Inorganica Chimica Acta, 37 (1979) 201–207
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Anionic Perfluorophenyl Complexes of Gold(I) and Gold(III)

R. USON, A. LAGUNA, J. GARCIA and M. LAGUNA
Department of Inorganic Chemistry, University of Saragossa, Spain

Received March 14, 1979

The preparation of organogold(I) anions of the types $[AuRX]^-$, $[AuR_2]^-$ *and* $[AuRR']^-$ *(R, R' =* C_6F_5 *or 2,4,6-*$C_6F_3H_2$*; X = Cl, I, SCN, CN or* N_3*) is accomplished in which the tetrahydrothiophen group of AuR(tht) is substituted by X, R or R'.*

Organogold(III) complexes of the general formulae $[AuR_2X_2]^-$, $[AuRR'X_2]^-$, $[AuR_3X]^-$ *and* $[AuR_4]^-$ *(R, R' =* C_6F_5*, 2,3,4,6-*C_6F_4H *or 2,4,6-*$C_6F_3H_2$*; X = Cl, Br or I) are obtained either by oxidation of the above-mentioned gold(I) complexes or by substitution reactions of* $AuCl_3$*(tht).*

The assignment of the cis- *or, respectively,* trans-*configuration of the* $[AuR_2X_2]^-$ *derivatives is based on their IR spectra.*

Introduction

We have recently reported [1] that several anionic pentafluorophenyl gold(I) and gold(III) complexes were prepared by making use of the poor coordination capacity of tetrahydrothiophen (tht), which allows its facile displacement by anionic ligands (halide) or pentahaloaryl groups (C_6F_5 or C_6Cl_5), or by the oxidative addition of halogens or $Tl(C_6F_5)_2Br$ to pentahaloaryl gold(I) complexes. However, only few organoaurate complexes have so far been synthesized [2], and only one or two examples of some types, such as $[AuR_2]^-$, $[AuRX]^-$, $[AuR_3X]^-$ and $[AuR_4]^-$, are hitherto known.

On extending the above-mentioned methods we have been able to prepare novel anionic gold(I) complexes of the types $[Au(C_6F_5)X]^-$, $[AuR_2]^-$ and $[AuRR']^-$ (X being Cl, I, SCN, CN or N_3; R being 2,4,6-$C_6F_3H_2$ or 2,3,4,6-C_6F_4H or, respectively, R = C_6F_5 and R' = 2,4,6-$C_6F_3H_2$). We also describe the preparation of anionic gold(III) complexes of the general formulae $[AuR_2X_2]^-$ (R = C_6F_5 or 2,4,6-$C_6F_3H_2$; X = Cl, Br or I), $[AuRR'X_2]^-$ (R = C_6F_5; R' = 2,4,6-$C_6F_3H_2$; X = Br or I), $[Au(2,4,6\text{-}C_6F_3H_2)_3X]^-$ (X = Cl or Br) and $[Au(2,3,4,6\text{-}C_6F_4H)_4]^-$.

Experimental

IR spectra were recorded (over the range 4000–200 cm^{-1}) on a Perkin-Elmer 577 spectrophotometer using Nujol mulls between polyethylene sheets; conductivities were measured in 5×10^{-4} *M* acetone solutions with a Philips 9501/01 conductimeter; C, H and N analyses were carried out with a Perkin-Elmer 240 microanalyzer; Au was determined by ashing the samples with an aqueous solution of hydrazine.

The complexes which contain the cation $[PPN]^+$ [μ-Nitrido-bis(triphenylphosphorus)] give slightly high values for Au (~6%), although their C, H and N analyses are in good agreement with the expected ones (similarly, the calcination of an equimolecular mixture of AuCl(tht) and [PPN]Cl yields a residue which weighs *ca.* 4% more than the Au present in the sample).

The yields, analytical results, melting points and conductivities of the novel complexes are collected in Table I.

$Li(2,4,6\text{-}C_6F_3H_2)$ and $Li(2,3,4,6\text{-}C_6F_4H)$ were prepared by reacting the corresponding Br-derivatives with n-butyllithium at –78 °C, as described elsewhere for LiC_6F_5 [3].

Preparation of the Complexes

[PPN] $[Au(C_6F_5)X]$ *(X = Cl, I, SCN,* N_3*)*

To an ethanol solution of $Au(C_6F_5)$(tht) at room temperature was added an equimolecular amount of [PPN]X (for X = I a little less than the stoichiometric amount was added), prepared by reacting [PPN]Cl with sodium or potassium salts of the respective anion. The haloorganoaurate(I) complexes precipitated as white crystals, which were filtered off and washed with small amounts of ethanol. New quantities of the complexes were obtained on evaporating the filtrate. The complexes are soluble in acetone, dichloromethane and chloroform, slightly soluble in ethanol, but insoluble in ether and n-hexane.

