CHLOROBIS(POLYFLUOROPHENYL)THALLIUM(III) COMPLEXES AND THEIR REACTIONS WITH GOLD(I) AND TIN(II) COMPOUNDS

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Summary

The reaction of $TlCl_3$ with RLi leads to complexes of the general formula TlR_2Cl ($R = C_6F_5$, p-C_6F_4H, m-C_6F_4H, $2,4,6$-$C_6F_3H_2$, p-C_6FH_4 or m-$CF_3C_6H_4$). Some of these undergo oxidative addition reactions with gold(I) complexes to give polyfluorophenyl derivatives of the types AuR_2ClL and $Au(C_6F_5)R_2(tht)$ (tht = tetrahydrothiophen), and with $SnCl_2$ to give oily materials from which stable solids of the general formula $Q[SnR_2Cl_3]$ can be isolated by addition of QCl ($Q = Et_4N$ or Ph_3BzP).

Introduction

The use of $Tl(C_6F_5)_2Br$ as a reagent which is capable of transferring its two aryl groups to transition- or post-transition-metal complexes is well established [1—6]. However, the preparation [7] of $Tl(C_6F_5)_2Br$ starting from $TlCl_3$ and C_6F_5MgBr leads to a dark product which must be repeatedly recrystallized and gives therefore only moderate yields (~45%). The reaction of $Tl(C_6F_5)_2Br$ with AgCl can be used for the synthesis [7] of $Tl(C_6F_5)_2Cl$, whose arylating capacity has hitherto not been studied. The preparation of $Tl(C_6F_4H)_2Br$ and $Tl(C_6F_3H_2)_2Br$ from the corresponding Grignard compounds has recently been reported [8].

Herein we describe the preparation of complexes of the type TlR_2Cl ($R = C_6F_5$; $2,3,5,6$-C_6F_4H; $2,3,4,6$-C_6F_4H; $2,4,6$-$C_6F_3H_2$; 4-C_6FH_4; 3-$CF_3C_6H_4$) obtained by arylation of $TlCl_3$ with the corresponding RLi. These reactions, which take place smoothly, give higher yields than those with Grignard compounds. Moreover, oxidative addition of some of these complexes to gold(I) or tin(II) compounds leads to novel gold(III) and tin(IV) complexes.

Discussion and results

a) Preparation of TlR_2Cl

The reaction (1 : 2) of $TlCl_3$ with RLi in ether solution leads, according to

eq. 1, to biarylthallium chloride, which for $R = 4\text{-}C_6FH_4$ is only slightly soluble

$$TlCl_3 + 2\ RLi \rightarrow 2\ LiCl + TlR_2Cl \qquad (1)$$

$(R = C_6F_5, 2,3,5,6\text{-}C_6F_4H, 2,3,4,6\text{-}C_6F_4H, 2,3,6\text{-}C_6F_3H_2, 4\text{-}C_6FH_4, 3\text{-}CF_3C_6H_4)$

and is therefore precipitated with the formed LiCl, from which it can be separated by extraction with warm acetone. In all the other cases the precipitated LiCl is removed by filtration and the corresponding TlR_2Cl can be crystallized by evaporation of the solvent. The solubility of the triarylthallium compounds in organic solvents decreases with the number of ring substituents. Their acetone or nitromethane solutions are non-conducting and their molecular weights in benzene (whenever the compound is soluble enough) correspond to the dimeric complexes $[TlR_2Cl]_2$, which are probably chloro-bridged, though there could be greater association in the solid state [9].

b) Oxidative additions to gold(I) complexes
 Oxidative addition of TlR_2Cl to $AuClPPh_3$ leads, as shown in to eq. 2, to the

$$TlR_2Cl + AuClPPh_3 \xrightarrow{\text{benzene}} TlCl + AuR_2ClPPh_3 \qquad (2)$$

