

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

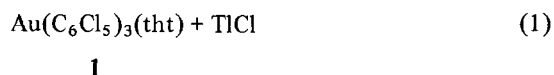
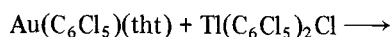
Complex	Yield (%)	Analysis, found (calc.) (%)				Λ_M^a	Molecular weight ^b found (calc.)	Melting point (°C)
		C	H	N	Au			
Au(C ₆ Cl ₅) ₃ (tht) (1)	71	25.4 (25.6)	1.2 (0.8)		19.4 (19.05)	8	993 (1033)	150(d)
[N(PPh ₃) ₂][Au(C ₆ Cl ₅) ₃ Cl] (2)	68	41.85 (42.7)	2.1 (2.0)	0.95 (0.9)	13.45 (12.95)	102		145(d)
[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.

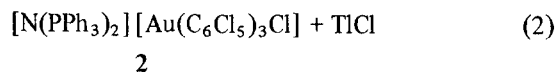
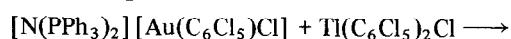
0.2 mmol), [N(PPh₃)₂]SCN (0.119 g, 0.2 mmol), [PPh₃Me]Br (0.071 g, 0.2 mmol) or [PPh₂Me₂]I (0.068 g, 0.2 mmol). The mixture was stirred at room temperature for 1 h. The solution was evaporated to ca. 5 ml and hexane was added to precipitate a white solid of 2, 5, 6 or 7.

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)



1



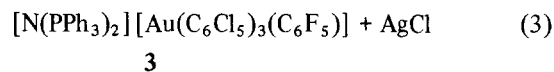
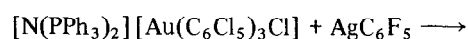
2

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.

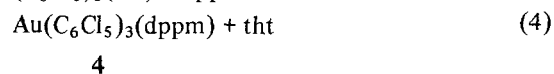
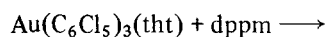
Attempts to introduce a fourth C₆Cl₅ group have failed. Neither the (1:1) reaction between [N(PPh₃)₂][Au(C₆Cl₅)₃Cl] and AgC₆Cl₅ at room temperature nor refluxing of toluene solutions of [NBu₄][Au(C₆Cl₅)₂] and Tl(C₆Cl₅)₂Cl has led to the synthesis of [Au(C₆Cl₅)₄]⁻, as is the case for the pentafluorophenyl 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



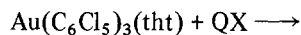
3

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))



4



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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