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PREPARATION AND PROPERTIES OF ARYLGOLD COMPOUNDS. SCOPE AND LIMITATIONS OF THE AURATION REACTION

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Summary

Several ligand-free monoarylgold dichlorides $(R—C_6H_4—AuCl_2)_2$ (R = H, Me, Et, i-Pr, t-Bu, Ph) have been prepared from arenes and $AuCl_3$; contrary to earlier reports, addition of ligands is not necessary in order to obtain thermally stable products. The auration is inhibited if the arenes contain potentially coordinating substituents. The properties and reactions of the arylgold dichlorides are discussed.

Introduction

The first synthesis of monoarylgold(III) compounds was reported by Kharasch [1,2], who described the so-called auration reaction:

(R = H, CH_3, C_6H_5, 1-OH-2-$COOCH_3$, 1-NO_2-2-OCH_3)

Except for R = H, the compounds were isolated as monomeric hydrates $R—C_6H_4—AuCl_2 \cdot H_2O$.

This reaction is of interest as potential route to arylgold compounds (cf. mercuration). Liddle and Parkin [3,4], when reinvestigating Kharasch's work, isolated the products as ligand-stabilized arylgold compounds, since they considered the ligand-free compounds to be unstable. Recently some of Kharasch's results have been questioned [5]. In this paper we describe the reactions of gold(III) chloride with a series of substituted benzenes in the absence of stabilizing ligands. Arenes containing both hydrocarbon substituents and substituents having a potentially coordinating atom or group were used as substrates.

Results and discussion

Reaction of $AuCl_3$ with hydrocarbon-substituted benzenes

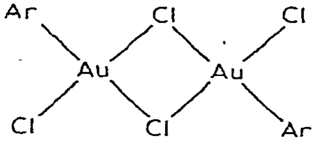
When a large excess of an aromatic hydrocarbon is added to a suspension of $AuCl_3$ in CCl_4 at room temperature, the suspension usually turns red/brown immediately. When after a short time diethyl ether is added to stop the reaction, a yellow solution containing the ether complex of the monoarylgold dichloride is obtained, together with a brown precipitate of an ether complex of $HAuCl_4$:

$$ArH + (AuCl_3)_2 \xrightarrow[2.\,Et_2O]{1.\,CCl_4} ArAuCl_2 \cdot Et_2O + HAuCl_4 \cdot xEt_2O \downarrow$$

Contrary to Kharasch's observations, very little HCl evolution takes place. Following low temperature work-up, the filtered solutions yield yellow ligand-free monoarylgold dichlorides.

Characterization of the isolated reaction products

Molecular weight determinations of compounds I and IV by cryoscopy in benzene showed them to be dimeric, probably involving intramolecular gold—chlorine coordination, analogous to alkylgold(III) halides [6]:



The remaining compounds are assumed also to be dimeric.

TABLE 1

SPECTROSCOPIC DATA AND DECOMPOSITION TEMPERATURES FOR MONOARYLGOLDDICHLORIDES

Compound	IR (cm^{-1})				NMR (δ in ppm)			Dec. temp. (°C)
	C—Au [a]		Au—Cl		Aryl	Side-chain		
$C_6H_5AuCl_2$ [b] (I)	448	377	368	322	7.15 [d] 7.35 [e]			130
4-Me—$C_6H_4AuCl_2$ (II)	489	378	365		7.11, 7.14, 7.45, 7.48 [f, g]	2.56		90
4-Et—$C_6H_4AuCl_2$ (III)	501	377		320	6.88 [h]	2.52	1.17	120
4-i-Pr—$C_6H_4AuCl_2$ (IV)	460	369		319	7.00 [i]	2.92	1.20	155
4-t-Bu—$C_6H_4AuCl_2$ (V)	460	364		331	6.96, 7.04, 7.12, 7.20 [d, g]	1.25		45
4-Ph—$C_6H_4AuCl_2$ (VI)	500	368			7.2-7.5 [i]			80
$C_6H_5AuCl_2 \cdot py$ [c]	478	357	355					155
4-Me—$C_6H_4AuCl_2 \cdot py$ [c]	495	362	355					164

[a] Y mode (Whiffen) [7]. [b] Described by Kharasch [1]. [c] According to [3]. [d] In DMF. [e] In Et_2O. [f] In CCl_4. [g] *AA'BB'* pattern. [h] In DMSO. [i] In $CDCl_3$.