$Bu_4N[Au(C_6F_5)X]$ *(X = I, CN)*

An equimolecular mixture of $Au(C_6F_5)$(tht) and $[Bu_4N]X$ was dissolved in dichloromethane or ethanol at room temperature and stirred for 2 h, whereupon it was evaporated to dryness. The resulting oil was stirred with ether at low temperature to

TABLE I. Analytical Data for Complexes.

	Complex	Yield (%)	Analysis found (calcd.) (%)				Λ_M	M.p. (°C)
			C	H	N	Au		
1.	$[PPN][Au(C_6F_5)Cl]$	73	53.70 (53.77)	3.20 (3.22)	1.74 (1.50)		90	113
2.	$[PPN][Au(C_6F_5)I]$	70	49.40 (49.00)	2.53 (2.93)	1.19 (1.36)		93	141
3.	$Bu_4N[Au(C_6F_5)I]$	83	36.40 (36.03)	5.08 (4.95)	2.02 (1.91)	26.64 (26.86)	129	65
4.	$[PPN][Au(C_6F_5)SCN]$	81	54.33 (53.76)	3.24 (3.15)	3.00 (2.91)		112	136
5.	$Bu_4N[Au(C_6F_5)CN]$	40	43.98 (43.67)	5.54 (5.76)	4.48 (4.42)	30.94 (31.14)	130	56
6.	$[PPN][Au(C_6F_5)N_3]$	93	53.69 (53.40)	3.03 (3.20)	5.15 (5.93)		106	126
7.	$Bu_4N[Au(C_6F_5)(C_6F_3H_2)]$	38	44.49 (45.59)	4.60 (5.19)	2.02 (1.90)	25.49 (26.70)	94	96
8.	$Bu_4N[Au(C_6F_3H_2)_2]$	35	48.31 (47.93)	4.91 (5.74)	2.19 (2.00)	27.80 (28.07)	92	116(d)
9.	$Bu_4N[Au(C_6F_4H)_2]$	48	45.71 (45.60)	4.88 (5.19)	1.68 (1.90)	25.61 (26.71)	98	90
10.	*cis*-$Bu_4N[Au(C_6F_3H_2)_2Cl_2]$	66	43.61 (43.54)	4.89 (5.22)	1.84 (1.81)	25.81 (25.50)	82	94
11.	*trans*-$Bu_4N[Au(C_6F_3H_2)_2Cl_2]$	81	43.81 (43.54)	5.37 (5.22)	1.73 (1.81)	25.93 (25.50)	93	127
12.	*cis*-$Bu_4N[Au(C_6F_3H_2)_2Br_2]$	95	38.49 (39.04)	4.62 (4.68)	1.69 (1.62)	22.74 (22.86)	90	106(d)
13.	*trans*-$Bu_4N[Au(C_6F_3H_2)_2Br_2]$	80	38.39 (39.04)	4.66 (4.68)	1.73 (1.62)	22.59 (22.86)	86	106(d)
14.	*cis*-$Bu_4N[Au(C_6F_3H_2)_2I_2]$	98	34.43 (35.19)	3.90 (4.22)	1.56 (1.47)	20.48 (20.61)	94	87
15.	*trans*-$Bu_4N[Au(C_6F_3H_2)_2I_2]$	68	34.84 (35.19)	3.84 (4.22)	1.46 (1.47)	20.39 (20.61)	87	106(d)
16.	*trans*-$Bu_4N[Au(C_6F_5)(C_6F_3H_2)Br_2]$	60	36.35 (37.47)	3.69 (4.26)	1.73 (1.56)	22.41 (21.95)	101	108
17.	$Bu_4N[Au(C_6F_5)(C_6F_3H_2)I_2]$	95	33.53 (33.92)	3.54 (3.86)	1.56 (1.41)	19.14 (19.87)	88	104
18.	*cis*-$Bu_4N[Au(C_6F_5)_2Cl_2]$	79	40.33 (39.83)	4.38 (4.30)	1.61 (1.66)	23.61 (23.32)	88	92
19.	*trans*-$Bu_4N[Au(C_6F_5)_2Cl_2]$	91	39.71 (39.83)	4.66 (4.30)	1.53 (1.66)	22.97 (23.32)	93	131
20.	*cis*-$Bu_4N[Au(C_6F_5)_2Br_2]$	95	35.43 (36.02)	3.94 (3.88)	1.83 (1.50)	20.98 (21.10)	98	88(d)
21.	*trans*-$Bu_4N[Au(C_6F_5)_2Br_2]$	90	34.47 (36.02)	3.61 (3.88)	1.97 (1.50)	20.85 (21.10)	98	111
22.	*trans*-$Bu_4N[Au(C_6F_5)_2I_2]$	97	32.43 (32.73)	3.28 (3.53)	1.39 (1.36)	18.57 (19.17)	116	109
23.	*trans*-$[Au(PPh_3)_2][Au(C_6F_5)_2Br_2]$	60	41.39 (40.82)	2.54 (2.14)		26.70 (27.89)	70	121
24.	$Bu_4N[Au(C_6F_3H_2)_3Cl]$	33	46.32 (47.04)	4.77 (4.88)	1.65 (1.61)	22.62 (22.69)	87	136
25.	$Bu_4N[Au(C_6F_3H_2)_3Br]$	15	45.19 (44.75)	4.40 (4.64)	1.60 (1.53)	20.93 (21.58)	101	135
26.	$Bu_4N[Au(C_6F_4H)_4]$	14	45.49 (46.38)	3.82 (3.89)	1.16 (1.35)	18.73 (19.02)	89	180

