pentachlorophenyl)-gold(III) complexes to be reported. The ready displacement of tht by other neutral or anionic ligands leads to the synthesis of $\text{Au}(\text{C}_6\text{Cl}_5)_3(\text{Ph}_2\text{PCH}_2\text{PPh}_2)$ or $\text{Q}[\text{Au}(\text{C}_6\text{Cl}_5)_3\text{X}]$ ($\text{Q} = \text{N}(\text{PPh}_3)_2$, PPh_3Me or PPh_2Me_2 ; $\text{X} = \text{C}_6\text{F}_5$, SCN , Br or I).

Introduction

During recent years less attention has been dedicated to the synthesis and study of gold(I) and gold(III) pentachlorophenyl derivatives than to the pentafluorophenyl analogues [1, 2]. So far, no gold compound containing more than two C_6Cl_5 groups [3, 4] has been reported, whilst tri- and tetrakis-pentafluorophenyl gold derivatives have recently been described [5].

In this paper we report the synthesis of $\text{Au}(\text{C}_6\text{Cl}_5)_3(\text{tht})$ (tht = tetrahydrothiophen), which can be used for the preparation of other neutral or anionic triaryl derivatives, such as $\text{Au}(\text{C}_6\text{Cl}_5)_3(\text{dppm})$ ($\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$) or $[\text{Au}(\text{C}_6\text{Cl}_5)_3\text{X}]^-$ ($\text{X} = \text{Cl}$, Br , I , SCN , C_6F_5).

Experimental

Instrumentation and general experimental techniques were as described earlier [4]. ^{31}P NMR spectra (H_3PO_4 as external reference) were recorded on a Varian XL200 spectrometer in CDCl_3 . The yields, melting points, C, H, N and Au analyses, conductivities and molecular weights of the novel complexes are listed in Table I.

Preparation of the Complexes

$\text{Au}(\text{C}_6\text{Cl}_5)_3(\text{tht})$ (1)

To a solution of $\text{Au}(\text{C}_6\text{Cl}_5)(\text{tht})$ [4] (0.452 g, 1 mmol) in 50 ml of toluene was added $\text{Ti}(\text{C}_6\text{Cl}_5)_2\text{Cl}$ [6] (0.738 g, 1 mmol) and the mixture was refluxed for 2 h. After removal of the precipitated TiCl the yellow solution was evaporated to dryness and the resulting complex **1** was recrystallized from diethylether–hexane.

$[\text{N}(\text{PPh}_3)_2][\text{Au}(\text{C}_6\text{Cl}_5)_3\text{Cl}]$ (2)

Addition of $\text{Ti}(\text{C}_6\text{Cl}_5)_2\text{Cl}$ [6] (0.148 g, 0.2 mmol) to a solution of $[\text{N}(\text{PPh}_3)_2][\text{Au}(\text{C}_6\text{Cl}_5)\text{Cl}]$ [4] (0.188 g, 0.2 mmol) in 30 ml of dichloromethane led (after a few seconds) to a yellow coloured liquid. The mixture was stirred at room temperature for 10 h, and the precipitated TiCl was filtered off. Concentration of the filtrate to ca. 3 ml and subsequent slow addition of diethylether (20 ml) led to crystallization of complex **2**.

$[\text{N}(\text{PPh}_3)_2][\text{Au}(\text{C}_6\text{Cl}_5)_3(\text{C}_6\text{F}_5)]$ (3)

To a freshly prepared diethylether solution (30 ml of $\text{Ag}(\text{C}_6\text{F}_5)$ [7] (0.4 mmol) was added **2** (0.608 g, 0.4 mmol). The mixture was stirred at room temperature for 90 min. After filtering off the AgCl the solution was concentrated to 5 ml. Addition of hexane (20 ml) led to the precipitation of **3**.

