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DIHALO PENTAFLUOROPHENYL TETRAHYDROTHIOPHEN GOLD(III) COMPLEXES, THEIR PREPARATION AND REACTIONS

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Summary

The complex $Au(C_6F_5)(tht)$ undergoes oxidative addition when treated in solution with halogens, to give $Au(C_6F_5)X_2(tht)$ (X = Cl, Br or I). The tetrahydrothiophen ligand of the latter can be displaced by neutral or anionic ligands to give, respectively, the neutral complexes $Au(C_6F_5)X_2L$ (L = Group IVB, VB or VIB ligand) or the anionic complexes $[Au(C_6F_5)X_2X']^-$ (X' = Cl or SCN).

Introduction

A well established method for the synthesis of arylgold(III) complexes of the general formula $Au(C_6F_5)X_2L$ (L = Group VB donor [1], isocyanide [2] or carbene [2]) involves the oxidative addition of halogens to the corresponding arylgold(III) complexes $Au(C_6F_5)L$, though in some cases cleavage of the Au—C bond leads to the formation of AuXL or, with an excess of the halogen, to AuX_3L. If L is a readily displaceable ligand, such as tetrahydrothiophen (tht), the resulting complexes $Au(C_6F_5)X_2(tht)$ are excellent precursors for the preparation of other neutral or anionic arylgold(III) complexes, as has already been reported for the corresponding arylgold(I) complex [3,4].

Some of the neutral gold(III) complexes described below cannot be prepared by direct oxidation of the corresponding gold(I) complex $Au(C_6F_5)L$. Furthermore, the anionic complexes $[Au(C_6F_5)X_3]^-$ and $[Au(C_6F_5)X_2X']^-$ are described for the first time.

Results and discussion

The reaction of equimolecular amounts of halogens (X = Cl, Br or I) to dichloromethane solutions of $Au(C_6F_5)(tht)$ proceeds readily according to eq. (1)

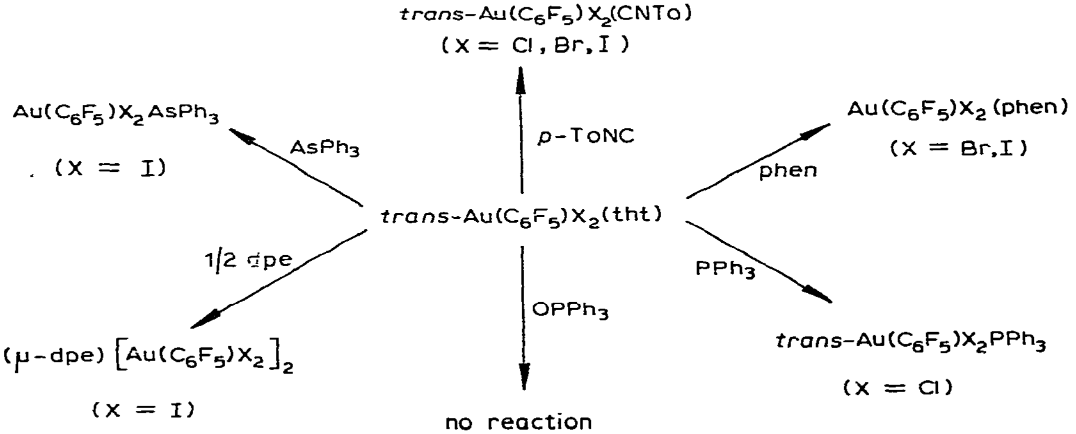
$$Au(C_6F_5)(tht) + X_2 \rightarrow Au(C_6F_5)X_2(tht) \quad (1)$$

The resulting dihalocomplexes are obtained as white (X = Cl), yellow (X = Br), or red crystals (X = I). They are soluble in most organic solvents, but not in aliphatic hydrocarbon and are non-conducting in acetone. Though the bromo and iodo derivatives are a little more stable than the corresponding gold(I) starting complex and can be satisfactorily stored at low temperature (—20° C), when left standing at room temperature and in atmospheric moisture they decompose during a few days. However, since the dichloro complex, which is generally obtained contaminated with metallic gold, is less stable, it is best to study their reactions with freshly prepared solutions (eq. 1).

Their IR spectra exhibit two bands located at 365 and 345 cm^{-1} (X = Cl) or 270 and 245 cm^{-1} (X = Br) assignable to ν_{assym}(X—Au—X) and ν_{sym}(X—Au—X). This shows that this method leads to the *trans*-isomer [5]. However, a slow transformation into the *cis*-isomer takes place in solution. Thus, after 7 h stirring at room temperature a dichloromethane solution of the dibromocomplex contains ca. 50% of each isomer; as may be seen from the appearance of a band at 222(br) cm^{-1}, which is characteristic of the *cis*-configuration. It was not possible to assign the structure of the diodo complex, since the vibrations due to ν(Au—I), expected below 200 cm^{-1}, are outside the range of our spectrophotometer.