The IR spectra of the isolated monoarylgold dichlorides show the presence of gold—chlorine and gold—carbon [7] bonds, in agreement with the IR data for some monomeric $RAuCl_2 \cdot L$ complexes [3], and are in accord with *para* substitution. All other frequencies of $(PhAuCl_2)_2$ fit the assignments given by Whiffen [7], and those for PhCu [8] and PhAg [9]. In view of the fact that the reaction is likely to proceed via electrophilic attack of the metal salt on the aromatic system, as in mercuration [10], thallation [11] and plumbylation [12], one would expect in addition to the *para* isomer some of *ortho* and, to a much lesser extent, *meta* isomer. However, the electronic effects of the ring substituents in combination with large steric effects due to the bulky incoming gold species will lead to very small partial-rate factors for their formation. The total absence of the *meta* and *ortho* isomers cannot be inferred from the IR data, but for the case in which steric factors are least important, viz. II, the ^{13}C NMR spectrum of the PPh_3 complex shows the exclusive presence of the *para* isomer.

In the PMR spectra the aromatic protons appear as a complicated multiplet. The absence of an *ortho* shift in these arylgold compounds, in contrast to the large downfield shift in the corresponding ArCu and ArAg [9] compounds, may be accounted for by the low polarity [13,14] of the gold—carbon bond [15].

Properties of monoarylgold dichlorides

Thermal behaviour. The decomposition temperatures of the ligand-free arylgold dichlorides are lower than or about equal to those of the corresponding compounds $ArAuCl_2 \cdot L$ [3,4] (cf. Table 1), but the significance of this observation is questionable since it is known [9] that the thermal stability of group IB arylmetal compounds is considerably reduced by the presence of small amounts of impurities.

The thermal decomposition products of solid $PhAuCl_2$ (I) were found to be metallic gold, monochlorobenzene (95%), 1,4-dichlorobenzene (3%) and traces of polychlorinated benzene and of 1,2- and 1,3-dichlorobenzene. Products II—VI decomposed similarly to give mainly 4-chloroarenes. Notably, there was no formation of biaryls, which would be expected if radical processes occurred. Other possibilities, e.g. reductive elimination of ArCl and/or reductive eliminatio of chlorine followed by attack of the free halogen on ArAu(I) are under investigation.

We believe the thermal instability of the $ArAuCl_2$ compounds to be the main reason for the low preparative yields (see Table 2). If the reaction is allowed to continue (i.e. when no ether is added), it finally yields only polychlorinated arenes (cf. [1]), in a process probably involving unstable polyauration products $Ar(AuCl_2)_n$ (cf. polymercurated products [16]). This reaction will consume some of the formed $ArAuCl_2$ in the short interval preceding ether addition.

Chemical reactions. In protic solvents such as MeOH fast decomposition to the parent arenes occurs. In some cases, viz. II, III and V, the auration products are unstable in $CHCl_3$. Addition of D_2O (or H_2O) results in almost immediate decomposition, but no ArD (or ArH) is formed. Instead, only ArCl is found, which suggests that water coordination occurs and that this leads to accelerated decomposition. This may explain why Kharasch's work-up procedure, involving water, gave very low yields. The products appear to be insensitive to oxygen.

In benzene the pure dimeric products react readily with phosphine ligands, forming complexes of the type $ArAuCl_2 \cdot L$, identical to those described by Liddle and Parkin [3,4].