$(R = C_6F_5, 2, 3, 5, 6\text{-}C_6F_4H, 2, 4, 6\text{-}C_6F_3H_2)$

precipitation of TlCl and the formation of the corresponding gold(III) complexes. However, when $R = 4\text{-}C_6FH_4$ or $3\text{-}CF_3C_6H_4$ the unchanged starting compounds are recovered even after 24 h refluxing in benzene or acetone.
 Analogous reactions with AuCl(tht) (tht = tetrahydrothiophen) lead to $AuR_2Cl(tht)$, and its neutral ligand can readily be replaced by L to give e.g. Au-$(C_6F_3H_2)_2Cl(PPh_3)$. All the novel gold(III) complexes, which are air- and moisture-stable crystals, are non-conducting in acetone.
 The splitting of the bands characteristic of the aryl group (at 1110, 1010 and 840 cm^{-1} for $C_6F_3H_2$ and at 1100 and 850 cm^{-1} for $2,3,5,6\text{-}C_6F_4H$) indicates that the complexes are the *cis*-isomers. This is in accord with observations made for trifluorophenylgold(III) complexes [2c] and with the behaviour of *cis*-Au-$(C_6F_5)_2ClPPh_3$ [10]. The $\nu(Au\text{—}Cl)$ vibration appear in every case as a single band in the 330—320 cm^{-1} region.
 The reaction represented by eq. 2 take place via a binuclear intermediate compound [2a] in which Au and Tl are linked by halogen-bridges. This requires that the gold starting complex contains a potentially bridging-ligand (e.g. a halogen atom) or a neutral ligand which dissociates to leave a free coordination site. $AuClPPh_3$ fulfills the first condition and therefore undergoes oxidative additions, whilst $Au(C_6F_5)PPh_3$, which does not meet any of these conditions, does not react. Thus, if benzene solutions of $Au(C_6F_5)PPh_3$ and $Tl(C_6F_3H_2)_2Cl$ are refluxed for eight hours no TlCl is precipitated and unchanged starting materials are recovered. Moreover, $Au(C_6F_5)(tht)$, which contains the readily displaceable tht ligand, dissociation of which will leave a free coordination site, undergoes oxidative addition reaction according to eq. 3.

$$TlR_2Cl + Au(C_6F_5)(tht) \rightarrow TlCl + Au(C_6F_5)\ R_2(tht) \qquad (3)$$
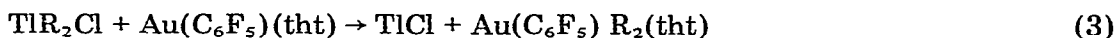
$(R = 2, 3, 4, 6\text{-}C_6F_4H; 2, 4, 6\text{-}C_6F_3H_2)$

The reaction leads to mixed triarylgold(III) derivatives of the general formula $AuRR'_2L$; a type of complex of which there are very few examples in the only hitherto described triarylcomplexes being $Au(C_6F_5)_3PPh_3$ [11] and $Au(C_6F_5)_2(C_6Br_5)PPh_3$ [12].

In the IR spectra of the novel triarylcomplexes $Au(C_6F_5)R_2(tht)$ some of the vibrations due to R are split, and the R groups must therefore be mutually *cis*. The complexes are air- and moisture-stable crystals, soluble in most organic solvents but insoluble in n-hexane. Their acetone solutions are non-conducting.

c) Oxidative addition to $SnCl_2$

Refluxing of acetone solutions of $SnCl_2$ and TlR_2Cl leads, according to eq. 4,

$$TlR_2Cl + SnCl_2 \xrightarrow{-TlCl} SnR_2Cl_2 \xrightarrow{QCl} Q[SnR_2Cl_3] \qquad (4)$$
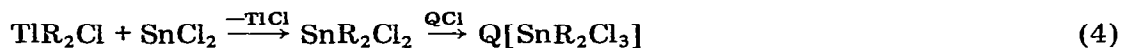
$(R = C_6F_5; 2, 3, 5, 6-C_6F_4H; 2, 4, 6-C_6F_3H_2; Q = Ph_3BzP; Et_4N)$

to neutral complexes SnR_2Cl_2 which can be isolated as oils by evaporating the solvent; the properties of the C_6F_5 derivative are identical with those previously reported [1]. Addition of QCl to acetone solutions of SnR_2Cl_2 leads to the formation of $Q[SnR_2Cl_3]$ (see eq. 4) which can be isolated by evaporation of the solvent. The obtained white crystals are air- and moisture-stable and are soluble in several organic solvents, slightly soluble in benzene, and insoluble in hexane. The conductivities of their acetone and nitromethane solutions are those of 1 : 1 electrolytes.

