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SYNTHESIS AND REACTIONS OF DI-μ-HALO- OR -PSEUDOHALO-TETRAKIS(PENTAFLUOROPHENYL)DIGOLD(III)

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Summary

$Bu_4N[Au(C_6F_5)_2X_2]$ (X = Cl or Br) has been used to prepare $[Au(C_6F_5)_2X]_2$. These complexes have been found to react with (a) salts MX′ to give $[Au(C_6F_5)_2X']_2$ or $[Au(C_6F_5)_2(acac)]$ (X′ = SCN, N_3 or CF_3COO); (b) neutral ligands to give $[Au(C_6F_5)_2Clpy]$ or $[Au(C_6F_5)_2(L-L)]^+$ $[Au(C_6F_5)_2Cl_2]^-$ (L–L = bipy, phen or pdma), and (c) $Bu_4N[AuR_2]$ (R = C_6F_5, 2,4,6-$C_6F_3H_2$) to give $Bu_4N[Au(C_6F_5)_2RCl]$.

Introduction

Although the dimeric diethylgold bromide, prepared 75 years ago, was the first reported organogold derivative [1] only a few compounds of the type $[AuR_2X]_2$ have been described. All of them are alkyl derivatives [3] except for the complex with R = $C_{12}H_8$ [2]. They were generally prepared by the reaction between a gold(III) halide, or its complexes, and an excess of an alkyl Grignard or alkyl-lithium reagent, though the yields are consistently poor (< 30%).

In the present paper we describe the synthesis of $[Au(C_6F_5)_2X]_2$ (X = Cl or Br), obtained by chloride abstraction (with $AgClO_4$) from the recently reported [4] organoaurate(III) complexes $Bu_4N[Au(C_6F_5)_2X_2]$. Substitution reactions of $[Au(C_6F_5)_2Cl]_2$ with MX lead to the novel binuclear complexes $[Au(C_6F_5)_2X]_2$ (X = N_3, SCN or CF_3COO) or to the monomeric AuR_2X (X = acac), while the cleavage of the chloro-bridges with neutral ligands yields complexes of the types $[Au(C_6F_5)_2(L-L)][Au(C_6F_5)_2Cl_2]$ (L–L = 1,10-phenanthroline, 2,2′-bipyridyl or *o*-phenylenebis(dimethylarsine)) or $[Au(C_6F_5)_2ClL]$ (L = pyridine).

Results and discussion

Organoaurate(III) of the type $Bu_4N[Au(C_6F_5)_2X_2]$ were used in all cases as starting reagents. The preparations of the *cis*- and *trans*-derivatives with X = Cl or Br have been described [4]. *trans*-$Bu_4N[Au(C_6F_5)_2(SCN)_2]$ (I) was obtained from the dichloro derivative by an exchange reaction, as in eq. 1.

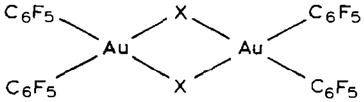
$$\textit{trans}\text{-}Bu_4N[Au(C_6F_5)_2Cl_2] + 2KSCN \rightarrow 2KCl + \underset{(I)}{\textit{trans}\text{-}Bu_4N[Au(C_6F_5)_2(SCN)_2]} \qquad (1)$$

Complex I is a yellow air- and moisture-stable solid, which is conducting in acetone (1/1 electrolyte), (see Table 1). Its IR spectrum shows a single band at 2115m cm^{-1}, assignable [5] to $\nu(C{\equiv}N)$, for which determination of the internal standard ratio [6] gives 0.39, indicating that the two SCN groups are linked via the S atoms. In the 800 cm^{-1} region a single band at 790 cm^{-1} due to the C_6F_5 groups [4] reveals these are mutually *trans*. Refluxing of a dichloromethane solution of I causes a slow isomerization to *cis*, as observed [4] for other *trans*-dihalo-organoaurate(III) complexes. The IR spectrum of II is characterized by two absorptions, at 805s and 792s cm^{-1}, arising from the two mutually *cis* C_6F_5 groups, along with the vibration $\nu(C{\equiv}N)$ at 2118m cm^{-1}, with a shoulder at 2125m cm^{-1} (internal standard ratio [6]: 0.35).

Attempts to synthesize the diazido derivative by reaction 1 using NaN_3 proved unsuccessful; a mixture of the complexes with $X = N_3$ and Cl, which could not be resolved, was obtained even when the reaction was carried out in refluxing acetone.