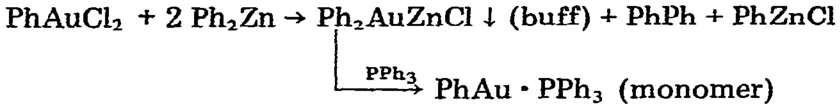
Although SO_2 is known to insert into the silver—carbon bond of ArAg compounds [9] and into the gold—carbon bond of 2-vinylphenylgold · PPh_3 [17], $(4\text{-}i\text{-}Pr{-}C_6H_4{-}AuCl_2)_2$ (IV) appears not to react with sulfur dioxide and under our conditions the starting material was recovered unchanged.

We also treated $(PhAuCl_2)_2$ with CO, as a possible route to PhAu(I):

$$PhAuCl_2 + CO \rightarrow PhAu + COCl_2$$

($AuCl_3$ is known to react with CO at elevated temperatures to give AuCl [18]). No reaction was observed between $PhAuCl_2$ and CO at 0°C during 20 h, at 1 atm or 40 atm CO pressure. Higher temperatures could not be used because of thermal decomposition of $PhAuCl_2$.

We did succeed in synthesizing phenylgold(I) compounds from $PhAuCl_2$ and Ph_2Zn. Addition of PPh_3 to the buff-coloured reaction product from $PhAuCl_2$ and Ph_2Zn gave $PhAu \cdot PPh_3$ [cf. 19]. Addition of a large excess of diphenylzinc to $PhAuCl_2$ gave red Ph_3AuZn [20]:



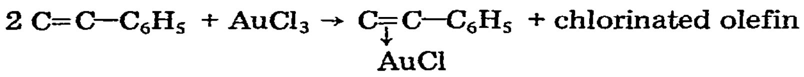
$$\begin{aligned} &PhAuCl_2 + 2\,Ph_2Zn \rightarrow Ph_2AuZnCl\downarrow \text{ (buff)} + PhPh + PhZnCl \\ &\qquad\qquad\qquad\qquad\qquad \xrightarrow{PPh_3} PhAu \cdot PPh_3 \text{ (monomer)} \end{aligned}$$

$$PhAuCl_2 + 3\,Ph_2Zn \rightarrow Ph_3AuZn\downarrow \text{ (red) (cyclic dimer)}$$

The phenylgoldzinc compounds obtained this way are identical to those made by the reaction of Ph_2Zn with $AuCl_3$ or AuCOCl [20]. The reactions of these arylgoldzinc compounds with mono- and bidentate ligands will be reported later.

Reactions of $AuCl_3$ with arenes containing a potentially coordinating substituent

Aromatic olefins. In these cases no simple auration takes place, and other reactions occur which depend on the nature of the substituent. When this is an olefinic group, a complex between AuCl and the arene is formed, evidently because reduction of $AuCl_3$ is preferred over the auration:

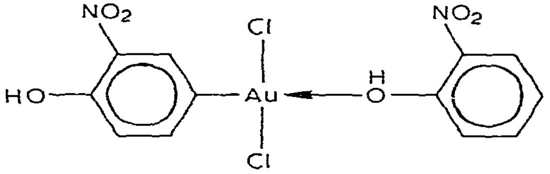


$$2\,C{=}C{-}C_6H_5 + AuCl_3 \rightarrow \underset{\substack{\downarrow \\ AuCl}}{C{=}C}{-}C_6H_5 + \text{chlorinated olefin}$$

With styrene at —20°C, a cream-coloured product was isolated which according to analysis and IR spectra is a π complex of styrene and AuCl. The complex is unstable above 0°C, and above 70°C it decomposes immediately into gold and a monosubstituted aryl compound containing chlorine but no olefinic group. The mechanism of the initial reduction of $AuCl_3$ by styrene may be similar to that accepted for the reduction of $CuCl_2$ in the chlorination of olefins by this compound [21]. Formation of olefin—gold(I) complexes from $AuCl_3$ and aliphatic olefins has been described by Hüttel and coworkers [22]. Reaction of $AuCl_3$ with allylbenzene yielded a similar π complex, which has an even lower thermal stability, and decomposes immediately above 10°C.

Arylcyanides. Treatment of $AuCl_3$ with cyanobenzenes gives results confirming Calderazzo's statement that coordination complexes of the type $R—C_6H_4—C{\equiv}N \cdot AuCl_3$ are formed [5].

