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DIHALOPERHALOARYL(TRIPHENYLARSINE)GOLD(III) COMPLEXES

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Summary

When $C_6Cl_5AuAsPh_3$ reacts with halogens, oxidation of the gold(I) complex and formation of $X_2Au(C_6Cl_5)AsPh_3$ (X = Cl, Br, I) take place. However, when $C_6F_5AuAsPh_3$ reacts with halogens, oxidation is only observed in the case of Cl_2, whilst I_2 (totally) and Br_2 (partially) split the Au—C bond. This behaviour is contrary to that observed with $C_6F_5AuPPh_3$ and halogens, where the tendency to split the Au—C bond decreases in the sequence Cl > B > I.

Introduction

The only dihaloperhaloaryl derivatives of gold(III) described hitherto are $Br_2Au(C_6F_5)PPh_3$ [1], and $Cl_2Au(C_6F_5)PPh_3$ [2], and further, the complexes of general formula $X_2Au(Ar_x)PPh_3$ (Ar_x = C_6F_5, C_6Cl_5, and X = Cl, Br, I) prepared by us.

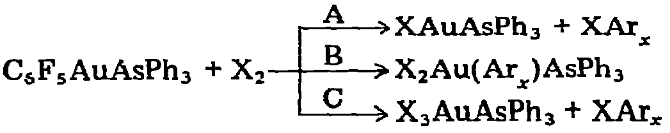
As far as we know, all such compounds prepared previously had triphenylphosphine as a ligand. In this study we describe the oxidation of $Ar_xAuAsPh_3$ complexes with halogens or with thallium(III) chloride, resulting in the isolation of the corresponding dihalides, $X_2Au(Ar_x)AsPh_3$.

Results and discussion

Oxidation reactions with halogens or with $TlCl_3$

The results of the oxidation reactions under various conditions are collected in Table 1.

When Ar_x = C_6F_5, and the oxidation is carried out with halogen, the reaction may take three different courses:



$$C_6F_5AuAsPh_3 + X_2 \begin{cases} \xrightarrow{A} XAuAsPh_3 + XAr_x \\ \xrightarrow{B} X_2Au(Ar_x)AsPh_3 \\ \xrightarrow{C} X_3AuAsPh_3 + XAr_x \end{cases}$$

TABLE 1

OXIDATION OF $Ar_xAuAsPh_3$ WITH HALOGENS OR $TlCl_3$

$Ar_xAuAsPh_3$	Oxidant	Reaction Products
$C_6F_5AuAsPh_3$	Cl_2 (1.6/1)	*trans*-$Cl_2Au(C_6F_5)AsPh_3$
$C_6F_5AuAsPh_3$	Br_2 (1.5/1)	$Br_3AuAsPh_3$ + $Br_2Au(C_6F_5)AsPh_3$
$C_6F_5AuAsPh_3$	I_2 (2/1)	$I_3AuAsPh_3$ + $IAuAsPh_3$
$C_6F_5AuAsPh_3$	$TlCl_3$ (1/1)	*cis*-$Cl_2Au(C_6F_5)AsPh_3$ + TlCl
$C_6Cl_5AuAsPh_3$	Cl_2 (1.75/1)	*trans*-$Cl_2Au(C_6Cl_5)AsPh_3$ [a]
$C_6Cl_5AuAsPh_3$	Br_2 (2.5/1)	$Br_2Au(C_6Cl_5)AsPh_3$
$C_6Cl_5AuAsPh_3$	I_2 (2/1)	$I_2Au(C_6Cl_5)AsPh_3$
$C_6Cl_5AuAsPh_3$	$TlCl_3$ (1/1)	*cis*-$Cl_2Au(C_6Cl_5)AsPh_3$ + TlCl

[a] Crystallizes with ca. 1 mole CCl_4.

Process A takes place with increasing probability according to the sequence Cl < Br < I, which is the exact opposite of the tendency observed [3] with PPh_3 as opposed to $AsPh_3$ as a ligand.

When $Ar_x = C_6Cl_5$ only the dihalides can be isolated, although the dibromo and diiodo derivatives are obtained in low yields. The sole products which could be separated by column chromatography are listed in Table 1. Attempts to crystallize characterizable products from other fractions proved unsuccessful and ill-defined oils remained after the evaporation of the solvent.

