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POLYFLUOROPHENYLGOLD(I) COMPLEXES

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Summary

Neutral polyfluorophenyl complexes of the type RAuL and RAuL—LAuR and anionic complexes of the type $[AuR_2]^-$ (R = 2,3,5,6-C_6F_4H, 2,4,6-$C_6F_3H_2$, 3,6-$C_6F_2H_3$, 4-C_6FH_4 or 3-$CF_3C_6H_4$) are obtained by the reaction of ClAuL (L = PPh_3, P(cyclohexyl)$_3$, $AsPh_3$ or tetrahydrothiophen; L—L = $Ph_2PCH_2PPh_2$ or $Ph_2PCH_2CH_2PPh_2$) with an organolithium derivative and/or the replacement of the initial ligands L by other mono- or bi-dentate ligands.

The outcome of the reaction of $[AuR_2]^-$ with $[Au(PCy_3)_2]^+$ (Cy = cyclohexyl), depends on the nature of the ligand R; thus with R = 3,6-$C_6F_2H_3$ the product is $[Au(PCy_3)_2][AuR_2]$, while with R = 2,4,6-$C_6F_3H_2$, the product is $[Au(PCy_3)(2,4,6\text{-}C_6F_3H_2)]$.

Introduction

In recent years there have been several studies of organogold(I) complexes containing monofluoro- [1,2] and pentafluoro-phenyl groups [2—7] but complexes containing other polyfluorophenyl groups have received little attention, and little information on their stability is available. Furthermore, few organoaurate complexes, especially of the type $[AuR_2]^-$ have been described, and all of them were isolated as tetra-n-butylammonium salts [7,8]. $[Au(PPh_3)_2][Au(C_6F_5)_2Br_2]$ is the only known organoaurate(III) which includes a gold containing cation [8]. Previous attempts to prepare other such gold(I) complexes proved unsuccessful.

We describe below the preparation of (i) neutral mononuclear complexes of the type RAuL (R = 2,3,5,6-C_6F_4H, 2,4,6-$C_6F_3H_2$, 3,6-$C_6F_2H_3$, 4-C_6FH_4, 3-$CF_3C_6H_4$; L = PPh_3, PCy_3 or $AsPh_3$), (ii) neutral binuclear complexes of the type RAuL—LAuR (L—L = bis(diphenylphosphine)methane (dpm), 1,2-bis(diphenylphosphine)ethane (dpe)), (iii) anionic complexes of the type $Bu_4N[AuR_2]$ (R being 3,6-$C_6F_2H_3$ or 3-$CF_3C_6H_4$), and (iv) $[Au(PCy_3)_2][Au(3,6\text{-}C_6F_2H_3)_2]$.

Results and discussion

Organolithium derivatives RLi react with gold(I) chloro complexes in ether to give neutral gold(I) derivatives of the type RAuL (eq. 1).

$$\mathrm{ClAuL + RLi \rightarrow RAuL + LiCl} \quad (1)$$

(R = 2,3,5,6-C_6F_4H, 2,4,6-$C_6F_3H_2$, 3,6-$C_6F_2H_3$, 4-C_6FH_4, 3-$CF_3C_6H_4$; L = PPh_3, $AsPh_3$, tht (tetrahydrothiophen))

This method can also be used for the preparation of related non-fluorinated compounds, e.g. those with R = α-naphthyl. (The derivatives with R = 4-C_6FH_4 and 3-$CF_3C_6H_4$ were made previously by reaction of the chloro complex with the corresponding organomagnesium derivative [1]).