We recently showed that the reaction with $AgClO_4$ (1/2) of the anions $[Au(C_6F_5)X]^-$ and $[Au(C_6F_5)_3X]^-$ containing pseudohalide ligands ($X = SCN$ or N_3) leads to the precipitation of half of the pseudohalide as its silver salt and the formation of the binuclear monobridged complex $X[Au(C_6F_5)]_2$ or $X[Au(C_6F_5)_3]_2$ [7]. Starting from both *cis*- or *trans*-$Bu_4N[Au(C_6F_5)_2X_2]$, a similar process gives the doubly-bridged binuclear derivatives III and IV (see eq. 2).

$$2\ \textit{cis}\text{-}Bu_4N[Au(C_6F_5)_2X_2] + 2AgClO_4 \longrightarrow 2AgX + 2[Bu_4N]ClO_4 +$$



(2)

(X = Cl (III), Br (IV))

The reaction takes place in dichloromethane/ether with precipitation of AgX. The mixture of $[Bu_4N]ClO_4$ and the binuclear complex obtained from the solution can be separated by making use of the insolubility of the ammonium salt in diethyl ether.

For X = SCN, reaction 2 seemingly takes a similar course, though owing to the insolubility of $[Au(C_6F_5)_2SCN]_2$ (V), the resulting mixture of AgSCN and V could not be resolved. However, complex V and the derivatives containing $X = N_3$ or CF_3COO can be prepared by an exchange reaction of the neutral binuclear complex III, as depicted in eq. 3.

$$[Au(C_6F_5)_2Cl]_2 + 2MX \rightarrow 2MCl + [Au(C_6F_5)_2X]_2 \qquad (3)$$

$(MX = KSCN, NaN_3, AgCF_3COO;\ X = SCN\ (V), N_3\ (VI), CF_3COO\ (VII))$

An alternative route to complex V, which gives higher yields, is the exchange between complex III and $Au(SCN)PPh_3$ (eq. 4).

$$[Au(C_6F_5)_2Cl]_2 + 2Au(SCN)PPh_3 \rightarrow 2Au(Cl)PPh_3 + [Au(C_6F_5)_2SCN]_2 \qquad (4)$$

The binuclear complexes III–VII are white or yellow (VI) air- and moisture-stable solids, which slowly decompose in polar solvents, such as acetone, with precipitation of metallic gold. Complexes III, IV and VII are soluble in acetone, benzene, chloroform, dichloromethane and diethyl ether, but insoluble in aliphatic hydrocarbons. Their molecular weights in chloroform (see Table 1) are consistent with the proposed formulae, Complexes V and VI are only slightly soluble in organic solvents.

In acetone complexes III–V and VII show a measurable conductivity, but this is clearly lower than expected for 1/1 electrolytes (The conductivity of VI could not be determined because of its insolubility.). This is probably due to a partial cleavage of the bridges by the molecules of the solvent to form ions (see eq. 5).

$$[Au(C_6F_5)_2X]_2 + 2L \rightleftharpoons [Au(C_6F_5)_2L_2]^+ + [Au(C_6F_5)_2X_2]^- \qquad (5)$$

As may be seen from Table 1 the extent bridge cleavage increases in the sequence $X = CF_3COO < SCN < Br < Cl$.

Complex III shows two bands at 300m and 285m,sh cm^{-1}, which in the light of the D_{2h} symmetry, are assignable to $\nu(Au{-}Cl)_{bridge}$. These values are lower than these observed for $\nu(Au{-}Cl)_{terminal}$ in *cis*-$[Au(C_6F_5)_2Cl_2]^-$ [4], as is also the case for other chloro complexes; e.g. for *cis*-$AuMe_2ClL$ the vibration due to $\nu(Au{-}Cl)$ appears at 287–273 cm^{-1} [8], while for $[AuMe_2Cl]_2$ the two bands arising from $\nu(Au{-}Cl)_{bridge}$ are at 273 and 245 cm^{-1} [9]. This indicates that C_6F_5 has a lower *trans*-influence than CH_3. The vibrations assignable to $\nu(Au{-}Br)_{bridge}$ are expected [10] to be below the range of our instrument (200 cm^{-1}) and could not be observed.

