

PREPARATION OF ORGANOGOLD(III) COMPLEXES BY OXIDIZING DICHLORO-, OR BIS(PENTAFLUOROPHENYL)- μ -BIS(DIPHENYLPHOS- PHINO)ETHANEDIGOLD(I)

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Summary

The oxidation of compounds of the type X Au(dpe)AuX [dpe = 1,2-bis(diphenylphosphino)ethane] leads to organogold(III) complexes. When X is Cl, treatment with $\text{BrTl(C}_6\text{F}_5)_2$ leads to oxidative addition of two C_6F_5 groups to each gold atom and formation of $\text{Cl(C}_6\text{F}_5)_2\text{Au(dpe)Au(C}_6\text{F}_5)_2\text{Cl}$, which by metathesis with KBr or KI gives the corresponding bromo (or iodo) derivative. When X is C_6F_5 oxidation with halogens leads in the case of $\text{X}' = \text{Cl}$ or Br to formation of $\text{X}'_2(\text{C}_6\text{F}_5)\text{Au(dpe)Au(C}_6\text{F}_5)\text{X}'_2$ whereas, for $\text{X}' = \text{I}$ reductive elimination of IC_6F_5 takes place to give IAu(dpe)AuI .

Introduction

Recent studies of the oxidative addition of halogens to gold(I) complexes of the type $\text{R}_\text{x}\text{AuL}$ ($\text{R}_\text{x} = \text{C}_6\text{F}_5$, C_6Cl_5 or C_6Br_5 ; $\text{L} = \text{PPh}_3$ or AsPh_3) [1-3] have shown that the outcome depends both on R_x and on L. Thus, the product may be either $\text{X}_2\text{R}_\text{x}\text{AuL}$, resulting from the oxidative addition, or X AuL , resulting from subsequent reductive elimination of XR_x , or, when an excess of the halogen is used, X_3AuL produced by secondary oxidation by halogen. Mixtures of the compounds are obtained in some cases, when these processes take place at comparable speeds.

On the other hand, the reaction of $\text{BrTl(C}_6\text{F}_5)_2$ with chlorogold(I) complexes such as X AuL (L being PPh_3 or AsPh_3) leads to $\text{X(C}_6\text{F}_5)_2\text{AuL}$ [4,5], but the subsequent substitution of the chlorine by bromine or iodine can only be accomplished with satisfactory yield when $\text{L} = \text{AsPh}_3$. In the case $\text{L} = \text{PPh}_3$, only the introduction of Br can be carried out successfully.

This paper describes the results of the oxidation of gold(I) complexes of the type X Au(dpe)AuX . The gold(I) complexes X Au(dpe)AuX ($\text{X} = \text{C}_6\text{F}_5$ or I), as well as the gold(III) complexes $\text{X}_2(\text{C}_6\text{F}_5)\text{Au(dpe)Au(C}_6\text{F}_5)\text{X}_2$ ($\text{X} = \text{Cl}$ or Br), and $\text{X(C}_6\text{F}_5)_2\text{Au(dpe)Au(C}_6\text{F}_5)_2\text{X}$ ($\text{X} = \text{Cl}$, Br or I) are reported for the first time.

