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Bimetallic Gold–Silver Pentachlorophenyl Complexes

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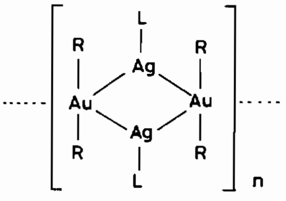
Abstract

A study of the reactions of several aurate(I) compounds with silver perchlorate shows that only bis(pentachlorophenyl)aurate(I) leads to stable bimetallic $[AuAg(C_6Cl_5)_2 \cdot L]_n$ (L = nil, tht, py, phen) complexes. The ionic $[Ag(py)_2][Au(C_6Cl_5)_2]$ is also described. A brief discussion about the general stability and reactivity of this class of bimetallic complexes is included.

Introduction

Recently [1] we reported the preparation and structure of bimetallic Au–Ag polyfluorophenyl complexes containing the moiety (A).



A

($R = C_6F_5, C_6F_3H_2$; L = O, N, S, P-donor ligand, alkene, alkyne or arene)

They are polymeric in nature since the $(AuAg)_2$ rings are linked by Au···Au short contacts to form infinite metal-atom chains. A study by Mössbauer spectroscopy [2] of some of them revealed that the $[AuR_2]^-$ groups are acting as Lewis bases; electron density of the 6s and 6p Au orbitals is withdrawn from the gold atom to the silver centres. In the present paper we describe the results of our search for other suitable $Q[AuR_2]$ precursors, successful only for $R = C_6Cl_5$.

TABLE I. Analytical Data for Complexes I–VII.

	Complex	Yield (%)	D.P. (°C)	Analysis (found (calc) (%))			
				C	H	N	Au + Ag
I	$[AuAg(CN)_2]_n$	90	290	6.65 (6.75)		7.7 (7.85)	84.7 (85.4)
II	$[AuAg(C_6Cl_5)_2]_n$	90	240	18.05 (17.95)			37.4 (37.95)
III	$[AuAg(C_6Cl_5)_2tht]_n$	95	150	21.4 (21.55)	0.75 (0.9)		33.8 (34.2)
IV	$[AuAg(C_6Cl_5)_2py]_n$	83	173	22.85 (23.15)	0.4 (0.55)	1.5 (1.6)	34.1 (34.55)
V	$[AuAg(C_6Cl_5)_2phen]_n$	96	255	28.75 (29.3)	0.7 (0.8)	2.5 (2.85)	30.6 (31.0)
VI	$[AuAg(C_6Cl_5)_2(OCMe_2)]_n$	75	250	20.4 (20.9)	0.7 (0.7)		35.35 (35.35)
VII	$[Ag(py)_2][Au(C_6Cl_5)_2]$	92	170	27.0 (27.45)	1.2 (1.05)	2.75 (2.90)	31.45 (31.7)

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Experimental

The instrumentation employed and general experimental techniques were as described earlier [1]. The yields, melting points and C, H, N and Au + Ag analyses of the novel complexes are listed in Table I.

Preparation of the Complexes

$[AuAg(CN)_2]_n$, (I)

$AgClO_4$ (0.104 g, 0.5 mmol) was added to a solution of $(NBu_4)[Au(CN)_2]$ (0.246 g, 0.5 mmol) in a mixture of dichloromethane (20 ml) and diethylether (10 ml) or in 30 ml of acetone and stirred at room temperature for 2 h. The white precipitate of (**I**) was filtered off and washed with 2 X 5 ml of diethylether.

$[AuAg(C_6Cl_5)_2]_n$, (II)

$AgClO_4$ (0.041 g, 0.2 mmol) was added to a solution of $(NBu_4)[Au(C_6Cl_5)_2]$ [3] (0.188 g, 0.2 mmol) in 20 ml of dichloromethane. After 6 h stirring at room temperature the yellow precipitate of (**II**) was filtered off and washed with 2 X 5 ml of diethylether.