For the SCN derivative V the vibration due to $\nu(C{\equiv}N)$ at 2170vs cm^{-1}, is displaced towards higher frequency than when it acts as a terminal ligand (I and II), in accord with previous observations [7,11]. Similarly, for VI the $\nu(N{\equiv}N)$ bond is shifted towards higher frequencies (2095s cm^{-1}), than in complexes with $Au{-}N_3$ terminal bonds [4,7,11].

The trifluoroacetato complex VII is characterized by a band at 1645m cm^{-1}, assignable to $\nu_{asym}(CO_2)$ [2], while the vibration arising from $\nu_{sym}(CO_2)$ is probably masked by absorptions due to the C_6F_5 group. Complexes III–VII show also two absorptions due to the C_6F_5 groups (at 825–810s and 815–795s cm^{-1}), indicating a *cis*-configuration [4].

If reaction 3 is carried out with Tl(acac), precipitation of TlCl is observed and $Au(C_6F_5)_2(acac)$ (VIII) can be isolated from the solution. The white complex VIII is monomeric in chloroform and non-conducting in acetone. Its IR spectrum exhibits three strong bands at 1570, 1560 and 1530 cm^{-1}, assignable to the acac ligand, in accord with those observed for *cis*-$AuMe_2(acac)$ [12]. The presence of two bands at 825s and 812s cm^{-1} confirms the expected *cis*-configuration.

The chloro-bridges of III are readily cleaved by neutral ligands. Reaction with monodentate ligands, such as pyridine (py) or PPh_3, results in symmetric cleavage of the bridges, as represented in eq. 6.

$$[Au(C_6F_5)_2Cl]_2 + 2L \rightarrow 2\ cis\text{-}Au(C_6F_5)_2ClL \qquad (6)$$

$(L = py\ (IX),\ PPh_3)$

TABLE 1

ANALYTICAL DATA FOR COMPLEXES I–XIV

Complex		Yield (%)	M.p. (°C)	Analyses (Found (calcd.) (%))				Λ_M (ohm^{-1} cm^2 mol^{-1})	Mol. wt. Found (calcd.)
				C	H	N	Au		
trans-$Bu_4N[Au(C_6F_5)_2(SCN)_2]$	(I)	90	112	40.77 (40.50)	4.04 (4.08)	4.70 (4.72)	22.31 (22.14)	107	–
cis-$Bu_4N[Au(C_6F_5)_2(SCN)_2]$	(II)	52	62	41.20 (40.50)	4.16 (4.08)	4.72 (4.72)	22.46 (22.14)	108	–
$[Au(C_6F_5)_2Cl]_2$	(III)	80	100 (d)	25.71 (25.44)	–	–	35.05 (34.77)	43	1099 (1133)
$[Au(C_6F_5)_2Br]_2$	(IV)	60	77 (d)	23.83 (23.59)	–	–	32.51 (32.24)	32	1150 (1222)
$[Au(C_6F_5)_2SCN]_2$	(V)	65	132 (d)	26.23 (26.50)	–	2.43 (2.38)	32.81 (33.43)	20	–
$[Au(C_6F_5)_2N_3]_2$	(VI)	35	170 (d)	25.14 (25.15)	–	7.03 (7.33)	34.81 (34.37)	–	–
$[Au(C_6F_5)_2(CF_3COO)]_2$	(VII)	65	115 (d)	25.50 (26.11)	–	–	30.91 (30.58)	15	1180 (1288)
$Au(C_6F_5)_2(acac)$	(VIII)	80	110 (d)	32.20 (32.40)	1.24 (1.12)	–	31.68 (31.26)	3	695 (630)
cis-$Au(C_6F_5)_2Clpy$	(IX)	70	160 (d)	30.75 (31.63)	1.00 (0.78)	2.10 (2.17)	30.35 (30.51)	4	704 (646)
cis,cis-$[Au(C_6F_5)_2bipy][Au(C_6F_5)_2Cl_2]$	(X)	75	230 (d)	31.62 (31.68)	0.87 (0.63)	2.42 (2.17)	30.69 (30.56)	89	–
cis,cis-$[Au(C_6F_5)_2phen][Au(C_6F_5)_2Cl_2]$	(XI)	84	232 (d)	32.12 (32.93)	0.92 (0.61)	2.00 (2.13)	30.37 (30.00)	91	–
cis,cis-$[Au(C_6F_5)_2pdma][Au(C_6F_5)_2Cl_2]$	(XII)	80	205	28.90 (28.78)	1.60 (1.14)	–	27.18 (27.76)	109	–
$Bu_4N[Au(C_6F_5)_3Cl]$	(XIII)	78	180 (d)	41.79 (41.84)	3.22 (3.72)	1.49 (1.44)	20.11 (20.18)	105	–
cis-$Bu_4N[Au(C_6F_5)_2(C_6F_3H_2)Cl]$	(XIV)	65	110 (d)	43.14 (43.44)	3.77 (4.07)	1.35 (1.49)	20.80 (20.95)	97	–

