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ortho-, *meta-* AND *para*-NITROPHENYLGOLD(I) COMPLEXES

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Summary

Treatment of $[BzPh_3P][AuCl_2]$ with $[Hg(x\text{-}C_6H_4NO_2)_2]$ ($x = o$, m, or p) gives anionic gold(I) complexes of the type $[BzPh_3P][Au(R)Cl]$ (R = *o*-, *m*- or $p\text{-}C_6H_4NO_2$, $Bz = C_6H_5CH_2$). The chloro ligand in $[Au(o\text{-}C_6H_4NO_2)Cl]^-$ can be replaced by bromo or iodo ligands by use of NaBr or NaI. The anions $[Au(R)Cl]^-$ react with neutral monodentate ligands, L, to give neutral mononuclear complexes [Au(R)L] ($R = o\text{-}C_6H_4NO_2$, $L = PPh_3$, $AsPh_3$; $R = m\text{-}C_6H_4NO_2$, $L = PPh_3$) and with 1,2-bis(diphenylphosphino)ethane (dpe) to give $[Au_2(R)_2(dpe)]$ ($R = o\text{-}C_6H_4NO_2$). The corresponding $[Au(p\text{-}C_6H_4NO_2)Cl]^-$ reacts with PPh_3 or $AsPh_3$ to give mixtures containing [AuClL]. The anionic *ortho*-nitrophenylgold(I) complex is much more stable than its *meta*- or *para*-nitrophenyl isomers. These are thought to be the first reports of nitrophenylgold(I) complexes.

Introduction

Most arylgold(I) complexes are of the type [Au(R)L], and they have mainly been prepared from organolithium or Grignard reagents [1–3]. A route involving $[Au(Me)PPh_3]$, HBF_4 and organomercury compounds [4] allows the synthesis of complexes of the types $[R(AuPPh_3)_2]BF_4$ or $[Au(R)PPh_3]$ depending on the nature of the aryl group R.

We describe here a new way of obtaining (halo)arylaurate(I) complexes using organomercury compounds as arylating agents. The only reported [2,3] anionic complexes of the type $[Au(R)X]^-$ are pentafluorophenyl derivatives, which were prepared by a two-step sequence:

$$[AuCl(tht)] + RLi \rightarrow [Au(R)(tht)] \xrightarrow[-tht]{+X^-} [Au(R)X]^-$$

(where tht = tetrahydrothiophene and $R = C_6F_5$)

Our method allows the synthesis of this type of complexes in a single step, and avoids the use of organolithium compounds, which are not suitable for the synthesis

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of all organogold(I) complexes. Thus for example, *ortho*-, *meta*- and *para*-nitrophenyl lithium are highly unstable [5] because of the presence of the reactive nitro group, and only the *ortho*-substituted derivative has been prepared in good yield. We have been able to make *ortho*- *meta*- and *para*-nitrophenylgold(I) complexes, and these make possible a study of the dependence of the stabilities of those organogold(I) complexes on the position of the nitro group in the phenyl ring.

Furthermore, starting from the anionic complexes we have been able to make the neutral complexes [Au(R)L].

An additional objective in this work was to extend the use of organomercury compounds to the preparation of organogold(I) complexes, as we have done to the preparation of gold(III) [6,7] and tin(IV) [8].

Results and discussion

Anionic complexes

When equimolecular amounts of $[BzPh_3P][AuCl_2]$ and $[Hg(o\text{-}C_6H_4NO_2)_2]$ are refluxed in acetone for 15 h a transmetallation reaction occurs:

$$[AuCl_2]^- + [HgR_2] \rightarrow [Au(R)Cl]^- + [Hg(R)Cl]$$

This gives the anionic complex $[BzPh_3P][Au(o\text{-}C_6H_4NO_2)Cl]$ (I) along with unreacted $[BzPh_3P][AuCl_2]$ which is always present even when an excess of $[HgR_2]$ (Au/Hg = 1/2.5) is used and the reflux is maintained for three days. We were unable to resolve this mixture because of the similar solubilities of the two complexes. In order to displace the above equilibrium we used Me_4NCl as a symmetrizing agent to give the insoluble salt $(Me_4N)_2[Hg_2Cl_6]$:

$$4[Hg(R)Cl] + 2Cl^- \rightarrow 2[HgR_2] + [Hg_2Cl_6]^{2-}$$

In this way the reaction is completed after 6 h refluxing in acetone and a half of the $[HgR_2]$ used can be recovered.