Nitrophenols, nitrobenzene and phenol. The foregoing results seem to suggest that the presence of any, even weakly, coordinating substituent in the aromatic substrate prevents the auration. It was therefore surprising that nitrophenols and $AuCl_3$ react to form auration products. Auration of *o*-nitrophenol resulted in the formation of an orange product. Analysis, IR and PMR spectra indicate the following structure:



Metathesis with iodine produced 1-iodo-3-nitro-4-hydroxybenzene and *o*-nitrophenol in a 1 : 1 ratio, in accord with the proposed structure. Auration of *p*-nitrophenol yielded a similar product, the substitution occurring *ortho* to the OH group. On the other hand, the auration of phenol did not lead to a well-defined arylgold species. Neither did nitrobenzene undergo auration, confirming earlier observations [1]. In view of these apparently anomalous results, the study of the scope of the auration reaction is being continued.

Conclusion

The auration of alkyl-substituted arenes leading to monoarylgold(III) compounds shows features consistent with its being an electrophilic aromatic substitution. Auration is, however, not as versatile a synthetic tool as mercuration, since the normal reaction is inhibited by the presence of an even weakly coordinating group.

Experimental

Unless stated otherwise, experiments were carried out under dry, oxygen-free nitrogen. NMR spectra were recorded on a Varian HA-100 spectrometer at —30°C by Miss T. Volp. IR spectra were recorded at 0°C with a Perkin—Elmer 457 spectrometer. Decomposition temperatures were determined on a Kofler Hotstage. Analyses were carried out under supervision of Mr. W.J. Buis at the microanalytical department of the Institute for Organic Chemistry, TNO, Utrecht. Solvents were purified and stored under nitrogen.

Gold trichloride was prepared in batches of 15 g using the standard procedure [23]. Chlorine was passed over finely divided gold in a glass tube at 250°C. The product, crystallizing in long ruby-red needles, was sufficiently pure for our purposes. Analysis found: Au, 64.5; Cl, 35.0. $AuCl_3$ calcd.: Au, 64.93; Cl, 35.06%.

Phenylgold dichloride (general auration procedure): To a suspension of finely powdered $AuCl_3$ (3.0 g, 10 mmol) in CCl_4 at 20°C was added 3.5 g (45 mmol) of benzene (generally a 4—10 fold excess of arene was used). After one minute, during which the mixture turned red/brown, 20 ml of diethyl ether was added. The clear yellow solution was separated from the brown deposit ($HAuCl_4 \cdot xEt_2O$). Evaporation of the solvent yielded a dark yellow product from which pure $(PhAuCl_2)_2$ was isolated by extraction with ether. The ether was removed and the residue was washed several times with pentane to remove decomposition products. Alternatively, pentane was added at —70°C to the partially evaporated ether solution, yielding a colourless precipitate containing ether. When stored under vacuum the precipitate gave the yellow $(PhAuCl_2)_2$.

Reactions of arylgold dichlorides

Reaction with sulfur dioxide. About 0.2 g of IV was kept for 3 h at —50°C in contact with a large excess of liquid SO_2, in which it is partially soluble. Slow evaporation of the SO_2 yielded unchanged starting material.

Reaction with carbon monoxide. CO was bubbled through a solution of 0.2 g of $PhAuCl_2$ in ether at 0°C. After 24 h the solvent was evaporated. The IR spectrum of the residue was identical with that of the starting compound, except for 2 very weak absorptions in the region of coordinated CO (2165 and 2185 cm^{-1}). No phosgene was evolved. Alternatively, 0.2 g of $PhAuCl_2$ in ether was treated for 16 hours at 0°C with CO at 40 atm. Again, the only difference between starting compound and product was the presence of two very weak CO bands in the IR spectrum, indicating the presence of a very small amount of coordinated CO.