$\text{Au}(\text{C}_6\text{Cl}_5)_3(\text{dppm})$ (4)

A solution of **1** (0.206 g, 0.2 mmol) and bis-(diphenylphosphino)methane (dppm) (0.076 g, 0.2 mmol) in 30 ml of dichloromethane was stirred at room temperature for 1 h. Concentration to ca. 5 ml and addition of hexane (20 ml) led to the precipitation of **4**.

$\text{Q}[\text{Au}(\text{C}_6\text{Cl}_5)_3\text{X}]$ $\text{Q} = \text{N}(\text{PPh}_3)_2$, $\text{X} = \text{Cl}$ (2) or SCN (5); $\text{Q} = \text{PPh}_3\text{Me}$, $\text{X} = \text{Br}$ (6) or $\text{Q} = \text{PPh}_2\text{Me}_2$, $\text{X} = \text{I}$ (7)

To a solution of **1** (0.206 g, 0.2 mmol) in 30 ml of dichloromethane was added $[\text{N}(\text{PPh}_3)_2]\text{Cl}$ (0.115 g,

TABLE I. Analytical Data for Complexes

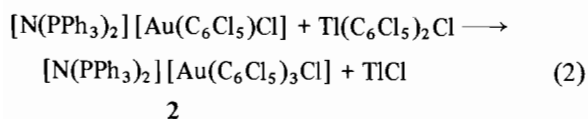
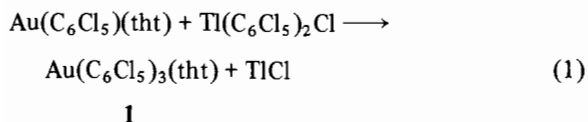
Complex	Yield (%)	Analysis, found (calc.) (%)				Λ_M^a	Molecular weight found (calc.) ^b	Melting point (°C)
		C	H	N	Au			
Au(C ₆ Cl ₅) ₃ (tht) (1)	71	25.4 (25.6)	1.2 (0.8)		19.4 (19.05)	8	993 (1033)	150(d)
[N(PPh ₃) ₂][Au(C ₆ Cl ₅) ₃ Cl] (2)	68	41.85 (42.7)	2.1 (2.0)	0.95 (0.9)	13.45 (12.95)	102		145(d)
[N(PPh ₃) ₂][Au(C ₆ Cl ₅) ₃ (C ₆ F ₅)] (3)	80	43.5 (43.65)	2.3 (1.85)	1.15 (0.85)	12.2 (11.95)	90		175
Au(C ₆ Cl ₅) ₃ (dppm) (4)	60	38.6 (38.85)	1.1 (1.65)		15.1 (14.8)	4	1250 (1329)	156
[N(PPh ₃) ₂][Au(C ₆ Cl ₅) ₃ SCN] (5)	60	42.45 (42.85)	2.15 (1.95)	1.35 (1.8)	12.4 (12.8)	93		70
[PPh ₃ Me][Au(C ₆ Cl ₅) ₃ Br] (6)	78	34.7 (34.15)	1.9 (1.4)		14.7 (15.1)	100		100(d)
[PPh ₂ Me ₂][Au(C ₆ Cl ₅) ₃ I] (7)	75	29.8 (29.85)	1.65 (1.25)		15.75 (15.3)	101		114

^aIn acetone (ohm⁻¹ cm² mol⁻¹).^bIn chloroform.

0.2 mmol), [N(PPh₃)₂]SCN (0.119 g, 0.2 mmol), [PPh₃Me]Br (0.071 g, 0.2 mmol) or [PPh₂Me₂]I (0.068 g, 0.2 mmol). The mixture was stirred at room temperature for 1 h. The solution was evaporated to ca. 5 ml and hexane was added to precipitate a white solid of **2**, **5**, **6** or **7**.