give a white solid which was recrystallized from dichloromethane–hexane. The complexes are soluble in most organic solvents, but not in ether and hexane.

$Bu_4N[Au(C_6F_5)(2,4,6\text{-}C_6F_3H_2)]$

$Au(C_6F_5)(tht)$ (1.70 g, 3.75 mmol) was added to a solution of $Li(2,4,6\text{-}C_6F_3H_2)$ (7 mmol) in 50 ml of ether and stirred for 35 min at −78 °C. A small quantity of precipitated metallic gold was filtered off and the filtrate was added to a solution of $[Bu_4N]Br$ (1.20 g, 3.75 mmol) in 10 ml of ether at −20 °C. On allowing to warm to room temperature a white precipitate was obtained which was recrystallized from dichloromethane–ether. The complex is soluble in dichloromethane, benzene and acetone, but insoluble in ether and hexane.

$Bu_4N[AuR_2]$ ($R = 2,4,6\text{-}C_6F_3H_2$, $2,3,4,6\text{-}C_6F_4H$)

AuCl(tht) (3 mmol) was added to a solution of LiR (12 mmol) in 50 ml of ether at −78 °C and stirred for 20 min, whereupon the solution was allowed to warm to room temperature and stirred for another 30 min. Traces of precipitated metallic gold were removed and the filtrate was added to a solution of $[Bu_4N]Br$ (2.8 mmol) in 10 ml of ether. The resulting white precipitate was recrystallized from dichloromethane–ethanol. The complexes are soluble in most organic solvents, but not in ether, ethanol and hexane.

trans-*$Bu_4N[AuR_2X_2]$ ($R = C_6F_5$, $2,4,6\text{-}C_6F_3H_2$; $X = Cl, Br, I$)*

A stoichiometric amount of the halogen in carbon tetrachloride solution was added dropwise to a solution of $Bu_4N[AuR_2]$ in dichloromethane. After 10 min stirring at room temperature the solvent was evaporated and the residue was recrystallized from dichloromethane–hexane. The complexes are soluble in dichloromethane and acetone, little soluble in benzene and ether, but insoluble in ethanol and hexane.

cis-*$Bu_4N[AuR_2X_2]$* ($R = C_6F_5$, $2,4,6\text{-}C_6F_3H_2$; $X = Cl, Br, I$)

Dichloromethane solutions of the respective *trans*-isomers were refluxed for 10 h (X = Cl), 2 h (X = Br) of 30 min (X = I) and the resulting *cis*-derivative was recrystallized from dichloromethane–hexane. Their solubilities are as for the *trans*-isomers.

cis-*$Bu_4N[AuR_2Cl_2]$ ($R = C_6F_5$, $2,4,6\text{-}C_6F_3H_2$)*

A stoichiometric amount of $TlCl_3$ was added to a suspension of $Bu_4N[AuR_2]$ in ether, whereupon the starting product dissolved instantaneously and TlCl precipitated. After 10 min stirring at room temperature and subsequent filtration the filtrate was evaporated to dryness and the resulting white residue was recrystallized from dichloromethane–hexane.

trans-*$[Au(PPh_3)_2]$ $[Au(C_6F_5)_2Br_2]$*

A mixture of $Bu_4N[Au(C_6F_5)_2Br_2]$ (0.252 g, 0.27 mmol) and $[Au(PPh_3)_2]ClO_4$ (0.221 g, 0.27 mmol) was dissolved in 30 ml of dichloromethane. After 2 h stirring at room temperature the solution was evaporated to give an oil which was destroyed by vigorously stirring with ether. The resulting yellowish-white solid was washed with benzene to eliminate the $[Bu_4N]ClO_4$ and recrystallized from dichloromethane–ether. The complex is soluble in acetone and dichloromethane, little soluble in chloroform, but insoluble in benzene, ethanol, ether and hexane.