When L = PPh_3, reaction 1 proceeds readily, but with ligands of poor coordinating capacity such as $AsPh_3$ or tetrahydrothiophen (tht) there is some decomposition to metallic gold which results in much lower yields. The stability of the resulting compounds decreases in the sequence $PPh_3 > AsPh_3 >$ tht, and the tetrahydrothiophen derivatives could not be isolated. They are stable in solution below —20°C, and these solutions can be used for preparative purposes. Thus, addition of triphenylphosphine to such solutions gives the corresponding $RAuPPh_3$ derivatives. The arsine ligand $AsPh_3$ can also be replaced by a phosphine (eq. 2).

$$\mathrm{RAuL' + L \rightarrow RAuL + L'} \quad (2)$$

(R = $C_6F_3H_2$ or $C_6F_2H_3$; L' = $AsPh_3$ or tht; L = PPh_3 or PCy_3)

Similarly, the addition of a bidentate ligand, e.g. bis(diphenylphosphine)-methane (dpm) or 1,2-bis(diphenylphosphine)ethane (dpe) to an ether solution of the tht or $AsPh_3$ derivatives gives binuclear complexes, as shown in eq. 3.

$$\mathrm{2\,RAuL' + L{-}L \rightarrow RAuL{-}LAuR + 2\,L'} \quad (3)$$

L' = tht or $AsPh_3$; L—L = dpm or dpe)

All the neutral mono- and bi-nuclear complexes can be isolated as white crystals. They are thermally less stable than the corresponding pentafluorophenyl complexes, and the thermal stability decreases with the number of fluorine atoms in the aromatic ring. They are non-conducting in acetone solution.

Anionic complexes of the $[AuR_2]^-$ type are formed by the reaction of lithium polyfluorophenyl derivatives with ether solutions of ClAutht and subsequent addition of Bu_4NBr, according to eq. 4.

$$\mathrm{ClAutht + RLi(excess) \xrightarrow{Bu_4NBr} Bu_4N[AuR_2]} \quad (4)$$

(R = $C_6F_2H_3$ or $CF_3C_6H_4$)

Again the complexes are less stable than those with R = C_6F_5 [7], C_6F_4H or $C_6F_3H_2$ [8], and can be stored only for a few days even at low temperature. As may be seen from Table 1, their conductivities in acetone solutions are as expected for uni-univalent electrolytes.

Reaction 1 does not take place when $ClAuPCy_3$ is treated with $C_6F_2H_3Li$,

TABLE 1

ANALYTICAL DATA FOR COMPLEXES I—XVI

Complex		Yield		Analysis (found (calcd.) (%))				M.p.	Λ_M
		a	b	C	H	Au	N		
I	$C_6F_4HAuPPh_3$	65	—	47.47 (47.38)	2.53 (2.65)	32.36 (32.38)	—	145	0.4
II	$C_6F_3H_2AuPPh_3$	60	80	49.39 (48.85)	2.77 (2.90)	32.90 (33.38)	—	130	0.9
III	$C_6F_2H_3AuPPh_3$	65	85	50.34 (50.36)	2.80 (3.17)	33.70 (34.42)	—	125	0
IV	$C_6FH_4AuPPh_3$	35	—	51.16 (52.00)	3.45 (3.47)	35.03 (35.53)	—	150 (dec.)	0
V	$CF_3C_6H_4AuPPh_3$	50	—	49.93 (49.73)	3.16 (3.17)	31.98 (32.62)	—	152 (dec.)	0.2
VI	$C_{10}H_7AuPPh_3$	68	—	56.81 (57.34)	3.69 (3.78)	32.90 (33.59)	—	161 (dec.)	0.3
VII	$C_6F_3H_2AuPCy_3$	—	75	47.00 (47.37)	5.88 (5.79)	31.74 (32.37)	—	110 (dec.)	3
VIII	$C_6F_3H_2AuAsPh_3$	40	—	45.83 (45.44)	2.31 (2.70)	30.42 (31.05)	—	120 (dec.)	0.9
IX	$C_6F_2H_3AuAsPh_3$	60	—	46.10 (46.77)	2.47 (2.94)	30.82 (31.96)	—	110 (dec.)	1.3
X	$(C_6F_3H_2Au)_2dpm$	—	80	43.68 (44.24)	2.75 (2.80)	38.63 (39.22)	—	90	1.2
XI	$(C_6F_3H_2Au)_2dpe$	—	82	43.27 (43.28)	2.59 (2.67)	36.89 (37.36)	—	180 (dec.)	0
XII	$(C_6F_2H_3Au)_2dpe$	—	85	44.78 (44.80)	2.93 (2.90)	38.05 (38.68)	—	132 (dec.)	1.2
XIII	$(C_{10}H_7Au)_2dpe$	—	30	51.88 (52.78)	2.96 (3.65)	38.50 (37.64)	—	195 (dec.)	8
XIV	$Bu_4N[Au(C_6F_2H_3)_2]$	51	—	51.44 (50.52)	6.50 (6.35)	29.01 (29.57)	1.98 (2.10)	80 (dec.)	93
XV	$Bu_4N[Au(CF_3C_6H_4)_2]$	52	—	49.32 (49.38)	6.02 (6.07)	26.72 (27.00)	6.02 (6.07)	82 (dec.)	90
XVI	$[Au(PCy_3)_2]$- $[Au(C_6F_2H_3)_2]$	67	—	48.81 (48.81)	5.78 (6.14)	32.41 (33.36)	—	130	93