Alternatively we used [Hg(R)Cl] as the reagent, according to the equation:

$$2[AuCl_2]^- + 2[Hg(R)Cl] + 2Cl^- \rightarrow 2[Au(R)Cl]^- + [Hg_2Cl_6]^{2-}$$

In practice we always use a moderate excess of $[HgR_2]$ or [Hg(R)Cl] and a great excess of Me_4NCl over the stoichiometric amounts (see Experimental). While this paper was being written the same technique was reported for the synthesis of ethynylplatinum(II) complexes [9].

When $[AuCl_2]^-$ and $[Hg(m\text{-}C_6H_4NO_2)_2]$ are mixed in acetone solution at room temperature a copious precipitation of metallic gold is observed. If the temperature is lowered to −50°C the starting complexes are recovered after 6 h stirring. However a clean transmetallation reaction occurs when the temperature is maintained at 0–4°C for 30 h and gives the anionic complex $[BzPh_3P][Au(m\text{-}C_6H_4NO_2)Cl]$ (II). At room temperature II slowly decomposes in solution or in the solid state to give metallic gold.

If $[Hg(p\text{-}C_6H_4NO_2)_2]$ is used as arylating agent the transmetallation occurs to give $[BzPh_3P][Au(p\text{-}C_6H_4NO_2)Cl]$ (III) along with a substantial amount of metallic gold irrespective of whether the reaction is carried out in acetone under reflux (1 h), at room temperature (1 h), or at 0°C (24 h). In all cases the yields of III are approx. 30–40%. III is stable in the solid state and in solution only when it is pure, otherwise

TABLE 1

ANALYTICAL AND OTHER DATA FOR COMPLEXES I–IX

Complex [a]		M.p. (°C)	Colour	Λ_M [c]	Analyses (Found (calc.) (%))				Yield (%)
					C	H	N	Au	
$[BzPh_3P][AuRCl]$	(I)	145	yellow	85	51.98 (52.59)	3.84 (3.70)	2.11 (1.98)	27.98 (27.82)	90
$[BzPh_3P][AuR'Cl]$	(II)	[b]	white	94	52.60 (52.59)	3.65 (3.70)	1.97 (1.98)	26.30 (27.82)	66
$[BzPh_3P][AuR''Cl]$	(III)	125(d)	white	102	53.30 (52.59)	3.87 (3.70)	1.78 (1.98)	27.25 (27.82)	37
$[BzPh_3P][AuRBr]$	(IV)	124	yellow	93	50.71 (49.49)	3.48 (3.48)	1.94 (1.86)	25.63 (26.18)	72
$[BzPh_3P][AuRI]$	(V)	103	yellow	86	46.59 (46.58)	3.24 (3.28)	1.95 (1.75)	24.78 (24.64)	76
$[AuR(PPh_3)]$	(VI)	133	yellow	0	49.55 (49.58)	3.38 (3.29)	2.73 (2.41)	33.51 (33.88)	68
$[AuR'(PPh_3)]$	(VII)	153(d)	white	0	48.63 (49.58)	3.30 (3.29)	2.52 (2.41)	33.88 (33.88)	60
$[Au_2R_2(dpe)]$	(VIII)	172	yellow	0	44.31 (44.03)	3.14 (3.11)	2.79 (2.70)	36.77 (38.00)	62
$[AuR(AsPh_3)]$	(IX)	104	yellow	3	46.41 (46.17)	3.17 (3.06)	2.57 (2.44)	31.60 (31.50)	51

[a] R = o-$C_6H_4NO_2$, R′ = m-$C_6H_4NO_2$, R″ = p-$C_6H_4NO_2$. [b] See text. [c] On approx. 10^{-4} *M* solution in acetone, (ohm^{-1} cm^2 mol^{-1}).

slow decomposition takes place. The well known stabilization effect of *ortho*-substituents in aryl complexes (*ortho* effect) [7,10] is evident.