Experimental

IR spectra were recorded (over the range 4000—200 cm^{-1}) on a Perkin-Elmer 597 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured in 5×10^{-4} M acetone or nitromethane solutions with a Philips PW 9501/01 conductimeter. Molecular weights were measured in benzene solutions with a Hitachi Perkin Elmer, model 115, osmometer. C, H and N analyses were carried out with a Perkin-Elmer 240 microanalyzer. Au was determined by ashing the samples in a crucible together with an aqueous solution of hydrazine.

The yields, melting points, analytical results, conductivites and molecular weights (in benzene) for the novel complexes are given in Table 1.

Ether solutions of RLi (R = *p*- and *m*-C_6F_4H, 2,4,6-$C_6F_3H_2$, *p*-C_6FH_4 or *m*-$CF_3C_6H_4$) were prepared by treating the respective bromo-derivative with n-butyllithium at —78°C, as described for C_6F_5Li [13].

Preparation of TlR_2Cl

To a solution of 12 mmol of RLi in ether (~50 ml) at —78°C under nitrogen were added 6 mmol of anhydrous $TlCl_3$. After 30 min stirring the solution was slowly brought to room temperature and filtered, and the filtrate was hydrolyzed with ~10 ml of acidified water (two drops of conc. HCl being added). After removal of the organic layer the solution was dried with anhydrous $MgSO_4$ and evaporated to dryness. The resulting residue was recrystallized from hot benzene (complex I) or dichloromethane-hexane (complexes II—IV).

TABLE 1

ANALYTICAL DATA FOR COMPLEXES I–XIV

Complex	Yield (%)	M.p. (°C)	Anal. found (calcd.) (%)				Λ_M (ohm^{-1} cm^2 mol^{-1})	Mol. wt. found (calcd.)
			C	H	N	Au		
I Tl(C$_6$F$_5$)$_2$Cl	83	220	25.82 (25.11)	—	—	—	—	—
II Tl(p-C$_6$F$_4$H)$_2$Cl	67	241	27.37 (26.98)	0.34 (0.38)	—	—	4^a	1090 (538)
III Tl(m-C$_6$F$_4$H)$_2$Cl	75	180	27.57 (26.98)	0.34 (0.38)	—	—	1^a	1132 (538)
IV Tl(2,4,6-C$_6$F$_3$H$_2$)$_2$Cl	75	166	29.21 (28.71)	0.88 (0.80)	—	—	2^a	1028 (502)
V Tl(p-C$_6$FH$_4$)$_2$Cl	70	>300	34.14 (33.52)	1.53 (1.87)	—	—	c	c
VI Tl(m-CF$_3$C$_6$H$_4$)$_2$Cl	85	298	31.62 (31.72)	1.63 (1.50)	—	—	0^b	c
VII Au(p-C$_6$F$_4$H)$_2$ClPPh$_3$	60	230(d)	44.96 (45.14)	1.96 (2.06)	—	26.01 (26.03)	—	—
VIII Au(2,4,6-C$_6$F$_3$H$_2$)$_2$ClPPh$_3$	50	235(d)	47.75 (47.50)	2.38 (2.53)	—	23.90 (24.86)	0^a	—
IX Au(2,4,6-C$_6$F$_3$H$_2$)$_2$Cl(tht)	45	89	33.04 (33.20)	1.76 (1.38)	—	34.77 (33.80)	4^a	—
X Au(C$_6$F$_5$)(m-C$_6$F$_4$H)$_2$(tht)	50	120(d)	34.64 (35.22)	1.39 (1.34)	—	25.43 (26.25)	3^a	—
XI Au(C$_6$F$_5$)(2,4,6-C$_6$F$_3$H$_2$)$_2$(tht)	60	105(d)	36.20 (36.99)	1.83 (1.69)	—	28.13 (27.57)	5^a	—
XII [Ph$_3$BzP][Sn(C$_6$F$_5$)$_2$Cl$_3$]	60	110	48.24 (48.67)	2.34 (2.40)	—	—	89^a	—
XIII [Et$_4$N][Sn(p-C$_6$F$_4$H)$_2$Cl$_3$]	60	300	37.23 (36.76)	3.78 (3.40)	2.37 (2.15)	—	86^b	—
XIV [Ph$_3$BzP][Sn(2,4,6-C$_6$F$_3$H$_2$)$_2$Cl$_3$]	60	139	52.13 (52.80)	2.93 (3.10)	—	—	77^a	—