$[AuAg(C_6Cl_5)_2L]_n$, (L = tht (III), py (IV), or phen (V))

To a suspension of (**II**) (0.161 g, 0.2 mmol) in 20 ml of dichloromethane was added a solution of tetrahydrothiophene in hexane (0.1 M, 4 ml, 0.4 mmol), a solution of pyridine in hexane (0.1 M, 4 ml, 0.4 mmol) or monohydrate of 1,10-phenanthroline (0.040 g, 0.2 mmol) and stirred at room temperature for 24 h. The greenish-yellow (**III**), cream-coloured (**IV**) or pale-yellow (**V**) solid was filtered off and washed with 2 X 5 ml of diethylether.

$[AuAg(C_6Cl_5)_2(OCMe_2)]_n$, (VI)

The reaction was carried out as for (**II**), though acetone (20 ml) was used as solvent. The red solid of (**VI**) was filtered off and washed with 2 X 5 ml of diethylether.

$[Ag(py)_2][Au(C_6Cl_5)_2]$, (VII)

To a suspension of (**IV**) (0.177 g, 0.2 mmol) in 20 ml of dichloromethane was added a solution of pyridine in hexane (0.1 M, 10 ml, 10 mmol) and stirred at room temperature for 2 h. The white complex (**VII**) was filtered off and washed with 2 X 5 ml of diethylether.

Results and Discussion

On studying the reactions between stoichiometric amounts of several aurate precursors and $AgClO_4$ in dichloromethane solution, we obtained the following results:

(*i*) If the aurate contains one or two chloride ions, as in $(NBu_4)[AuCl_2]$ or $(PPN)[AuCl(C_6F_5)]$, the addition of $AgClO_4$ causes precipitation of AgCl mixed with metallic gold. In diethylether, only AgCl precipitates and the solution decomposes (slowly at low temperature, more rapidly at room temperature) under deposition of metallic gold, owing to the unstability of the covalent gold(I) perchlorato complex formed by the anion exchange.

(*ii*) With aurate(III) precursors, such as $(PPN)[Au(C_6F_5)_4]$ and $(NBu_4)[Au(C_6F_5)_3Br]$, no reaction is observed in the first case whereas anion exchange with precipitation of AgBr takes place in the second case.

(*iii*) Aurate(I) containing only Au–C bonds behave differently. Thus, the reaction between $(NBu_4)[Au(CH_3)_2]$ and $AgClO_4$ in CH_2Cl_2 solution immediately gives metallic gold and $(NBu_4)ClO_4$ can be recovered from the solution. With $(NBu_4)[Au(CN)_2]$ the immediate formation of a white solid is observed. This solid analyzes as $[AuAg(CN)_2]$ (**I**), though its white colour, the shift of the $\nu(C{\equiv}N)$ band to higher energies (2205 cm^{-1}; 2140 cm^{-1} in the $[Au(CN)_2]^-$ precursor), and the insolubility in common organic solvents, as well as its lack of reactivity with neutral ligands (tetrahydrothiophene, pyridine, in 50:1 excess), point to a polymeric material with bridging CN-groups as:

$$-N{\equiv}C-Au-C{\equiv}N-Ag-N{\equiv}C-Au-C{\equiv}N-$$

rather than to a bimetallic complex with $(AuAg)_2$ units.

(*iv*) Finally, the use of $(NBu_4)[Au(C_6Cl_5)_2]$ as a precursor seems to be the only way to prepare stable bimetallic complexes similar to those previously described [1]. The slow formation of a yellow solid (**II**), according to eqn. 1 takes place:

$$(NBu_4)[Au(C_6Cl_5)_2] + AgClO_4 \xrightarrow{CH_2Cl_2} \frac{1}{n}\underset{\textbf{II}}{[AuAg(C_6Cl_5)_2]_n} + (NBu_4)ClO_4 \quad (1)$$

Stirring of a suspension of (**II**) in dichloromethane or diethylether with a neutral ligand L (L = tetrahydrothiophene(tht), pyridine(py) or 1,10-phenanthroline(phen); tht and py in a 100% excess) causes the addition of the ligand, according to eqn. 2

$$[AuAg(C_6Cl_5)_2]_n + nL \longrightarrow [AuAg(C_6Cl_5)_2L]_n \quad (2)$$

[L = tht (III), py (IV), phen (V)]

No reaction was observed when L = olefin or acetylene (cyclooctadiene, norbornadiene, 3-hexyne, diphenylacetylene). Thus, refluxing for several days of chloroform suspension of (**II**) with an excess of any of these ligands renders the unchanged gold(I) precursor. Furthermore, if in the first reaction (eqn. 1) an arene (*e.g.* benzene) is substituted for dichloromethane, complex **(II)** is again recovered without formation of the addition product with L = C_6H_6.