The properties of the derivative with $L = PPh_3$ agree with those previously reported [13]. IX is a white solid, which in solution is monomeric and non-conducting. (Table 1). Its IR spectrum (two bands at 822s and 812s cm^{-1}) reveals the conservation of the *cis*-configuration of the C_6F_5 groups.

Bidentate ligands, such as 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen) or *o*-phenylenebis(dimethylarsine) (pdma) cause asymmetric cleavage, leading to ionic complexes, according to eq. 7

$$[Au(C_6F_5)_2Cl]_2 + L\text{–}L \rightarrow cis,cis\text{-}[Au(C_6F_5)_2L\text{–}L][Au(C_6F_5)_2Cl_2] \qquad (7)$$

$$(L\text{–}L = \text{bipy (X), phen (XI), pdma (XII)})$$

The products are white air- and moisture-stable solids, conducting in acetone. Their IR spectra show two bands at 335m and 318m cm^{-1}, corresponding to ν(Au–Cl), characteristic of the anion *cis*-$[Au(C_6F_5)_2Cl_2]$ [4]. Of the four expected bands in the 800 cm^{-1} region only three at ~ 820m, 810s and 800m cm^{-1} could be observed, probably owing to some overlap.

The chloro bridges of III are also cleaved by $[AuR_2]^-$ ($R = C_6F_5$ or $C_6F_3H_2$). As we recently showed [14], $[Au(C_6F_5)_2]^-$ can act as electron density donor towards silver centres, though in the present case the reaction is more complex, giving a precipitate of metallic gold and leading to transfer of an R group to the gold(III) centre, as may be seen from eq. 8.

$$[Au(C_6F_5)_2Cl]_2 + 2Bu_4N[AuR_2] \rightarrow 2Bu_4N[Au(C_6F_5)_2RCl] + 2Au + R\text{–}R \qquad (8)$$

$$(R = C_6F_5\ \text{(XIII)},\ 2,4,6\text{-}C_6F_3H_2\ \text{(XIV)})$$

The resulting organoaurate(III) complexes are white solids, which are conducting in acetone. Complex XIV shows two bands at 810m and 800m cm^{-1}, indicating a *cis*-configuration of the C_6F_5 groups. In the same region the spectrum of complex XIII is characteristic of a tris-pentafluorophenyl complex [15], with two bands at 815s and 795s,br cm^{-1}.

Experimental

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 5×10^{-4} *M* acetone solutions with a Philips PW 9501/01 conductimeter. Molecular weights were measured in chloroform solution with a Hitachi Perkin–Elmer 215 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, C, H, N and Au analyses, conductivities and molecular weights of the novel complexes are listed in Table 1.

Preparation of the complexes

trans-$Bu_4N[Au(C_6F_5)_2(SCN)_2]$ (I)

A solution of *trans*-$Bu_4N[Au(C_6F_5)_2Cl_2]$ [4] (0.422 g, 0.5 mmol) and KSCN (0.194 g, 2 mmol) in 50 ml of acetone was stirred for 2 h at room temperature. The precipitated KCl was filtered off and the filtrate was evaporated to dryness. The residue was extracted with 30 ml of dichloromethane and the insoluble excess of KSCN removed by filtration. Evaporation to dryness gave the yellow complex I, which was recrystallized from dichloromethane/hexane.

cis-$Bu_4N[Au(C_6F_5)_2(SCN)_2]$ *(II)*

A solution of I (0.445 g, 0.5 mmol) in 50 ml of dichloromethane was refluxed for 6 h. After evaporation to dryness the residue was recrystallized from dichloromethane/hexane. The first fractions contained complex II, and the last fractions were a mixture of I and II.

