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Tris(pentachlorophenyl) Gold(III) complexes

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Abstract

By reaction of $Tl(C_6Cl_5)_2Cl$ with $Au(C_6Cl_5)(tht)$ (tht = tetrahydrothiophen) or $[N(PPh_3)_2][Au(C_6Cl_5)Cl]$ the gold(III) complexes $[Au(C_6Cl_5)_3(tht)]$ or $[N(PPh_3)_2][Au(C_6Cl_5)_3Cl]$ 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 $Au(C_6Cl_5)_3(Ph_2PCH_2PPh_2)$ or $Q[Au(C_6Cl_5)_3X]$ ($Q = N(PPh_3)_2$, PPh_3Me or PPh_2Me_2; $X = C_6F_5$, 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 $Au(C_6Cl_5)_3(tht)$ (tht = tetrahydrothiophen), which can be used for the preparation of other neutral or anionic triaryl derivatives, such as $Au(C_6Cl_5)_3(dppm)$ (dppm = $Ph_2PCH_2PPh_2$) or $[Au(C_6Cl_5)_3X]^-$ (X = 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

$Au(C_6Cl_5)_3(tht)$ (1)

To a solution of $Au(C_6Cl_5)(tht)$ [4] (0.452 g, 1 mmol) in 50 ml of toluene was added $Tl(C_6Cl_5)_2Cl$ [6] (0.738 g, 1 mmol) and the mixture was refluxed for 2 h. After removal of the precipitated TlCl the yellow solution was evaporated to dryness and the resulting complex **1** was recrystallized from diethylether–hexane.

$[N(PPh_3)_2][Au(C_6Cl_5)_3Cl]$ (2)

Addition of $Tl(C_6Cl_5)_2Cl$ [6] (0.148 g, 0.2 mmol) to a solution of $[N(PPh_3)_2][Au(C_6Cl_5)Cl]$ [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 TlCl 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**.

$[N(PPh_3)_2][Au(C_6Cl_5)_3(C_6F_5)]$ (3)

To a freshly prepared diethylether solution (30 ml of $Ag(C_6F_5)$ [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**.

$Au(C_6Cl_5)_3(dppm)$ (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**.

$Q[Au(C_6Cl_5)_3X]$ $Q = N(PPh_3)_2$, $X = Cl$ (2) or SCN (5); $Q = PPh_3Me$, $X = Br$ (6) or $Q = PPh_2Me_2$, $X = I$ (7)

To a solution of **1** (0.206 g, 0.2 mmol) in 30 ml of dichloromethane was added $[N(PPh_3)_2]Cl$ (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			
$Au(C_6Cl_5)_3(tht)$ (**1**)	71	25.4 (25.6)	1.2 (0.8)		19.4 (19.05)	8	993 (1033)	150(d)
$[N(PPh_3)_2][Au(C_6Cl_5)_3Cl]$ (**2**)	68	41.85 (42.7)	2.1 (2.0)	0.95 (0.9)	13.45 (12.95)	102		145(d)
$[N(PPh_3)_2][Au(C_6Cl_5)_3(C_6F_5)]$ (**3**)	80	43.5 (43.65)	2.3 (1.85)	1.15 (0.85)	12.2 (11.95)	90		175
$Au(C_6Cl_5)_3(dppm)$ (**4**)	60	38.6 (38.85)	1.1 (1.65)		15.1 (14.8)	4	1250 (1329)	156
$[N(PPh_3)_2][Au(C_6Cl_5)_3SCN]$ (**5**)	60	42.45 (42.85)	2.15 (1.95)	1.35 (1.8)	12.4 (12.8)	93		70
$[PPh_3Me][Au(C_6Cl_5)_3Br]$ (**6**)	78	34.7 (34.15)	1.9 (1.4)		14.7 (15.1)	100		100(d)
$[PPh_2Me_2][Au(C_6Cl_5)_3I]$ (**7**)	75	29.8 (29.85)	1.65 (1.25)		15.75 (15.3)	101		114

[a] In acetone (ohm^{-1} cm^2 mol^{-1}). [b] In chloroform.