Oxidation with $TlCl_3$ leads to the respective dichlorides. The resulting isomer is, as when PPh_3 acts as a ligand [3], different from the isomer obtained by direct chlorination. It was not possible to assign structures to the dibromides and diiodides, since in these cases the metal—halogen vibrations are beyond the range of our spectrophotometer.

The *trans*-$Cl_2Au(C_6Cl_5)AsPh_3$ compound, obtained by direct chlorination, crystallizes with approximately 1 mole of CCl_4. When this material was recrystallized from diethyl ether—dichloromethane, CCl_4 was eliminated, resulting in the *cis*-isomer. This can clearly be seen from the IR spectra and the melting points, which coincide with those of the product obtained by oxidation with $TlCl_3$. Isomerization to the *cis* form does not, however, take place after *trans*-$Cl_2Au(C_6F_5)AsPh_3$ is refluxed in chloroform.

Reactions with CH_3I

$(C_6F_5)AuAsPh_3$ reacts with CH_3I to give a mixture of products, which we were unable to separate and identify.

The reaction of $(C_6Cl_5)AuAsPh_3$ with CH_3I results in the formation of $IAu(C_6Cl_5)(CH_3)AsPh_3$. Two different species of crystals were isolated, one yellow (m.p. 168°) and the other orange-red (m.p. 146°), which coincided in their analyses and IR spectra, and so are likely to be isomers. We have not so far tried to make any structural assignment.

Analytical results

As may be seen from the data in Table 2 all the complexes are non-conducting in acetone solution, with the exception of $I_2Au(C_6Cl_5)AsPh_3$ and $IAu(C_6Cl_5)(CH_3)AsPh_3$, which show conductivities which, though perceptible,

TABLE 2

ANALYTICAL DATA

Complex	m.p. (°C)	Λ_M (ohm^{-1} cm^2 mol^{-1})	Found (calcd.) (%)				Mol. wt. found (calcd.)
		acetone	C	H	Au	Cl	
$C_6Cl_5AuAsPh_3$ (I)	198 (dec.)	0	38.16 (38.30)	1.94 (2.01)	26.66 (26.18)	22.47 (23.55)	701 (753)
trans-$Cl_2Au(C_6Cl_5)AsPh_3$ (II)	113-115	8.8	30.36 (30.72)	1.47 (1.55)	20.10 (20.15)		*b*
cis-$Cl_2Au(C_6Cl_5)AsPh_3$ (III)	218-220 (dec.)	0	33.87 (35.01)	1.78 (1.84)	23.79 (23.92)	29.18 (30.14)	811 (823)
$Br_2Au(C_6Cl_5)AsPh_3$ (IV)	130	2.0	30.85 (31.59)	1.58 (1.66)	20.78 (21.50)		913 (912)
$I_2Au(C_6Cl_5)AsPh_3$ (V)	125 (dec.)	32.9 [c]	28.08 (28.64)	1.51 (1.50)	20.15 (19.57)		972 (1006)
$IAu(C_6Cl_5)(CH_3)AsPh_3$ (VI)	168 146 [a]	24.9 [c]	33.88 (33.57)	1.85 (2.03)	23.59 (22.86)		*b*
$C_6F_5AuAsPh_3$ (VII)	160-162	0	43.15 (43.00)	2.32 (2.26)	29.35 (29.39)		676 (670)
trans-$Cl_2Au(C_6F_5)AsPh_3$ (VIII)	157-159 (dec.)	3.4	38.94 (38.89)	2.25 (2.04)	26.48 (26.58)		803 (741)
$Br_2Au(C_6F_5)AsPh_3$ (IX)	145	9.3	34.76 (34.73)	1.80 (1.82)	22.83 (23.73)		890 (830)

[a] M.p.'s of the yellow and the orange-red isomers respectively. [b] Not soluble enough for determination. [c] $\Lambda_M = 0$ in benzene.

are lower than those expected for 1/1 electrolytes in acetone solution (≈ 140 ohm^{-1} cm^2 mol^{-1}). The diiodide is non-conducting in benzene solution, and its molecular weight is in good agreement with the calculated value. The iodide is scarcely soluble in benzene and therefore its molecular weight could not be determined. All the complexes are monomeric in benzene.