Complexes I–III show a strong IR band at approx. 300 cm^{-1} (I 309, II 303 and III 302 cm^{-1}) assignable to ν(AuCl).

Starting from I, it is possible to replace the chloro ligand by bromo or iodo using NaX salts, to give $[BzPh_3P][Au(o\text{-}C_6H_4NO_2)X]$ (X = Br (IV), I (V)). All the anionic complexes (I–V) show molar conductivities as expected for 1 : 1 electrolytes.

Neutral complexes

When complexes I or II are treated with PPh_3 in acetone neutral complexes $[Au(R)(PPh_3)]$ (R = $o\text{-}C_6H_4NO_2$ (VI), $m\text{-}C_6H_4NO_2$ (VII)) can be isolated.

$$[Au(R)Cl]^- + PPh_3 \rightarrow [Au(R)(PPh_3)] + Cl^-$$

However, the reaction of III with PPh_3 proceeds differently, and only $BzPh_3PCl$ can be isolated as a pure compound. A mixture of $[AuCl(PPh_3)]$ and other compound(s) containing the $p\text{-}C_6H_4NO_2$ group (IR) is also obtained and cannot be separated. Use of $AsPh_3$ gives similar results.

We made several attempts to prepare the corresponding $[Au(R)(PPh_3)]$ complex: (a) We tried to prepare $[Au(R)OClO_3]^-$ in situ by treating III with $NaClO_4$ or $AgClO_4$ thinking that the desired complex would then be formed upon addition of PPh_3. Using $NaClO_4$ we isolated $[BzPh_3P]ClO_4$, NaCl and the same mixture containing $[AuCl(PPh_3)]$, with $AgClO_4$ there was immediate precipitation of metallic gold; (b) by reacting $[AuCl(PPh_3)]$ with $[Hg(p\text{-}C_6H_4NO_2)_2]$ in refluxing acetone, but the starting gold complex was recovered almost quantitatively.

The reaction of I with 1,2-bis(diphenylphosphino)ethane (dpe) gave the dinuclear complex $[Au_2(o\text{-}C_6H_4NO_2)_2(dpe)]$ (VIII). When $AsPh_3$ was used only 7% yield of $[Au(o\text{-}C_6H_4NO_2)(AsPh_3)]$ (IX) was obtained along with unreacted I even when a large excess of the ligand is used. The corresponding equilibrium can be displaced by reacting I with $AsPh_3$ (1/2) in the presence of $NaClO_4$ $[(I)/NaClO_4 = 1/2]$ in tetrahydrofuran.

The neutral complexes VI–IX are stable at room temperature in the solid state and in solution, and also towards atmospheric moisture and daylight.

All the complexes show IR bands assignable to the NO_2 group, and these appear in the expected ranges for nitroaryl compounds ($\nu_{asym}(NO_2)$, 1490–1505 and $\nu_{sym}(NO_2)$, 1330–1340 cm^{-1}). This and the fact that no significant differences are observed between the three types of substituted derivatives may indicate that there is no appreciable intramolecular O ··· Au interaction in the *ortho*-substituted aryl complexes [7].

Table 1 presents analytical and other data for complexes I–IX.

Experimental

IR spectra were recorded on Perkin–Elmer 457 and a Nicolet MX-1 spectrophotometers using Nujol mulls between polyethylene sheets or KBr pellets. Conductivities were measured with a Phillips 9501 conductimeter. Melting points were determined on a Reichert apparatus and are uncorrected. C, H and N analyses were carried out with a Perkin–Elmer 240C microanalyzer. Au was determined by ashing the samples with an aqueous solution of hydrazine. Solvents were distilled before use.