The tetrahydrothiophen group can readily be displaced by other neutral ligands, such as C, N, P or As donors, according to the following scheme

SCHEME 1



Thus, the addition of *p*-tolylisocyanide leads to the corresponding gold(III) isocyanides, which are characterized by the appearance of an strong band at 2220 (X = Cl), 2255 (X = Br) or 2250 (X = I) cm^{-1} (assignable to the ν(C≡N) vibration). Furthermore, the location of the bands due to ν(Au—X) shows that no isomerization took place during the substitution (see Table 1).

Similarly, displacement of the tht group by 1,10-phenanthroline (phen) leads to the complexes Au(C_6F_5)X_2(phen), which are monomeric in solution (molecular-weight in chloroform: 739 (calcd. 704) for X = Br; 845 (calcd. 798) for X = I). We could not determine whether the phenanthroline group acts as a chelating ligand, but in the complex the absorptions due to ν(Au—Br) are somewhat shifted towards lower energies (see Table 1).

The reactions of the dichloroderivative with triphenylphosphine, and of the diiodo-complex with triphenylarsine or 1,2-bis(diphenylphosphino)ethane seem to be of special interest since they allow the preparation of compounds which could not be obtained by any other route. The reaction of halogens with the relevant gold(I) complexes gives rise to cleavage of the Au—C_6F_5 bond [7—9], though this behaviour is likely to be due to kinetic and not to thermodynamic causes, since the dihalo compounds once prepared are stable at room temperature and melt without decomposition.

The complex $Au(C_6F_5)Cl_2(PPh_3)$, obtained by this method, has a *trans*-configuration, as shown by its ν(Au—Cl) absorptions (see Table 1). Refluxing of chloroform solutions of the complex leads to slow transformation into the *cis*-isomer, which we previously prepared [7] by treating $Au(C_6F_5)PPh_3$ with $TlCl_3$; after three hours' refluxing only about 20% *cis*-isomer is obtained.

No reaction was observed with poorer donors, such as $OPPh_3$. Furthermore, attempts to prepare the binuclear complex $(C_6F_5)BrAu(\mu\text{-}Br)_2AuBr(C_6F_5)$ by displacing the tht group of the dibromo-derivative in refluxing chloroform proved unsuccessful and led to decomposition to metallic gold.

The tht group can also be displaced by anionic ligands, and thus the replacement by chloride leads to the synthesis of aurate(III) derivatives, as may be seen from eq. 2:

$$Au(C_6F_5)X_2(tht) + [Ph_3BzP]Cl \rightarrow [Ph_3BzP][Au(C_6F_5)X_2Cl] + tht \qquad (2)$$

X = Cl, Br; Bz = benzyl

The *trans*-configuration of the starting compound is also preserved in this case, as may be seen from the halogen—gold stretching vibrations of the dibromoderivative (Table 1).

Though $[Ph_3BzP]SCN$ seems to react in a similar way with $Au(C_6F_5)Br_2(tht)$ to give the anionic complex $[Au(C_6F_5)(SCN)Br_2]^-$, subsequent redistribution of the ligands finally yields $[Au(C_6F_5)(SCN)_2Br]^-$ and $[Au(C_6F_5)Br_3]^-$, according to eq. 3:

$$2\,Au(C_6F_5)Br_2(tht) + 2\,[Ph_3BzP]SCN \rightarrow$$
$$[Ph_3BzP][Au(C_6F_5)(SCN)_2Br] + [Ph_3BzP][Au(C_6F_5)Br_3] + 2\,tht \qquad (3)$$

The two products can be separated, the tribromoderivative being less soluble in ether. These aurate(III) complexes are air- and moisture-stable solids; their acetone solutions show conductivities characteristic of 1 : 1 electrolyts.

The presence of the SCN group in $[Au(C_6F_5)(SCN)_2Br]^-$ is supported by two strong bands at 2139 and 2130 cm^{-1} corresponding to ν(C≡N) [10]. Determination of the internal standard ratio [11] gives 0.5 or 0.8, respectively, which confirms the S-bonded structure of the complex. Other vibrations due to SCN could not be assigned since the cation shows several absorptions in the 820—650 and 520—400 cm^{-1} regions.

Experimental

The IR Spectra were recorded (over the range 4000—200 cm^{-1}) on a Perkin-Elmer 599 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured in $\sim 5 \times 10^{-4}$ *M* acetone solutions with a Philips