[a] By reaction with organolithium derivatives. [b] By substitution reactions of the neutral ligands.

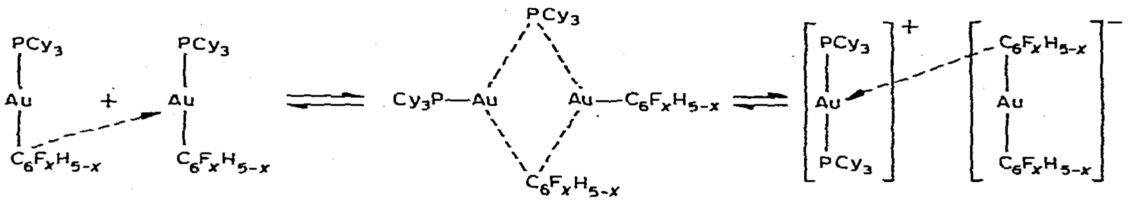
while the analysis of the product points to the formula ($Au(C_6F_2H_3)(PCy_3)$), the complex is conducting in acetone and nitromethane, and when the equivalent conductivity in nitromethane is plotted against the square root of the concentration a straight line with slope 128 is obtained, corresponding to a uni-univalent electrolyte [10]. This means that the complex has the formula $[Au(PCy_3)_2]$-$[Au(C_6F_2H_3)_3]$, and is formed according to eq. 5.

$$2\ ClAuPCy_3 + 2\ C_6F_2H_3Li \rightarrow [Au(PCy_3)_2][Au(C_6F_2H_3)_2] + LiCl \qquad (5)$$

The same compound is obtained on treating equimolecular amounts of Bu_4N-$[Au(C_6F_2H_3)_2]$ with $[Au(PCy_3)_2]ClO_4$ (eq. 6), as confirmed by the analyses, conductivities, melting points, and IR spectra.

$$Bu_4N[Au(C_6F_2H_3)_2] + [Au(PCy_3)_2]ClO_4 \rightarrow$$
$$[Bu_4N]ClO_4 + [Au(PCy_3)_2][Au(C_6F_2H_3)_2] \qquad (6)$$

SCHEME 1



However, the reaction with $Bu_4N[Au(C_6F_3H_2)_2]$ proceeds in a different way, to give the neutral complex $C_6F_3H_2AuPCy_3$ (see eq. 7), whose properties are identical with those of the compound obtained from the substitution reaction 2 when L′ = $AsPh_3$. This behaviour is analogous to that observed on treatment of $Bu_4N[Au(C_6F_5)_2]$ with $[Au(PPh_3)_2]ClO_4$ [8].

$$Bu_4N[Au(C_6F_3H_2)_2] + [Au(PCy_3)_2]ClO_4 \rightarrow [Bu_4N]ClO_4 + 2\ C_6F_3H_2AuPCy_3 \quad (7)$$

The interconversion ionic complex ⇌ neutral complex, which can clearly be seen from processes 5 and 7 requires the migration of the polyfluorophenyl groups from one gold atom to the other; this could take place as shown in Scheme 1, with formation of an intermediate compound in which the polyfluorophenyl group bridges two gold atoms, similar to complexes described by Nesmeyanov [11]. This points to the existence of binuclear complexes involving polyfluoroaryl groups. At present we are studying the possible existence of such polyfluorophenyl-bridged complexes.