$[BzPh_3P][Au(o\text{-}C_6H_4NO_2)Cl]$ (I)

A mixture of $[BzPh_3P][AuCl_2]$ (205.6 mg, 0.40 mmol), $[Hg(o\text{-}C_6H_4NO_2)_2]$ (115.1 mg, 0.26 mmol) and Me_4NCl (102 mg, 0.93 mmol) is refluxed in acetone (30 ml) for 6 h. The suspension is then concentrated to dryness, methylene chloride (8 ml) is added, and the suspension refluxed for further 30 min. It is then filtered and concentrated to 3 ml. Slow addition of diethyl ether gives a solid, which is filtered and washed with diethyl ether to give I.

$[BzPh_3P][Au(m\text{-}C_6H_4NO_2)Cl]$ (II)

To a cold (0°C) solution of $[BzPh_3P][AuCl_2]$ (85.6 mg, 0.14 mmol) in acetone (60 ml) $[Hg(m\text{-}C_6H_4NO_2)_2]$ (62.1 mg, 0.14 mmol) is added and the suspension stirred under nitrogen for 30 h at a temperature of 2–4°C. The resulting solution is concentrated to 10 ml under vacuum and filtered into cold diethyl ether (75 ml). The solution is cooled at −20°C to give a solid which is filtered off and washed with cold ether to give II.

$[BzPh_3P][Au(p\text{-}C_6H_4NO_2)Cl]$ (III)

To a solution of $[BzPh_3P][AuCl_2]$ (260 mg, 0.42 mmol) in cold acetone (20 ml, 0°C) $[Hg(p\text{-}C_6H_4NO_2)_2]$ (186 mg, 0.42 mmol) is added and the suspension stirred under nitrogen for 24 h at 0–4°C. The suspension is then concentrated to 10 ml and filtered into diethyl ether (50 ml). The resulting solid is recrystallized from methylene chloride/diethyl ether to give III.

$[BzPh_3P][Au(o\text{-}C_6H_4NO_2)Br]$ (IV)

NaBr (18.4 mg, 0.18 mmol) and I (80 mg, 0.11 mmol) are allowed to react in acetone (5 ml) at room temperature for 12 h. The resulting suspension is concentrated to dryness and the solid extracted with methylene chloride (4 ml). The extract is filtered and diethyl ether is added, to give a precipitate, which is filtered off and washed with diethyl ether to give IV.

$[BzPh_3P][Au(o\text{-}C_6H_4NO_2)I]$ (V)

NaI (25.2 mg, 0.17 mmol) and I (80 mg, 0.11 mmol) are allowed to react in acetone (4 ml) at room temperature for half an hour. The resulting suspension is treated as described for IV to give V.

$[Au(R)(PPh_3)]$ ($R = o\text{-}C_6H_4NO_2$ (VI), $m\text{-}C_6H_4NO_2$ (VII))

To a solution of I or II (75.8 mg, 0.11 mmol) in acetone (4 ml) is added a solution of PPh_3 (33.4 mg, 0.13 mmol) in acetone (4 ml). The resulting suspension is concentrated to 2 ml and diethyl ether (10 ml) is added. The solution is filtered, and concentrated to 3 ml, and n-hexane is added to give VI or VII.

$[Au_2(o\text{-}C_6H_4NO_2)_2(dpe)]$ (VIII)

To a solution of I (74.4 mg, 0.10 mmol) in acetone (4 ml) is added dpe (23 mg, 0.06 mmol). The resulting suspension is treated as described for VI or VII to give VIII.

$[Au(o\text{-}C_6H_4NO_2)(AsPh_3)]$ (IX)

I (144.6 mg, 0.20 mmol), $AsPh_3$ (126 mg, 0.41 mmol) and $NaClO_4$ (51 mg, 0.42

mmol) are allowed to react in THF (1 ml) at room temperature for 3 h. Diethyl ether (15 ml) is then added and the suspension filtered. The filtrate is concentrated to 2 ml and n-pentane is added to give IX.

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