0.2 mmol), $[N(PPh_3)_2]SCN$ (0.119 g, 0.2 mmol), $[PPh_3Me]Br$ (0.071 g, 0.2 mmol) or $[PPh_2Me_2]I$ (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

$Tl(C_6Cl_5)_2Cl$ [6] adds oxidatively to gold(I) derivatives, both neutral $Au(C_6Cl_5)(tht)$ (eqn. (1)) or anionic $[N(PPh_3)_2][Au(C_6Cl_5)Cl]$ (eqn. (2)), the two pentachlorophenyl groups being transferred to the gold(I) centre which thereby is oxidised to gold(III)

$$Au(C_6Cl_5)(tht) + Tl(C_6Cl_5)_2Cl \longrightarrow \underset{\mathbf{1}}{Au(C_6Cl_5)_3(tht)} + TlCl \qquad (1)$$

$$[N(PPh_3)_2][Au(C_6Cl_5)Cl] + Tl(C_6Cl_5)_2Cl \longrightarrow \underset{\mathbf{2}}{[N(PPh_3)_2][Au(C_6Cl_5)_3Cl]} + TlCl \qquad (2)$$

No substitution processes leading to other gold(I) compounds, as reported by the reaction of the thallium derivative with $AuCl(PPh_3)$, 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 C_6Cl_5 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 $\nu(Au-Cl)$ appears [9] at 320(m) cm^{-1}.

Attempts to introduce a fourth C_6Cl_5 group have failed. Neither the (1:1) reaction between $[N(PPh_3)_2][Au(C_6Cl_5)_3Cl]$ and AgC_6Cl_5 at room temperature nor refluxing of toluene solutions of $[NBu_4][Au(C_6Cl_5)_2]$ and $Tl(C_6Cl_5)_2Cl$ has led to the synthesis of $[Au(C_6Cl_5)_4]^-$, 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 $[Au(C_6Cl_5)_2]^-$ was obtained; in the second case, no reaction took place. Notwithstanding, a mixed tetra-aryl aurate(III) (**3**) can be obtained by arylating $[Au(C_6Cl_5)_3Cl]^-$ with AgC_6F_5. In this reaction (eqn. (3)) no formation of reduction products containing gold(I) can be observed

$$[N(PPh_3)_2][Au(C_6Cl_5)_3Cl] + AgC_6F_5 \longrightarrow \underset{\mathbf{3}}{[N(PPh_3)_2][Au(C_6Cl_5)_3(C_6F_5)]} + AgCl \qquad (3)$$

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))

$$Au(C_6Cl_5)_3(tht) + dppm \longrightarrow \underset{\mathbf{4}}{Au(C_6Cl_5)_3(dppm)} + tht \qquad (4)$$

$$Au(C_6Cl_5)_3(tht) + QX \longrightarrow Q[Au(C_6Cl_5)_3X] + tht \qquad (5)$$

$Q = N(PPh_3)_2$, $X = Cl$ (**2**) or SCN (**5**); $Q = PPh_3Me$, $X = Br$ (**6**); $Q = PPh_2Me_2$, $X = I$ (**7**).

Complexes **4**–**7** are white, air and moisture stable solids. Complex **4** is a non-electrolyte and monomeric in $CHCl_3$ solution. Its ^{31}P NMR spectrum is similar to that observed for $Au(C_6F_5)_3(dppm)$ [5] and, shows two doublets at $\delta = -26.49$ and $\delta = 21.67$ 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 $\nu(C{\equiv}N)$ appears at 2120(m) cm^{-1} in the IR spectrum of complex **5**, close to that observed [5] in the spectra of $[PPh_3Bz][Au(C_6F_5)_3(SCN)]$ (2125 cm^{-1}) and $[N(PPh_3)_2][Au(C_6F_5)_3(SCN)]$ (2135 cm^{-1}), suggesting that the SCN group is S-bonded. The $\nu(Au{-}Br)$ (complex **6**) or $\nu(Au{-}I)$ (complex **7**) are not observed, most probably they lay below the lower limit of our apparatus (200 cm^{-1}).

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