$[Au(C_6F_5)_2X]_2$ $X = Cl$ *(III) or* Br *(IV)*

Silver perchlorate (0.207 g, 1.0 mmol) was added to a solution of *cis*- or *trans*-$Bu_4N[Au(C_6F_5)_2X_2]$ [4] (1 mmol) (X = Cl: 0.844 g; Br: 0.933 g) in a mixture of 25 ml of diethyl ether and 25 ml of CH_2Cl_2, and the mixture was stirred for 2 h at room temperature with exclusion of light. The precipitated AgX was filtered off and the filtrate was evaporated to dryness. The residue was treated with 30 ml of diethyl ether and the insoluble $[Bu_4N]ClO_4$ was filtered off. Evaporation to dryness gave III or IV as a white solid, which was recrystallized from diethyl ether/hexane.

$[Au(C_6F_5)_2SCN]_2$ *(V)*

To a solution of III (0.549 g, 0.5 mmol) in 30 ml of acetone was added KSCN (0.098 g, 1 mmol). The mixture was stirred for 4 h at room temperature. The KCl was filtered off and the filtrate was evaporated to dryness to leave an oil. Prolonged stirring with hexane gave solid V (10% yield).

Better yields (65%) were obtained as follows. To a solution of $Au(SCN)PPh_3$ [16] (0.259 g, 0.5 mmol) in 30 ml of dichloromethane was added III (0.283 g, 0.25 mmol). The mixture was stirred for 2 h at room temperature during which V separated as a white solid. This was filtered off and extracted with dichloromethane. Concentration of the extract to ca. 8 ml and addition of 20 ml of hexane gave solid $AuClPPh_3$.

$[Au(C_6F_5)_2N_3]_2$ *(VI)*

A solution of III (0.113 g, 0.1 mmol) and NaN_3 (0.013 g, 0.2 mmol) in 30 ml of acetone was refluxed for 2 h. On cooling the yellow VI precipitated out. It was filtered off and washed with acetone and dichloromethane.

$[Au(C_6F_5)_2(CF_3COO)]_2$ *(VII)*

To a solution of III (0.170 g, 0.15 mmol) in 20 ml of ether was added AgO_2CCF_3 (0.066 g, 0.30 mmol). The mixture was stirred for 15 min at room temperature, the precipitated AgCl was filtered off, and the filtrate was evaporated to dryness. The resulting oil was taken up in 8 ml of dichloromethane and 20 ml of hexane were added to precipitate the white complex VII.

cis-$Au(C_6F_5)_2(acac)$ *(VIII)*

To a solution of (III) (0.170 g, 0.15 mmol) in 20 ml of diethyl ether was added Tl(acac) (0.091 g, 0.3 mmol). The mixture was stirred for 2 h at room temperature and the TlCl was filtered off. The filtrate was evaporated to dryness to give the white VIII, which was recrystallized from dichloromethane/hexane.

cis-$Au(C_6F_5)_2Clpy$ (IX)

Pyridine (0.016 g, 0.2 mmol) was added to a solution of III (0.113 g, 0.1 mmol) in 40 ml of ether, and the mixture was stirred for 30 min at room temperature. The solution was evaporated to dryness and the white residue IX was recrystallized from dichloromethane/hexane.

cis-,cis-$[Au(C_6F_5)_2(L–L)][Au(C_6F_5)_2Cl_2]$ (L–L = bipy(X); phen (XI) or pdma (XII))

To a solution of III (0.113 g, 0.1 mmol) in 40 ml of ether was added 0.1 mmol of the bidentate ligand (2,2′-bipyridyne: 0.016 g; 1,10-phenanthroline: 0.019 g; or *o*-phenylenebis(dimethylarsine): 0.029 g). The mixture was stirred for 15 min at room temperature, and the precipitated white complexes (X–XII) were filtered off. Concentration to ca. 8 ml and addition of hexane gave further quantities of X–XII. The products, were recrystallized from dichloromethane/hexane.

$Bu_4N[Au(C_6F_5)_2RCl]$ R = C_6F_5 (XIII) or 2,4,6-$C_6F_3H_2$ (XIV)

Complex III (0.113 g, 0.1 mmol) was added to a solution of $Bu_4N[AuR_2]$ [4] (0.2 mmol) (R = C_6F_5: 0.155 g; 2,4,6-$C_6F_3H_2$: 0.140 g) in 20 ml of dichloromethane. After 1 h stirring at room temperature the precipitated metallic gold was filtered off. The filtrate was evaporated to dryness and the white XIII or XIV was recrystallized from dichloromethane/hexane.

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