TABLE 2

ANALYTICAL DATA

Complex	m.p. (°C)	Λ_M ($\text{ohm}^{-1} \text{cm}^2$ mol^{-1}) acetone	Analysis found (calcd.) (%)				Mol. wt. found (calcd.)
			C	H	Au	X (Cl, Br)	
$\text{C}_6\text{F}_5\text{Au}(\text{dpe})\text{AuC}_6\text{F}_5$ (I)	199	nil	40.91 (40.50)	2.59 (2.14)	33.04 (34.96)		^a
<i>trans</i> - $\text{Cl}_2(\text{C}_6\text{F}_5)_2\text{Au}(\text{dpe})\text{Au}(\text{C}_6\text{F}_5)_2\text{Cl}_2$ (II)	168 (dec.)	4.71	35.52 (35.97)	1.97 (1.90)	32.87 (31.05)	11.15 (11.17)	1229 (1268)
$\text{Br}_2(\text{C}_6\text{F}_5)_2\text{Au}(\text{dpe})\text{Au}(\text{C}_6\text{F}_5)_2\text{Br}_2$ (III)	163 (dec.)	61.36	30.17 (31.55)	1.63 (1.67)	27.18 (27.23)	23.46 (22.09)	1457 (1445)
$\text{IAu}(\text{dpe})\text{AuI}$ (IV)	274 (dec.)	^a	29.93 (29.84)	2.42 (2.31)	36.66 (37.65)		^a
$\text{Cl}(\text{C}_6\text{F}_5)_2\text{Au}(\text{dpe})\text{Au}(\text{C}_6\text{F}_5)_2\text{Cl}$ (V)	175 (dec.)	43.46	39.10 (39.21)	1.89 (1.58)	24.79 (25.72)		1405 (1531)
$\text{Br}(\text{C}_6\text{F}_5)_2\text{Au}(\text{dpe})\text{Au}(\text{C}_6\text{F}_5)_2\text{Br}$ (VI)	189 (dec.)	80.05	36.38 (37.06)	1.86 (1.49)	24.85 (24.31)		1610 (1620)
$\text{I}(\text{C}_6\text{F}_5)_2\text{Au}(\text{dpe})\text{Au}(\text{C}_6\text{F}_5)_2\text{I}$ (VII)	163 (dec.)	97.37	34.76 (35.02)	1.50 (1.41)	23.07 (22.98)		1680 (1714)

^a Not soluble enough for determination.

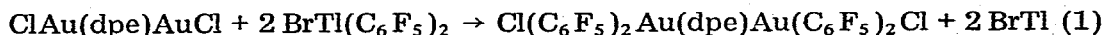
Results and discussion

(a) Oxidation of $(C_6F_5)Au(dpe)Au(C_6F_5)$ with halogens

The results of these reactions are summarized in Table 1. Reaction with both chlorine and bromine, even in excess, leads to gold(III) complexes, while treatment with a stoichiometric amount of iodine causes cleavage of the Au—C bond and gives the gold(I) complex $IAu(dpe)AuI$. The IR spectrum reveals that the resulting compound is *trans*- $Cl_2(C_6F_5)Au(dpe)Au(C_6F_5)Cl_2$. No information about the structure of the dibromo derivative could be obtained with our spectrophotometer (range $4000-250\text{ cm}^{-1}$).

(b) Oxidation of $ClAu(dpe)AuCl$ with $BrTi(C_6F_5)_2$

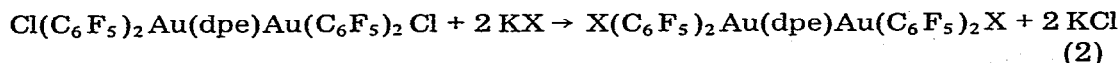
When a benzene solution of $ClAu(dpe)AuCl$ and $BrTi(C_6F_5)_2$ [6] is heated under reflux, $TiBr$ is precipitated and transfer of the two C_6F_5 groups occurs according to eqn. 1.



When $BrTi(C_6F_5)_2$ is used for the oxidation of $ClAuL$ (L being PPh_3 or $AsPh_3$) the product is *cis*- $Cl(C_6F_5)_2AuL$ [5], as shown by the splitting of bands characteristic of the C_6F_5 groups (especially those at 950 and 800 cm^{-1}), but there was no such splitting in the case of the product of eqn. 1.

(c) Substitution reactions

Potassium bromide or iodide reacts with an acetone solution of $Cl(C_6F_5)_2Au(dpe)Au(C_6F_5)_2Cl$ according to eqn. 2.



No reduction to metallic gold or gold(I), as observed for the similar reaction of $Cl(C_6F_5)_2AuPPh_3$ [5] with iodide, was detected.

(d) Properties of the complexes

The analytical data, melting points, conductivities and molecular weights of the complexes are listed in Table 2. The high conductivities of complexes III, V, VI and VII are noteworthy. All the complexes are thermally very stable. They show no trace of decomposition after weeks of exposure to daylight and atmospheric moisture. Their solutions are similarly stable.