IR spectra

The vibrations which could be assigned to the C_6Cl_5 group [3, 4] and which are not masked by vibrations of the triphenylarsine group are collected in Table 3.

The *cis*-dichloro derivatives $Cl_2Au(Ar_x)PPh_3$ [3] show two absorption bands at 312 m(br) and 295 m cm^{-1} ($Ar_x = C_6F_5$), and at 318 m and 294 m cm^{-1} ($Ar_x = C_6Cl_5$), whereas *trans*-$Cl_2Au(C_6Cl_5)PPh_3$ exhibits a single band at 365 m cm^{-1}. In the triphenylarsine complexes it was not possible to identify the bands characteristic of *cis*-isomers, since the absorptions of the triphenylarsine group are around 300 cm^{-1}. Nevertheless, the dichloro derivatives, obtained by direct chlorination, show an absorption at 365 m cm^{-1} [$Cl_2Au(C_6Cl_5)$-$AsPh_3$], or at 330 m cm^{-1} [$Cl_2Au(C_6F_5)AsPh_3$] which is assignable to ν(Au—Cl) in the *trans* isomers, in agreement with the above-mentioned observations [3].

$IAu(C_6Cl_5)(CH_3)AsPh_3$ exhibits bands at 2900 w and 2980 w cm^{-1} characteristic of CH_3. In the region 1150-1200 cm^{-1} where two bands due to the bending modes of the CH_3 group are to be found [5] the presence of bands due to the $AsPh_3$ prevents a definite assignment.

The spectrum of *trans*-$Cl_2Au(C_6Cl_5)AsPh_3$, prepared by direct chlorination of $C_6Cl_5AuAsPh_3$ in CCl_4, shows two bands at 760 m and 780 m cm^{-1}, not observed in any other complex. The position of these bands coincides with a very strong and broad band between 750 and 770 cm^{-1} which is observed in the spectrum of carbon tetrachloride. On recrystallizing the compound from diethyl ether—dichloromethane, the two bands, and also the band at 365 m cm^{-1}, disappear, which indicates that not only CCl_4 has been removed, but that the *trans*-isomer has also isomerised to *cis*-$Cl_2Au(C_6Cl_5)AsPh_3$. This was also confirmed by the melting point determination (Table 2).

TABLE 3

VIBRATIONS DUE TO THE LIGAND C_6Cl_5

Complex	Frequencies (cm^{-1})					
$C_6Cl_5AuAsPh_3$	1330 s	1320 vs	1290 s	1225 w	835 m	660 m
trans-$Cl_2Au(C_6Cl_5)AsPh_3$	1330 s [a]		1290 m	1210 w	835 w	675 m
cis-$Cl_2Au(C_6Cl_5)AsPh_3$	1330 s [a]		1290 m	1210 vw	835 w	[b]
$Br_2Au(C_6Cl_5)AsPh_3$	1330 s [a]		1290 m	1210 w	840 w	675 s
$I_2Au(C_6Cl_5)AsPh_3$	1325 s [a]		1290 m	1205 w	830 w	670 m (sh)
$IAu(C_6Cl_5)(CH_3)AsPh_3$		1320 vs [a]	1290 s	1230 w	835 m	670 s

[a] Asymmetric band. [b] Probably masked by the $AsPh_3$ vibration at 685 cm^{-1}.

Experimental

IR spectra were recorded on a Beckman IR 20A spectrophotometer (over the range 4000-250 cm^{-1}) using Nujol mulls between polyethylene sheets. Molecular weights were measured in benzene solution with a Hitachi—Perkin—Elmer 115 osmometer, and the conductivities ($\approx 5 \times 10^{-4}$ *M* solutions) with a Philips PW 9501/01 conductimeter. C, H and N analyses were carried out with a Perkin—Elmer 240 microanalyzer.