Reaction of $AuCl_3(tht)$ with $Li(2,4,6\text{-}C_6F_3H_2)$

$AuCl_3(tht)$ (1.00 g, 2.55 mmol) was added to a solution of $Li(2,4,6\text{-}C_6F_3H_2)$ (15.3 mmol) in 50 ml of ether at −78 °C, whereupon $[Bu_4N]Br$ (0.82 g, 2.55 mmol) was added. The solution was allowed to warm to room temperature and stirred for 20 min. The resulting precipitate was filtered off, washed with ether, recrystallized from dichloromethane–hexane and identified as $Bu_4N[Au(C_6F_3H_2)_2]$ (62% yield).

The ether filtrate was evaporated to dryness to give a white residue which was recrystallized from ether–hexane and identified as $Bu_4N[Au(C_6F_3H_2)_3Br]$ (15% yield). It is soluble in most organic solvents, but not in hexane.

Reaction of $AuCl_3(tht)$ with $Li(2,3,4,6\text{-}C_6F_4H)$

To a solution of $Li(2,3,4,6\text{-}C_6F_4H)$ (15.0 mmol) in 50 ml of ether at −78 °C was added $AuCl_3(tht)$ (1.00 g, 2.55 mmol) and 5 min later $[Bu_4N]Br$ (0.82 g, 2.55 mmol) whereupon the mixture was allowed to warm to room temperature. After 20 min the precipitate was filtered off, washed with ether, recrystallized from dichloromethane–hexane and finally identified as $Bu_4N[Au(C_6F_4H)_2]$ (34% yield).

The filtrate was evaporated to dryness to give a solid which was identified as a mixture of $Bu_4N[Au(C_6F_4H)_4]$ and a small amount of $Bu_4N[Au(C_6F_4H)_2]$ which could be separated because of its lower solubility in ether. The gold(III) complex which was recrystallized from ether–hexane (14% yield) is soluble in most organic solvents, but not in hexane.

Reaction of $Bu_4N[Au(C_6F_5)_2]$ with $Tl(C_6F_5)Cl$

A mixture of $Bu_4N[Au(C_6F_5)_2]$ (0.38 g, 0.5 mmol) and $Tl(C_6F_5)_2Cl$ (0.28 g, 0.5 mmol) in 50 ml of benzene at 80 °C was refluxed for 4 h until formation of a white precipitate was observed. The precipitate was filtered off and identified as a mixture of TlCl and $Bu_4N[Au(C_6F_5)_4]$, which could be separated by washing with acetone wherein TlCl (90% of the total Tl) is insoluble. The acetone filtrate which contains the gold(III) complex was evaporated to dryness and the residue was extracted with dichloromethane–hexane.

The evaporation to dryness of the benzene solution yielded a mixture of $Bu_4N[Au(C_6F_5)_2]$ and $Bu_4N[Au(C_6F_5)_4]$ which was separated as described elsewhere [1]. The ir spectrum of the solution revealed the presence of decafluorobiphenyl. Yields: gold(I) complex 13%, gold(III) complex 53%.

Reaction of $Bu_4N[Au(2,4,6\text{-}C_6F_3H_2)_2]$ with Tl-$(2,4,6\text{-}C_6F_3H_2)_2Cl$

A mixture of $Bu_4N[Au(C_6F_3H_2)_2]$ (0.63 g, 0.9 mmol) and $Tl(C_6F_3H_2)_2Cl$ [4] (0.45 g, 0.9 mmol) was dissolved in 40 ml of benzene at 80 °C and refluxed for 2.5 h, whereafter *ca.* 50% of the thallium precipitated as TlCl and was filtered off. The evaporation of the filtrate yielded a residue which could partly be dissolved on treatment with 25 ml of ether; the remaining white insoluble compound was identified as $Bu_4N[Au(C_6F_3H_2)_2]$ (31% yield). To the ether solution were added 5 ml of hexane whereupon it was carefully evaporated under reduced pressure. The first fraction (0.2 g) contained $Bu_4N[Au(C_6F_3H_2)_3Cl]$ along with traces of a thallium complex (probably $Tl(C_6F_3H_2)_3$ [4] according to its ir spectrum) whilst the other fractions consisted of the pure aurate(III) complex (33% yield), which is soluble in most organic solvents, but not in hexane.