The resulting yellow **(II)**, greenish-yellow **(III)**, cream-coloured **(IV)**, or respectively, pale-yellow **(V)** complexes are air- and moisture-stable. They are insoluble in organic solvents such as dichloromethane, chloroform, hexane, benzene, toluene, diethylether and acetone.

In acetone suspension, complex **(II)** is quickly converted into an insoluble red solid $[AuAg(C_6Cl_5)_2(OCMe_2)_x]_n$, albeit after 8 h refluxing in acetone x < 1. Refluxing of complexes **(III)** and **(IV)** in acetone gives rise to an exchange of their neutral ligands under formation of red solids, though the substitution is not quantitative. However, the pure complex $[AuAg(C_6Cl_5)_2\cdot(OCCH_3)]_n$ **(VI)** can be obtained if in the preparation according to eqn. 1 acetone is used instead of CH_2Cl_2.

Complex **(IV)** reacts with a great excess of pyridine (50:1) to give the ionic complex **(VII)** (eqn. 3):

$$[AuAg(C_6Cl_5)_2\cdot py]_n + py \rightleftarrows n[Ag(py)_2][Au(C_6Cl_5)_2] \qquad (3)$$

which is a white, air- and moisture-stable solid at room temperature, that is soluble in acetone (its 5×10^{-4} M acetone solution has a conductivity of 72 ohm^{-1} cm^2 mol^{-1}).

The IR spectra of the resulting complexes show the absorptions which are characteristic of the pentachlorophenyl group [4, 5]. The ionic complexes $(NBu_4)[Au(C_6Cl_5)_2]$ and **(VII)** exhibit two bands at 833(s) and 612 (m) cm^{-1}, assignable to the X-sensitive vibration of X-C_6Cl_5 and, respectively, to metal–carbon stretching vibration. In the spectra of the polynuclear complexes **II–VI** these vibrations are slightly displaced towards higher energies (recorded at 840–838(s) and 615(m) cm^{-1}) as has also previously been observed for the complexes with C_6F_5 or $C_6F_3H_2$ [1].

Comparison of the results with those obtained previously [1] allows us to establish the following points:

(1) With precursors $[AuXX']^-$, where X = R, X' = halide or X = X' = halide, it is not possible to prepare Au–Ag bimetallic complexes of type **A**, since silver halide precipitates in every case.

(2) For X = C-ligand, with potentially bidentate ligands such as cyanide, the ligand free-end is a better donor than the gold atom, and polymeric materials without Au–Ag bonds are precipitated.

(3) For X = alkyl or aryl ligands, only when the Au–C bonds are strong (or inert) enough can the $(AuAg)_2$ rings be formed and preserved. Therefore the alkyl aurate(I) compounds are to be ruled out, a total decomposition being observed for $[AuMe_2]^-$.

(4) Only polyhalophenyl aurate(I) fulfill all the necessary conditions to give stable bimetallic complexes, with the silver atoms as the electrophilic and the gold atoms of the $[AuR_2]^-$ groups as the nucleophilic part. They show a gradation in their properties which correlates with the presumptive electronegativity of the R groups. With R = C_6F_5 the donation of electron density is not sufficient to stabilize the neutral ligand-free compound $[AuAgR_2]_n$, which can be readily isolated with R = $C_6F_3H_2$ or C_6Cl_5. Therefore, the reactivity of the silver centres towards neutral ligands is higher for R = C_6F_5. A variety of neutral ligands including olefins, acetylenes and arenes can be incorporated to give $[AuAgR_2L]_n$, whilst neither olefins, acetylenes or arenes give stable compounds with R = $C_6F_3H_2$ or C_6Cl_5. The C_6Cl_5 complexes are the most reluctant to further react with other than the neutral ligands of the Vb and VIb groups.

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