TABLE 1

ANALYTICAL DATA FOR COMPLEXES I–XV

	Complex	Yield (%)	Analysis found (calcd.) (%)				Λ_M	M.p. (°C)	ν(Au–X) (cm^{-1})
			C	H	N	Au			
I	$Au(C_6F_5)Cl_2(tht)$	51	22.09 (22.96)	1.26 (1.54)		36.84 (37.66)	0.2	—	365m, 345w
II	$Au(C_6F_5)Br_2(tht)$	58	19.03 (19.62)	1.25 (1.32)		32.21 (32.18)	3	110(d)	270m, 245w
III	$Au(C_6F_5)I_2(tht)$	75	16.75 (17.01)	1.09 (1.14)		27.48 (27.91)	0.4	95(d)	—
IV	$Au(C_6F_5)Cl_2(CNTo)$	68	30.09 (30.46)	1.53 (1.28)	2.41 (2.54)	35.74 (35.68)	5	131(d)	368m, 350m
V	$Au(C_6F_5)Br_2(CNTo)$	80	26.20 (26.24)	1.16 (1.10)	2.04 (2.19)	30.10 (30.73)	12	148(d)	265m, 240m
VI	$Au(C_6F_5)I_2(CNTo)$	68	22.87 (22.87)	0.86 (0.96)	1.78 (1.90)	26.58 (26.79)	12	145(d)	—
VII	$Au(C_6F_5)Br_2(phen)$	80	31.04 (30.70)	1.16 (1.14)	3.86 (3.97)	27.80 (27.97)	1	245(d)	235m, 205m
VIII	$Au(C_6F_5)I_2(phen)$	75	27.84 (27.09)	1.00 (1.01)	3.11 (3.51)	24.94 (24.68)	15	194(d)	—
IX	$Au(C_6F_5)Cl_2(PPh_3)$	61	42.17 (41.34)	2.48 (2.17)		29.14 (28.29)	0.6	156	365m, 335m
X	$Au(C_6F_5)I_2(AsPh_3)$	83	31.76 (31.16)	1.64 (1.64)		20.89 (21.32)	15	121	—
XI	$(\mu\text{-dpe})[Au(C_6F_5)I_2]_2$	68	27.48 (27.93)	1.44 (1.48)		24.32 (24.10)	14	133	—
XII	$[Ph_3BzP][Au(C_6F_5)Cl_3]$	67	44.80 (45.19)	2.79 (2.69)		23.25 (23.91)	112	205(d)	362m, 345w, 315m
XIII	$[Ph_3BzP][Au(C_6F_5)Br_3]$	48	38.62 (38.89)	2.47 (2.31)		19.89 (20.58)	112	167	260w, 235m, 225m
XIV	$[Ph_3BzP][Au(C_6F_5)Br_2Cl]$	89	41.60 (40.79)	2.51 (2.42)		20.94 (21.60)	109	190	315m, 255m, 230m
XV	$[Ph_3BzP][Au(C_6F_5)(SCN)_2Br]$	30	42.92 (43.33)	2.48 (2.42)	2.81 (3.06)	21.02 (21.56)	122	112	235m

PW 9501/01 conductimeter. C, H and N analyses were carried out with a Perkin-Elmer 240 microanalyzer, Au was determined by ashing the samples together with an aqueous solution of hydrazine.

The yields, analytical results, melting points, conductivities and ν(Au—X) frequencies for the new compounds are listed in Table 1.

Preparation of the complexes

$Au(C_6F_5)X_2(tht)$. 1 mmol of the appropriate halogen, either dissolved in ~3 cm^3 of carbon tetrachloride (X = Cl or Br) or as solid (X = I), was added to a dichloromethane solution of $Au(C_6F_5)(tht)$ (0.45 g, 1 mmol). After 1 h stirring under nitrogen the solution was evaporated at reduced pressure and the resulting complexes (I—III) were recrystallized from ether-hexane.

Because of the poor stability of the dichloro-derivative, $Au(C_6F_5)Cl_2(tht)$, all its reactions were carried out at 0°C with freshly prepared solutions.

$Au(C_6F_5)X_2L$. To a solution of $Au(C_6F_5)X_2(tht)$ in 30 cm^3 of ether or dichloromethane an equimolar amount of the ligand L was added with stirring during 30 min. Thereafter the solvent was evaporated and the residue was recrystallized from dichloromethane-hexane. The complexes are white (X = Cl, complex IV and IX), yellow (X = Br, complex V and VII) or red (X = I, complex VI, VIII and X) crystals.

The 1,2-bis(diphenylphosphino)ethane complex (XI) was obtained similarly, although a 1 : 2 molar ratio of diiodo-complex: ligand was used.

The 1,10-phenanthroline derivatives (VII and VIII) are not very soluble in dichloromethane, and so addition of the ligand gives rise to their partial precipitation. Further quantities of these compounds could be obtained by evaporation of the solvent.

$[Ph_3BzP][Au(C_6F_5)X_2Cl]$. 1 mmol of $[Ph_3BzP]Cl$ was added $Au(C_6F_5)X_2$-(tht) (1 mmol) in 50 cm^3 of dichloromethane and the solution was stirred for 1 h at room temperature. After evaporation of the solvent the residue was recrystallized from dichloromethane-hexane to give a off-white (X = Cl, XII) or yellow solid (X = Br, XIV). The bromo-derivative is less soluble and crystallizes out at the beginning of the evaporation.

$[Ph_3BzP][Au(C_6F_5)Br_3]$ and $[Ph_3BzP][Au(C_6F_5)(SCN)_2Br]$. 1 mmol of $[Ph_3BzP]SCN$ was added to a solution of $Au(C_6F_5)Br_2(tht)$ (1 mmol) in 50 cm^3 of chloroform and stirred for 1 h at room temperature. Evaporation of the solvent and treatment of the residue with ether left a yellow insoluble complex, which was recrystallized from dichloromethane-hexane and identified as XIII (48%). Complex XV (30%) was isolated from the ether solution and recrystallized from ether-hexane.

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