Results and Discussion

Gold(I) Complexes

The reaction of ethanol or dichloromethane solutions of pentafluorophenyltetrahydrothiophengold(I) with equimolecular amounts of n-butylammonium or μ-nitrido-bis(triphenylphosphorus) salts leads to the substitution of the neutral ligand (tht) by the anionic ligand, according to eqn. (1)

$$Au(C_6F_5)(tht) + QX \rightarrow Q[Au(C_6F_5)X] + tht \quad (1)$$

$$Q = Bu_4N, PPN; X = Cl, I, CN, SCN, N_3$$

In the case of iodide a little less than the stoichiometric amount is to be used, in order to avoid the cleavage of the Au–C_6F_5 bond and subsequent formation of $[AuI_2]^-$, as we have already reported elsewhere [1]. The crystallization of the aurate(I) complexes can greatly be facilitated by the use of the cation $[PPN]^+$.

On the other hand, the reaction of lithium polyfluorophenyl LiR (R = 2,4,6-$C_6F_3H_2$ or 2,3,4,6-C_6F_4H) with ether solutions of AuCl(tht) and subsequent addition of $[Bu_4N]Br$ gives rise to the formation of anionic bis(polyfluorophenyl)gold(I) complexes (eqn. (2))

$$AuCl(tht) + LiR(excess) \xrightarrow{[Bu_4N]Br} Bu_4N[AuR_2] \quad (2)$$

$$R = C_6F_3H_2, C_6F_4H$$

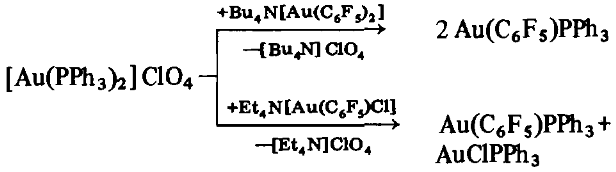
It is also possible to obtain organoanions with two different aryl-groups, according to eqn. (3)

$$Au(C_6F_5)(tht) + LiC_6F_3H_2 \xrightarrow{[Bu_4N]Br} Bu_4N[Au(C_6F_5)(C_6F_3H_2)] \quad (3)$$

This process is, however, not a general one, since reactions with LiC_6H_5 and NaC_5H_5 lead, along with a partial decomposition to metallic gold, to $Bu_4N[Au(C_6F_5)_2]$ and $Bu_4N[Au(C_6F_5)Br]$ as the only isolable products.

All the above-mentioned anionic gold(I) complexes are white air- and moisture-stable solids; their conductivities in acetone solution are those expected for uni–univalent electrolytes (see Table I).

$[Au(PPh_3)_2]ClO_4$ reacts with pentafluorophenylaurate(I) complexes in dichloromethane solution in a rather singular way since, although ammonium perchlorate is formed, the ionic species interchange ligands to form finally neutral gold(I) complexes, as may be seen from Scheme 1.



Scheme 1

Gold(III) Complexes

The oxidative addition of halogens (or thallium trichloride) to bis(polyfluorophenyl)aurate(I) complexes leads to the formation of the corresponding dihalobis(polyfluorophenyl)aurate(III) complexes, according to eqn. (4)

$$Bu_4N[AuRR'] + X_2 \text{ (or } TlCl_3) \rightarrow Bu_4N[AuRR'X_2] \text{ (+ TlCl)} \quad (4)$$

$$R = R' = C_6F_5, C_6F_3H_2; R = C_6F_5, R' = C_6F_3H_2; X = Cl, Br, I$$

As may be seen from their ir spectra (see below) oxidative addition reactions with halogens lead in every case to the *trans*-isomers, whilst treatment with $TlCl_3$ gives rise to the formation of the *cis*-isomers. Nevertheless solutions of the *trans*-dihalocompounds can be transformed into the *cis*-isomers by heating. For X = Cl the isomerization is slow and needs several hours refluxing, whilst for X = Br or I it can already be accomplished at room temperature or needs only a short time refluxing.

The oxidative addition reactions of anionic gold(I) complexes take place more readily than the previously reported ones of neutral gold(I) complexes [2]. Thus, whilst the latter require either refluxing or several hours treatment at room temperature the former are completed in a few minutes.

The *trans*-dihalogold(III) complexes are white (X = Cl), yellow (X = Br) or reddish-brown (X = I) solids, whilst the *cis*-isomers show paler shades. They are air- and moisture-stable and their conductivities in acetone solution are those expected for uni–univalent electrolytes.