TABLE 1

OXIDATION OF $C_6F_5Au(dpe)AuC_6F_5$ WITH X_2

Halogen	Molar ratio $X_2/Complex$	Endproduct
Cl_2	great excess	<i>trans</i> - $Cl_2(C_6F_5)Au(dpe)Au(C_6F_5)Cl_2$
Br_2	4/1	$Br_2(C_6F_5)Au(dpe)Au(C_6F_5)Br_2$
I_2	2/1	$IAu(dpe)AuI$

(e) IR spectra

The IR spectrum of each complex shows the bands characteristic of the relevant ligand, along with those due to the pentafluorophenyl group [7] (except for complex IV). The $\nu(\text{Au}-\text{Cl})$ frequency can unambiguously be assigned, since no absorptions due to (dpe) are to be found in the region $400\text{-}250\text{ cm}^{-1}$. Thus in the spectrum of $\text{Cl}_2(\text{C}_6\text{F}_5)\text{Au}(\text{dpe})\text{Au}(\text{C}_6\text{F}_5)\text{Cl}_2$ the band at 360 cm^{-1} is assigned to $\nu(\text{Au}-\text{Cl})$. This indicates that the compound is the *trans*-isomer, in accordance with observations on the spectra of $\text{Cl}_2(\text{C}_6\text{F}_5)\text{AuL}$ ($\text{L} = \text{PPh}_3$ [1] or AsPh_3 [2]). The absorptions due to $\nu(\text{Au}-\text{Br})$ and $\nu(\text{Au}-\text{I})$, which are to be expected to lie below 250 cm^{-1} [8,9] could not be recorded on our spectrophotometer (range $4000\text{-}250\text{ cm}^{-1}$). The vibration $\nu(\text{Au}-\text{Cl})$ which in $\text{Cl}(\text{C}_6\text{F}_5)_2\text{-Au}(\text{dpe})\text{Au}(\text{C}_6\text{F}_5)_2\text{Cl}$ is observed at 325 cm^{-1} disappears as reported after the treatment with KBr or KI.

Experimental

IR spectra were recorded on a Beckman IR 20 A spectrophotometer (over the range $4000\text{-}250\text{ cm}^{-1}$) using Nujol mulls between polyethylene sheets. Conductivities were measured in $4\text{-}5 \times 10^{-4}\text{ M}$ acetone solutions with a Philips PW 9501/01 conductimeter, and molecular weights in 0.12-0.40% benzene solutions with a Hitachi-Perkin-Elmer model 115 osmometer. Melting or decomposition points were determined with a Reichert apparatus (Austria). C and H analyses were made with a Perkin-Elmer 240 microanalyzer. Chlorine and bromine analyses were performed as described by White [10], though this was not possible for complexes V and VI for which the high fluorine contents prevented accurate determinations.

Preparation of ClAu(dpe)AuCl

This compound has been previously prepared from $[\text{AuCl}_4]\text{H}$ and (dpe) [11], but we started from ClAuAsPh_3 in order not to waste (dpe) in the reduction of Au^{III} to Au^{I} . (dpe) (3.76 g, 9.44 mmole) was added to a solution of ClAuAsPh_3 (10.16 g, 18.88 mmole) in 20 ml of dichloromethane. A white precipitate formed immediately. The mixture was stirred for 3 h, then the precipitate was filtered off, washed and dried to give 5.92 g of $\text{ClAu}(\text{dpe})\text{AuCl}$ [70% yield referred to (dpe)]. Attempts to replace the ligand of ClAuPPh_3 by (dpe), in ether (or in dichloromethane) at room temperature and in boiling ethanol [12] were unsuccessful.

 $\text{C}_6\text{F}_5\text{Au}(\text{dpe})\text{AuC}_6\text{F}_5$ (I)

$\text{ClAu}(\text{dpe})\text{AuCl}$ (3.02 g, 3.50 mmole) was added to a solution of BrMgC_6F_5 (prepared by Nield's method [13] from Mg shavings (0.24 g, 10 mmole) and bromopentafluorobenzene (1.82 ml, 14 mmole) in 40 ml of anhydrous ether) at room temperature. The suspended solid was dissolved by adding 100 ml of anhydrous THF. The solution was refluxed for 3 h then allowed to cool to room temperature. Water was added and the organic layer was separated. The solution was set aside overnight over activated charcoal and anhydrous magnesium sulfate, then filtered and reduced in vacuo to 50 ml. After addition of 20 ml of ethanol the solution was vacuum-concentrated to give white crystals of I (2.69 g, 68%

yield). Complex I is soluble in acetone and THF, slightly soluble in benzene, chloroform and dichloromethane, and insoluble in ether, ethanol and hexane.