I. $C_6Cl_5AuAsPh_3$

To a tetrahydrofuran solution of C_6Cl_5MgCl [6] (10 mmol), was added 20 ml of benzene and $ClAuAsPh_3$ (2.69 g, 5 mmol). The mixture was stirred under a dry N_2 stream at room temperature for 1 h; water was added to destroy the Grignard compound, and the organic layer was separated. The solution was set aside for one night with activated charcoal and anhydrous magnesium sulfate, then filtered and evaporated to dryness. After washing the solid residue with 100 ml of ethanol, a yellowish-white solid remained, which consisted mainly of complex I. It was washed twice with small portions of dichloromethane, and finally 2.19 g of I remained undissolved. A further 1.3 g were obtained upon adding ethanol to the CH_2Cl_2 solution, and washing with warm hexane. Complex I (total yield 46%) is obtained as colourless crystals, soluble in dichloromethane, chloroform, carbon tetrachloride, benzene and acetone; less soluble in diethyl ether, and insoluble in ethanol and hexane.

II. trans-$Cl_2Au(C_6Cl_5)AsPh_3$

A solution of complex I (0.75 g, 1 mmol) in 25 ml CCl_4 was prepared and cooled to 0°. Upon adding 10 ml of 0.35 *N* chlorine solution in CCl_4, II precipitated almost immediately as a yellow solid. The mixture was set aside for one hour, filtered, and the filtrate was twice washed with small portions of ethyl ether (72% yield). Complex II is soluble in acetone, dichloromethane and chloroform, not very soluble in ethyl ether and benzene, and insoluble in hexane. Its IR spectrum and analyses show that II contains approximately 1 mole of CCl_4. A solution of II in diethyl ether—dichloromethane becomes discoloured after a few minutes, and after evaporation of the solvent at room temperature III is obtained (see below).

III. cis-$Cl_2Au(C_6Cl_5)AsPh_3$

Complex I (0.75 g, 1 mmol) was added to a solution of $TlCl_3$ (0.31 g, 1 mmol) in 25 ml of chloroform and the solution was refluxed for 20 min. Precipitated TlCl was filtered off and the solution evaporated to dryness. The resulting yellow oil was dissolved in dichloromethane, ethanol added and the solution partially evaporated yielding complex III (0.68 g; 83% yield) as white crystals. It is soluble in dichloromethane, acetone and benzene, less soluble in carbon tetrachloride, and insoluble in ethanol, ethyl ether, and hexane.

IV. $Br_2Au(C_6Cl_5)AsPh_3$

A 1 *N* bromine solution in dichloromethane (5 ml) was added to I (0.75 g, 1 mmol) in 20 ml of the same solvent and the mixture was stirred at room temperature for 1 h. The resulting yellow precipitate was filtered and washed with n-hexane to give complex IV (0.33 g; 36% yield), soluble in dichloromethane, acetone and benzene, and insoluble in alcohol and hexane.

V. $I_2Au(C_6Cl_5)AsPh_3$

A solution of I (0.75 g, 1 mmol) and I_2 (0.5 g, 2 mmol) in 50 ml of dichloromethane was stirred at room temperature for 16 h. After adding alcohol and partially evaporating in vacuo, V was obtained as red crystals which were washed with alcohol and then with two small portions of ether (34% yield). It is soluble in benzene, dichloromethane, toluene, tetrahydrofuran and acetone, less soluble in diethyl ether, methanol and ethanol and insoluble in hexane.

VI. $IAu(C_6Cl_5)(CH_3)AsPh_3$

Complex I (0.6 g) was dissolved in 20 ml of freshly distilled CH_3I and the solution was stirred under nitrogen at room temperature for 24 h, carefully protected against light and atmospheric moisture. A small quantity of metallic gold formed during the reaction was filtered off. The solution was evaporated to dryness and the residue dissolved in dichloromethane—ethanol. The resulting solution was partially evaporated in vacuo to give complex VI in the form of a yellow solid, which was washed with ethanol and hexane (60% yield). Under the microscope two different species of crystals of VI could be distinguished, the yellow crystals of m.p. 168° and orange-red crystals of m.p. 146°. Both exhibit identical IR spectra (4000-250 cm^{-1}), and are thought to be isomers.