The tetrabutylammonium cation of some gold(III) complexes, but not of gold(I) complexes, can be substituted by the cation $[Au(PPh_3)_2]^+$. Thus, $Bu_4N[Au(C_6F_5)_2Br_2]$ reacts with equimolecular amounts of $[Au(PPh_3)_2]ClO_4$ to give, according to eqn. (5),

$$[Au(PPh_3)_2]ClO_4 + Bu_4N[Au(C_6F_5)_2Br_2] \rightarrow [Bu_4N]ClO_4 + [Au(PPh_3)_2][Au(C_6F_5)_2Br_2] \qquad (5)$$

a mixture of $[Bu_4N]ClO_4$ and $[Au(PPh_3)_2][Au(C_6F_5)_2Br_2]$, which can readily be resolved by extracting with benzene in which the gold(III) complex is insoluble. This process is, however, not a general one and we were not able to accomplish the same reactions with other cationic complexes, such $[Au(C_6F_5)_2(PPh_3)_2]ClO_4$ or $[Au(C_6F_5)_2diars]ClO_4$.

As has already been described [1] organoaurate(III) complexes can also be obtained by a different route, the arylation of $AuCl_3(tht)$ with lithium derivatives (see Scheme 2). The reaction of $AuCl_3(tht)$ with an excess of LiC_6F_4H and subsequent addition of $[Bu_4N]Br$ yields a mixture of $Bu_4N[Au(C_6F_4H)_2]$ and $Bu_4N[Au(C_6F_4H)_4]$, which can be separated by treatment with ether in which the aurate(I) complex is far less soluble. Nonetheless, after several recrystallizations the yields of the pure compounds continue to be quite low; 14% (aurate(III)) and 34% (aurate(I) complex). The arylation of $AuCl_3(tht)$ with $LiC_6F_3H_2$ is even more complicated leading not only to $Bu_4N[Au(C_6F_3H_2)_2]$ but also to $Bu_4N[Au(C_6F_3H_2)_3Br]$, probably because of a secondary metathesis between $[Au(C_6F_3H_2)_4]^-$ and $[Bu_4N]Br$. The mixture can be resolved since the gold(I) complex is far less soluble in ether. Nevertheless, if $[Bu_4N]ClO_4$ instead of the bromide derivative is used, only $Bu_4N[Au(C_6F_3H_2)_2]$ is formed (90% yield).

It can again be seen that complexes of the type $Bu_4N[AuR_2]$ ($R = C_6F_5$, $C_6F_3H_2$) do readily undergo oxidation, thus, the reaction with TlR_2Cl leads to gold(III) complexes, although the gold(I) derivatives do not contain any bridge-forming group [5]. However, these reactions are quite complex and so if equimolecular amounts of the two compounds ($R = C_6F_5$) are refluxed in benzene, a precipitate containing TlCl (90% of the total Tl) and $Bu_4N[Au(C_6F_5)_4]$ is formed which can be separated by washing with acetone wherein the former is less soluble. The benzene filtrate contains a mixture $Bu_4N[Au(C_6F_5)_2]$ and $Bu_4N[Au(C_6F_5)_4]$ which was separated as described elsewhere [1]. Traces of decafluorobiphenyl are also detected in the solution.

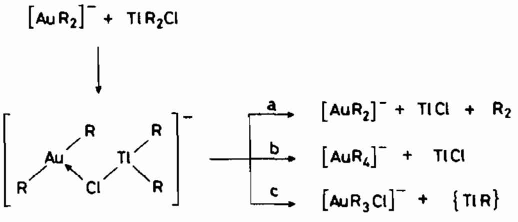
With $R = C_6F_3H_2$ the reaction takes an entirely different course. After 2.5 h refluxing in benzene and removal of the precipitate (TlCl: 50% of the total Tl) a mixture of $Bu_4N[Au(C_6F_3H_2)_2]$ (31%) and $Bu_4N[Au(C_6F_3H_2)_3Cl]$ (33%) can be separated from the filtrate, whilst another fraction yields $Bu_4N[Au(C_6F_3H_2)_3Cl]$ along with another thallium compound (which, in accordance with the ir spectrum, is probably $Tl(C_6F_3H_2)_3$ [4]).

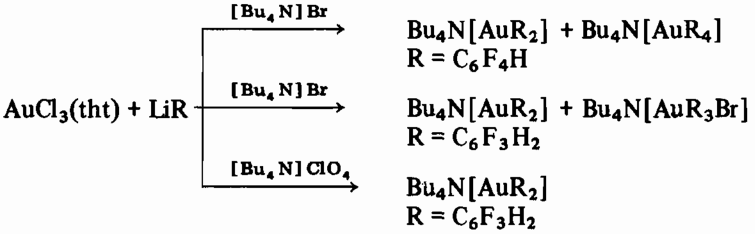
In agreement with previously reported observations [5, 6], this behaviour could be interpreted in the following way: the reactions are likely to take place through an inner-sphere mechanism *via* an intermediate complex as in Scheme 3, whereupon they can take three different routes.

a) by the cleavage of the Tl–R bonds with formation of R_2, precipitation of TlCl and regeneration of the gold(I) starting compound

b) by transfer of the two R groups to the gold atom with formation of the gold(III) complex and precipitation of TlCl, and

c) by transfer of a single R group with formation of $[AuR_3Cl]^-$ and {TlR}, which being very reactive [7] could react with some species in the solution





Scheme 2

TABLE II. Absorptions Assigned to the Coordinated 2,4,6-$C_6F_3H_2$ Group.