^{a} In acetone. ^{b} In nitromethane. ^{c} Not soluble enough.

For complex VI (R = m-CF$_3$C$_6$H$_4$) the synthesis was carried out as similarly but in 120 ml of ether.

Complex V (R = p-C$_6$FH$_4$), being even less soluble in ether, precipitated out together with LiCl. It was separated by treatment with acetone at 60°C and warm-filtration. The filtrate was hydrolyzed with a few drops of acidified water (HCl), and gave crystals of V upon evaporation.

Reactions of TlR$_2$Cl

a) With AuClPPh$_3$. A solution of 0.24 g (0.5 mmol) of AuClPPh$_3$ [14] in 50 ml of benzene and 0.5 mmol of TlR$_2$Cl (R = p-C$_6$F$_4$H or 2,4,6-C$_6$F$_3$H$_2$) was refluxed for 2 h. After removal of the precipitated TlCl the solution was evaporated to dryness and the resulting complex (VII or VIII) was recrystallized from dichloromethane-hexane.

No reaction took place when R was p-C$_6$FH$_4$ or m-CF$_3$C$_6$H$_4$, even after refluxing equimolecular amounts of the reagents in benzene or acetone solutions for 24 h.

b) With AuCl(tht). A solution of AuCl(tht) [15] (0.32 g, 1 mmol) and Tl(2,4,6-C$_6$F$_3$H$_2$)$_2$Cl (0.50 g, 1 mmol) in 50 ml of dichloromethane was stirred for 3 h at room temperature then filtered, and the filtrate was evaporated to dryness to give a colourless oil. Thus was crystallized by vigorous stirring with hexane. Complex IX was recrystallized from ether-hexane.

c) With Au(C$_6$F$_5$)(tht). 0.22 g (0.5 mmol) of Au(C$_6$F$_5$)(tht) [15] were added to a solution of 0.5 mmol of TlR$_2$Cl (R = m-C$_6$F$_4$H or 2,4,6-C$_6$F$_3$H$_2$) in 50 ml of benzene. After 3 h stirring at room temperature and 2 h refluxing the solution was filtered and evaporated to dryness to give a white solid. This was recrystallized from ether-hexane (Complexes X and XI).

d) With SnCl$_2$. 1 mmol of TlR$_2$Cl (R = C$_6$F$_5$, p-C$_6$F$_4$H or 2,4,6-C$_6$F$_3$H$_2$) was added to an acetone solution (30 ml) of SnCl$_2$ (0.19 g, 1 mmol) and the mixture was refluxed for 3 h then filtered and evaporated to dryness. The resulting oil (identified for R = C$_6$F$_5$ as Sn(C$_6$F$_5$)$_2$Cl$_2$ [1]) was dissolved in 20 ml of acetone. After addition of 1 mmol of QCl (Q = Et$_4$N, Ph$_3$BzP) and 1 h stirring at room temperature the solutions were again evaporated to dryness to give white solids which were recrystallized from dichloromethane-hexane. (Complexes XII—XIV).

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