VII. $C_6F_5AuAsPh_3$

$ClAuAsPh_3$ (8.08 g, 15 mmol) was added to 60 ml of an ether solution of C_6F_5MgBr [7] (22.5 mmol). After 30 min refluxing in a dry N_2 stream the mixture was hydrolysed and the organic layer separated. It was left standing overnight with activated charcoal and anhydrous magnesium sulfate, filtered and concentrated to ≈ 20 ml. VII separated as colourless crystals, which were washed several times with small portions of ethyl ether. Further crops of crystals were obtained from the solution upon adding ethanol and subsequent evaporation (80% yield). It is soluble in acetone, benzene, ethyl ether, dichloromethane, chloroform and carbon tetrachloride, and insoluble in ethanol and hexane.

VIII. trans-$Cl_2Au(C_6F_5)AsPh_3$

A 0.32 *N* chlorine solution in carbon tetrachloride (10 ml) was added to a solution of VII (0.67 g, 1 mmol) in 10 ml of the same solvent cooled to 0°. After 5 min stirring a turbidity could be observed, which as soon as the stirring was interrupted became a yellow oil. The solution was evaporated to dryness and the resulting oil was dissolved in ethyl ether. Complex VIII precipitated spontaneously in the form of a white solid which was filtered and washed with a small portion of ether. An additional crop of crystals was obtained by further concentrating and cooling (61% yield). VIII is soluble in dichloromethane, chloroform, acetone and benzene, not very soluble in ethyl ether, and insoluble in ethanol and hexane.

IX. $Br_2Au(C_6F_5)AsPh_3$

A 1 *N* bromine solution in dichloromethane (3 ml) was added to a solution of VIII (0.67 g, 1 mmol) in 3 ml of the same solvent. After 1 h stirring, ethyl ether was added drop by drop until a red crystalline product (0.16 g, 23% yield) separated. Its m.p. (102°) and IR spectrum coincide with those of $Br_3AuAsPh_3$ [8]. The red crystals were filtered off and the resulting solution was concentrated until the yellow crystals of IX separated (42% yield). It is soluble in dichloromethane, acetone, benzene, ethanol and ethyl ether, and insoluble in hexane.

Reaction of $C_6F_5AuAsPh_3$ *with* I_2

To a solution of complex VII (0.67 g, 1 mmol) in 5 ml of CH_2Cl_2 was added I_2 (0.50 g, 2 mmol). After 4 h stirring at room temperature a small quantity of a drab-coloured product was filtered off, and ethanol was added to the solution. Upon solvent evaporation a brown heterogeneous product (a) crystallized, which was filtered and was washed several times with hexane. The solution was concentrated and upon adding ethyl ether product (b) separated in the form of red crystals.

Compound (a), once washed with large portions of ethanol was obtained in the form of a yellowish-white powder, which does not contain C_6F_5 and whose melting point (200°) coincides with that of $IAuAsPh_3$. The red compound (b) does not contain C_6F_5 either, and its C and H analyses show that it mainly consists of $I_3AuAsPh_3$. Found C, 26.20; H, 1.56. Calcd.: C, 24.46; H. 1.71%. Not even by using stoichiometric amounts was it possible to isolate products other than these mentioned above.

References

1 L.G. Vaughan and W.A. Sheppard, J. Amer. Chem. Soc., 91 (1969) 6151.
2 A. Laguna, P. Royo and R. Usón, Rev. Acad. Ciencias Zaragoza, 27 (1972) 19.
3 R. Usón, A. Laguna and J. Pardo, Syn. React. Inorg. Metal-org. Chem., (1974) in press.
4 M.D. Rausch, F.E. Tibbets and H.B. Gordon, J. Organometal. Chem., 5 (1966) 493; J. Organometal. Chem., 21 (1970) 487.
5 G.E. Coates and C. Parkin, J. Chem. Soc. A, (1963) 421.
6 K. MacKinnon and B.O. West, Aust. J. Chem., 21 (1968) 2801.
7 E. Nield, R. Stephens and J.C. Tatlow, J. Chem. Soc., (1959) 166.
8 J.L. Burmeister and N.J. DeStefano, Inorg. Chem., 10 (1971) 998.
9 A.D. Westland, Can. J. Chem., 47 (1969) 4135.