$Bu_4N[Au(C_6F_3H_2)_2]$	1615(m)	1585(s)	1100(s)	995(vs)	985(vs)	830(s)
cis-$Bu_4N[Au(C_6F_3H_2)_2Cl_2]$	1615(m)	1590(s)	1115(s), 1105(s)	1010(vs)[a]	995(s)[a]	835(m), 830(m)
trans-$Bu_4N[Au(C_6F_3H_2)_2Cl_2]$	1615(m)	1590(s)	1110(s)	1005(vs)	990(s)	845(m)
cis-$Bu_4N[Au(C_6F_3H_2)_2Br_2]$	1620(m)	1595(s)	1115(s), 1108(s)	1010(vs)[a]	995(s)[a]	840(s), 830(s)
trans-$Bu_4N[Au(C_6F_3H_2)_2Br_2]$	1620(m)	1590(s)	1110(s)	1010(vs)	990(s)	840(s)
cis-$Bu_4N[Au(C_6F_3H_2)_2I_2]$	1620(m)	1590(s)	1120(s), 1110(s)	1015(vs)[a]	995(s)[a]	842(s), 835(s)
trans-$Bu_4N[Au(C_6F_3H_2)_2I_2]$	1615(m)	1590(s)	1105(s)	1005(vs)	990(s)	840(s)
$Bu_4N[Au(C_6F_3H_2)_3Cl\}$	1620(m)	1590(s)	1110(s)[a], 1105(s)	1015(vs)[a]	990(vs)[a]	840(m), 830(s), 820(m)
$Bu_4N[Au(C_6F_3H_2)_3Br]$	1620(m)	1590(s)	1110(s)[a], 1105(s)	1015(vs)[a]	990(vs)[a]	840(m), 830(s), 820(m)
$Bu_4N[Au(C_6F_5)(C_6F_3H_2)]$	1615(m)	1585(m)	1100(m)	995(m)	985(s)	835(m)
trans-$Bu_4N[Au(C_6F_5)(C_6F_3H_2)Br_2]$	1620(m)	1590(m)	1110(m)	1008(m)	992(m)	840(m)
trans-$Bu_4N[Au(C_6F_5)(C_6F_3H_2)I_2]$	1620(m)	1590(m)	1108(m)	1005(m)	990(m)	840(m)

[a] These bands are broader than for the bis(trifluorophenyl) derivative.

TABLE III. ν(Gold–Halide) and Internal Vibrations of Pseudohalide Ligands.

$[PPN][Au(C_6F_5)Cl]$	325(m)
cis-$Bu_4N[Au(C_6F_5)_2Cl_2]$	330(m), 315(m)
trans-$Bu_4N[Au(C_6F_5)_2Cl_2]$	365(s)
cis-$Bu_4N[Au(C_6F_5)_2Br_2]$	230(m), 220(m)
trans-$Bu_4N[Au(C_6F_5)_2Br_2]$	265(s)
trans-$[Au(PPh_3)_2][Au(C_6F_5)_2Br_2]$	265(m)
trans-$Bu_4N[Au(C_6F_5)(C_6F_3H_2)Br_2]$	265(m)
cis-$Bu_4N[Au(C_6F_3H_2)_2Cl_2\}$	320(m), 315(m)
trans-$Bu_4N[Au(C_6F_3H_2)_2Cl_2]$	360(m)
cis-$Bu_4N[Au(C_6F_3H_2)_2Br_2]$	220(m), 215(m)
trans-$Bu_4N[Au(C_6F_3H_2)_2Br_2\}$	260(m)
$Bu_4N[Au(C_6F_3H_2)_3Cl]$	315(m)
$[PPN][Au(C_6F_5)SCN\}$	2115(s), 470(w), 455(w), 440(w), 402(w
$Bu_4N[Au(C_6F_5)CN]$	2140(s), 425(w), 322(w), 230(m)
$[PPN\}[Au(C_6F_5)N_3]$	2050(s), 405(m)

The organoaurate(III) complexes are isolated as air- and moisture-stable solids. Their conductivities in acetone are those characteristic for uni–univalent electrolytes.