trans-Cl₂(C₆F₅)Au(dpe)Au(C₆F₅)Cl₂ (II)

A slow chlorine stream was bubbled for 1 h through a stirred suspension of complex I (1.12 g, 1 mmole) in 70 ml of dichloromethane at room temperature. The resulting yellow solution was vacuum concentrated after addition of ethanol to give complex II (0.6 g, 47% yield). Complex II is soluble in acetone, benzene, THF, dichloromethane, chloroform and carbon tetrachloride, very slightly soluble in ether, and insoluble in ethanol and hexane.

Br₂(C₆F₅)Au(dpe)Au(C₆F₅)Br₂ (III)

A solution of bromine (2 mmole) in 4 ml of dichloromethane was added to a suspension of complex I (0.56 g, 0.5 mmole) in 50 ml of the same solvent. The resulting yellow solution, which quickly turned orange and then red, was stirred for 1 h, then concentrated in vacuo to half its volume and diluted with ethanol to give complex III as orange-red crystals (0.52 g, 72% yield). III is soluble in acetone, benzene, THF, dichloromethane and chloroform, slightly soluble in carbon tetrachloride and ether, and insoluble in alcohol and hexane.

IAu(dpe)AuI (IV)

Iodine (0.12 g, 1 mmole) was added to a dichloromethane suspension of complex I (0.56 g, 0.5 mmole). Evaporating gave complex IV instead of the expected compound I₂(C₆F₅)Au(dpe)Au(C₆F₅)I₂. The preparation was repeated with an acetone solution (I is soluble in acetone) of complex I (0.5 mmole) and iodine (1 mmole), but this also after approx. 15 min gave yellowish-white crystals of complex IV (0.30 g, 56% yield). IV is slightly soluble in dichloromethane and insoluble in acetone, benzene, THF, chloroform, carbon tetrachloride, nitromethane, ethanol and ether.

Cl(C₆F₅)₂Au(dpe)Au(C₆F₅)₂Cl (V)

Addition of BrTi(C₆F₅)₂ (1.22 g, 2 mmole) to a stirred benzene solution (125 ml) of ClAu(dpe)AuCl (0.86 g, 1 mmole), was followed by refluxing for 3 h. The quantitative precipitate of TiBr₃ was centrifuged off and the pale yellow solution was evaporated to dryness. The residue was dissolved in the least possible amount of dichloromethane and addition of ethanol gave complex V as white crystals (0.81 g, 53% yield). V is soluble in acetone, benzene, THF and dichloromethane, slightly soluble in chloroform, carbon tetrachloride and ether, and insoluble in ethanol and hexane.

Br(C₆F₅)₂Au(dpe)Au(C₆F₅)₂Br (VI)

Complex V (0.60 g, 0.39 mmole) and KBr (0.11 g, 0.97 mmole) were dissolved in the minimum amount of acetone and the solution was refluxed for 3.5 h, then evaporated to dryness. The residue was redissolved in dichloromethane, and filtered. Complex VI (0.35 g, 31% yield) was obtained after adding ethanol and concentrating in vacuo. The white crystals of VI are soluble in acetone, benzene, THF, dichloromethane, chloroform and ether, and insoluble in carbon tetrachloride, ethanol and hexane.

$I(C_6F_5)_2Au(dpe)Au(C_6F_5)_2I$ (VII)

To a solution of complex V (0.40 g, 0.26 mmole) in 50 ml of acetone was added KI (0.13 g, 0.78 mmole) in 25 ml of the same solvent. The yellow solution was set aside for 14 h at room temperature. The white precipitate of KCl was filtered off and ethanol was added to the filtrate, which was vacuum concentrated to approx. 20 ml. A yellow precipitate of complex VII was obtained upon adding a few drops of hexane. (VII: 0.35 g, 65% yield.) VII is soluble in acetone, benzene, THF, dichloromethane, chloroform, carbon tetrachloride, ether and ethanol, and insoluble in hexane.

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