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 $\sim 5.10^{-4}$ *M* acetone solutions with a Philips PW 9501/01 conductimeter. C, H and N analyses were carried out with a Perkin—Elmer microanalyzer. Au was determined by ashing the samples together with an aqueous solution of hydrazine.

The yields, analytical results, melting points and conductivities are listed in Table 1.

Solutions of RLi (R = 2,3,5,6-C_6F_4H, 2,4,6-$C_6F_3H_2$, 3,6-$C_6F_2H_3$, 4-C_6FH_4, 3-$CF_3C_6H_4$ or α-naphthyl) were prepared, as described for C_6F_5Li [9], by slow addition of an equimolecular amount of n-butyllithium in ether to a solution of the corresponding bromo derivative in the same solvent at —78°C, and subsequent stirring for 30 min at the same temperature.

PREPARATION OF THE COMPLEXES

RAuL

Complexes of this type were prepared by two routes: (a) To a solution of RLi in ether at —78°C ClAuL was added in a 2/1 molar ratio, and the mixture was slowly allowed to warm to room temperature (45 min). The solution was treated with a few drops of water, filtered through anhydrous $MgSO_4$ and evaporated to dryness. The resulting white residue was recrystallized from dichloromethane/hexane (complexes I—IV, VIII, IX and XVI).

Solutions of RAutht (R = C_6F_4H, $C_6F_3H_2$ and $C_6F_2H_3$), which were prepared similarly, underwent decomposition when evaporated. They are stable only below —20°C.

(b) Stoicheiometric amounts of a phosphine were added to a dichloromethane or ether solution of RAuL (L = $AsPh_3$ or tht) and the mixture was stirred for 30 min at room temperature ($AsPh_3$) or at —20°C (tht). The resulting solutions were evaporated to dryness and the residue was recrystallized from dichloromethane/hexane (complexes II, III and VII).

The RAuL complexes are soluble in most organic solvents, but not in aliphatic hydrocarbons.

RAuL—LAuR

To a solution of RAutht in ether at —20°C (or of $RAuAsPh_3$ in dichloromethane at room temperature) was added diphosphine in a 2/1 molar ratio. The stirred mixture was allowed to warm to room temperature during 30 min, then evaporated to dryness. The resulting white solid was recrystallized from dichloromethane/hexane (complexes X—XIII).

The complexes are soluble in benzene, acetone and dichloromethane, not very soluble in ether, and insoluble in hexane.

$Bu_4N[AuR_2]$

3 mmol of ClAutht were added to a solution of 10 mmol of RLi in 50 ml of ether at —78°C. After 20 min stirring at this temperature, 3 mmol of Bu_4NBr were added and the mixture was allowed to warm to room temperature. After a few minutes a white compound was precipitated and this was filtered off and recrystallized from dichloromethane/hexane. Further quantities of the anionic complexes were obtained by evaporation of the ether filtrate.

Complexes XIV and XV are soluble in most organic solvents, not very soluble in ethanol and ether, and insoluble in aliphatic hydrocarbons.

$[Au(PCy_3)_2][Au(C_6F_2H_3)_2]$

A mixture of $[Au(PCy_3)_2]ClO_4$ (1 mmol) and $Bu_4N[Au(C_6F_2H_3)_2]$ (1 mmol) in 30 ml of dichloromethane was stirred for 20 min at room temperature then it was evaporated to dryness. The residue was washed with small portions of ethanol/water to remove $[Bu_4N]ClO_4$. After filtration, the solid was recrystallized from dichloromethane/hexane. Complex XVI is soluble in most organic solvents, but insoluble in ether, ethanol and hexane.

Complex XVI can also be obtained by method a.

$C_6F_3H_2AuPCy_3$

An equimolecular mixture of $[Au(PCy_3)_2]ClO_4$ and $Bu_4N[Au(C_6F_3H_2)_2]$ [8] in 30 ml of dichloromethane was stirred for 20 min at room temperature, evaporated to dryness, and the residue was washed with ether. The resulting white solid was identified as $[Bu_4N]ClO_4$. Complex VII was crystallized from the ether filtrate; it can also be obtained by method b.

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