IR Spectra

All the pentafluorophenyl complexes show the bands are characteristic of the bound pentafluorophenyl group, X-C_6F_5 [8, 9], at 1500, 1060, 950 and 800 cm^{-1}. The lather one, classified by Deacon and Green as "X-sensitive" [9] appears split in the *cis*-isomers, as has already been observed for platinum complexes [10]. Nonetheless, the structural assignment is based on the ν(gold–halogen) vibrations as may be seen below.

The presence of the 2,4,6-$C_6F_3H_2$ group is confirmed by the absorptions which are characteristic of this ligand (the most intense ones are listed in Table II). Some of these, especially those at ~1100 and ~800 cm^{-1} are single in the case of *trans*-$[AuR_2X_2]$ and in complexes containing only one $C_6F_3H_2$ group. Moreover, with decreasing symmetry these bands appear split into two (for compounds of the *cis*-$[AuR_2X_2]^-$ type) or, respectively, into three absorptions (for compounds of the $[AuR_3X]^-$ type).

The vibrations assignable to the 2,3,4,6-C_6F_4H group are for aurate(I) complexes at 1620(m), 1215(m), 1130(m), 1040(vs), 1000(vs) and 825(s) cm^{-1} and for aurate(III) complexes at 1625(m), 1215(m), 1135(m), 1045(vs), 1020(vs) and 830(s) cm^{-1}.

The *cis*- or *trans*- configuration of the dichloro- and dibromocomplexes can be distinguished by the bands due to the ν(Au–X) stretching mode. Thus, the two ir active bands (a_1 and b_1) which are to be expected for *cis*-isomers (C_{2v}) are located at approx. 330 and 315 cm^{-1} (X = Cl) or, respectively, at 230 and 215 cm^{-1} (X = Br) whilst the *trans*-isomers (D_{2h}) with a single ir active vibration (b_{2u}) show the absorption at approx. 360 (X = Cl) or, respectively, 260 cm^{-1} (X = Br) (see Table III). In this case we can again observe a difference of 100 ± 10 cm^{-1} between the corresponding vibrations due to X = Cl or, respectively, X = Br, as has been pointed out before [11].

The absorption due to ν(Au–I), expected to be below 200 cm^{-1}, could not be recorded on our spectrophotometer (range 4000–200 cm^{-1}). It was, nevertheless, possible to assign the *cis*- or *trans*-configuration of the diiodo derivatives both because of the route used for their synthesis and because of the similarities between the absorptions due to the C_6F_5 and $C_6F_3H_2$ groups of these compounds and of those of the dichloro- and dibromo-derivatives.

In $Bu_4N[Au(C_6F_3H_2)_3Br]$ the bands due to ν(Au–Br) could not be observed either, and are also likely to be beyond the range of our instrument.

Table III also lists the vibrations due to the pseudohalide ligands attached to the gold atom. They reveal [12, 13] that the SCN group acts as an isothiocyanate and is attached through its sulfur atom.

References

1 R. Uson, A. Laguna and J. Vicente, *Chem. Comm.*, 353 (1976); *J. Organometal. Chem.*, *131*, 471 (1977).

2 R. Uson, A. Laguna and J. Vicente, *Syn. React. Inorg. Metalorg. Chem.*, *7*, 463 (1977).

3 P. L. Coe, R. Stephens and J. G. Tatlow, *J. Chem. Soc. A*, 3227 (1962).

4 R. Uson, A. Laguna and T. Cuenca. Unpublished results.

5 R. Uson, P. Royo and A. Laguna, *J. Organometal. Chem.*, *69*, 361 (1974).

6 P. Royo, *Rev. Acad. Cienc. Zaragoza*, *27*, 235 (1972).

7 H. Kurosawa and R. Okawara, *Organometal. Chem. Rev. A*, *6*, 65 (1970).

8 D. A. Long and D. Steele, *Spectrochim. Acta*, *19*, 1955 (1963).

9 G. B. Deacon and J. H. S. Green, *Spectrochim. Acta*, *24*, 1125 (1968).

10 R. Uson, J. Fornies, J. Gimeno, P. Espinet and R. Navarro, *J. Organometal. Chem.*, *81*, 115 (1974).

11 R. Uson, A. Laguna and J. Vicente, *Rev. Acad. Cienc. Zaragoza*, *31*, 211 (1976).

12 N. J. Destefano and J. L. Burmeister, *Inorg. Chem.*, *10*, 998 (1971);
J. B. Melpolder and J. L. Burmeister, *Inorg. Chem.*, *11*, 911 (1972).

13 R. Uson, P. Royo and A. Laguna, *Syn. Inorg. Metal-org. Chem.*, *3*, 237 (1973).