Results and Discussion

Tl(C₆Cl₅)₂Cl [**6**] adds oxidatively to gold(I) derivatives, both neutral Au(C₆Cl₅)(tht) (eqn. (1)) or anionic [N(PPh₃)₂][Au(C₆Cl₅)Cl] (eqn. (2)), the two pentachlorophenyl groups being transferred to the gold(I) centre which thereby is oxidised to gold(III)

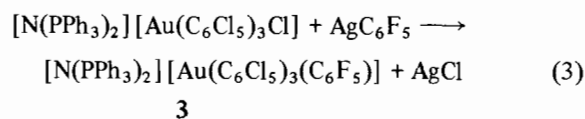


No substitution processes leading to other gold(I) compounds, as reported by the reaction of the thallium derivative with AuCl(PPh₃), could be observed [**3**].

Complexes **1** and **2** are white air- and moisture-stable solids at room temperature. Acetone solutions of **1** are non-conducting, solutions of **2** behave as 1:1 electrolytes. The molecular weight of **1** (isopiestic, in chloroform) is that expected for a monomeric complex. The IR spectra show the absorptions due to the

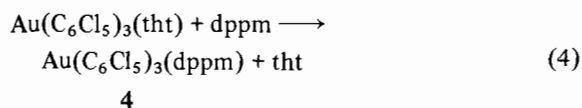
C₆Cl₅ groups [**8**] at ca. 1330(s), 1300(s), 845(m) and 685(s) cm⁻¹. Moreover, in the spectrum of **2** the vibration due to $\nu(\text{Au}-\text{Cl})$ appears [**9**] at 320(m) cm⁻¹.

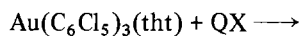
Attempts to introduce a fourth C₆Cl₅ group have failed. Neither the (1:1) reaction between [N(PPh₃)₂][Au(C₆Cl₅)₃Cl] and AgC₆Cl₅ at room temperature nor refluxing of toluene solutions of [NBu₄][Au(C₆Cl₅)₂] and Tl(C₆Cl₅)₂Cl has led to the synthesis of [Au(C₆Cl₅)₄]⁻, as is the case for the pentafluorophenyl derivatives [**5**]. In the first case, a mixture of the unreacted gold complex and the gold(I) anion [Au(C₆Cl₅)₂]⁻ was obtained; in the second case, no reaction took place. Notwithstanding, a mixed tetra-aryl aurate(III) (**3**) can be obtained by arylating [Au(C₆Cl₅)₃Cl]⁻ with AgC₆F₅. In this reaction (eqn. (3)) no formation of reduction products containing gold(I) can be observed



Complex **3** is a white solid and a 1:1 electrolyte in acetone solution (Table I).

The neutral ligand tht in complex **1** can readily be displaced by other neutral dppm = bis(diphenylphosphino)methane or anionic ligands (eqns. (4), (5))





Q = N(PPh₃)₂, X = Cl (2) or SCN (5); Q = PPh₃Me, X = Br (6); Q = PPh₂Me₂, X = I (7).

Complexes 4–7 are white, air and moisture stable solids. Complex 4 is a non-electrolyte and monomeric in CHCl₃ solution. Its ³¹P NMR spectrum is similar to that observed for Au(C₆F₅)₃(dppm) [5] and, shows two doublets at δ = -26.49 and δ = 21.67 ppm., the former corresponding to the gold-bonded P atom, the second to the uncoordinated P atom [10, 11]. Complexes 5–7 behave as 1:1 electrolytes in acetone solution. The vibration due to ν(C≡N) appears at 2120(m) cm⁻¹ in the IR spectrum of complex 5, close to that observed [5] in the spectra of [PPh₃Bz][Au(C₆F₅)₃(SCN)] (2125 cm⁻¹) and [N(PPh₃)₂][Au(C₆F₅)₃(SCN)] (2135 cm⁻¹), suggesting that the SCN group is S-bonded. The ν(Au–Br) (complex 6) or ν(Au–I) (complex 7) are not observed, most probably they lay below the lower limit of our apparatus (200 cm⁻¹).

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