Reaction with diphenylzinc. A twofold excess of Ph_2Zn in Et_2O was added to a solution of 0.2 g of $PhAuCl_2$ at —40°C. The solution turned black, and a brownish precipitate was slowly formed. The unstable (dec. 50°C) dry material which was obtained after three washings with ether, was treated with PPh_3 in ether. Extraction of the resulting brown material with ether followed by evaporation of the ether and several washings of the residue with pentane gave cream-

TABLE 2

DETAILS OF THE AURATIONS

Compound	Colour	Yield (%)	Analysis found (calcd.) (%)				Reaction time [a] (min)	T (°C)
			C	H	Au	Cl		
I	dark yellow	35	20.4 (20.89)	1.5 (1.46)	56.7 (57.09)	20.5 (20.52)	1	20
II	dark yellow	30	24.1 (23.57)	2.6 (1.96)	50.2 (54.67)	19.8 (19.71)	1/3	20
III	dark yellow	25	26.7 (25.75)	2.7 (2.43)	50.7 (52.80)	20.4 (19.01)	3	20
IV	light yellow	45	28.9 (27.92)	2.9 (2.86)	49.3 (50.89)	18.3 (18.32)	5	20
V	light yellow	50	30.9 (29.95)	3.3 (3.26)	48.0 (49.11)	16.6 (17.67)	3	0
VI	dark yellow	25	36.1 (34.22)	2.0 (2.15)	44.5 (46.7)	16.8 (16.84)	2	20

[a] Time between mixing the reactants and adding ether to stop the reaction.

coloured $PhAu \cdot PPh_3$, melting point 160°C (lit. [19] 164°C); the IR spectrum was identical with that of an authentic sample.

When a 4-fold excess of Ph_2Zn was added to a solution of $PhAuCl_2$ in ether at —40°C, a red compound was formed. This compound was shown to be impure Ph_3AuZn, by comparison with Ph_3AuZn obtained via reaction of AuCOCl and Ph_2Zn.

Styrene—AuCl complex

Adding styrene (13 g, 12.6 mmol) to $AuCl_3$ (1.9 g, 6.3 mmol) in 15 ml CCl_4 yielded a cream-coloured deposit when ether was injected after 3 h at —20°C. After 2 washings with pentane 1.2 g (3.6 mmol, 55%) of a crystalline product was obtained. Due to thermal instability no satisfactory analysis could be obtained.

Stirring styrene in ether with AuCl during 5 h at —20°C gave a colourless compound having an IR spectrum superimposable upon that of the starting materials (C=C shift 1630 → 1599 cm^{-1}, Au—Cl 330 cm^{-1}, no Au—C frequencies).

Cyanobenzene—AuCl$_3$ complexes

Yellow compounds were obtained using the general auration procedure. The same material was obtained when no ether was added. Use of an excess of $AuCl_3$ also failed to produce any auration product. $C_6H_5CN \cdot AuCl_3$ analysis found: C, 20.3, H, 1.2, Au, 49.1; Cl, 25.4; N, 3.3. $C_7H_5AuCl_3N$ calcd.: C, 20.69; H, 1.24; Au, 48.46; Cl, 26.17; N, 3.44%. Dec. temp. 153°C.

Auration of o-nitrophenol

Under the normal auration conditions, 3.25 mmol $AuCl_3$ and 1.5 mmol *o*-nitrophenol in 5 ml CCl_4 gave an orange-yellow solution from which an extremely hygroscopic compound was obtained by ether addition after 10 minutes. Analysis found: C, 24.5; H, 1.8; Au, 36.5; Cl, 15.3; N, 4.4; O, 17.4. $C_{12}H_9AuCl_2N_2O_6$ calcd.: C, 26.44; H, 1.66; Au, 36.14; Cl, 13.01; N, 5.14; O, 17.61%. IR: 435 (Au—C), 1539, 1330 ($ArNO_2$), 1190 (ArOH) 872, 835, 750 cm^{-1}.

Iodine in $CDCl_3$ was added to the dry compound to give a solution with an NMR-spectrum which was a superposition of the spectra of *o*-nitrophenol and 1-iodo-3-nitro-4-hydroxybenzene.

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