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REACTIONS OF COMPLEXES OF GOLD(I) WITH BIS(PENTAFLUOROPHENYL)THALLIUM(III) HALIDES

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Summary

The reactions of bis(pentafluorophenyl)thallium(III) halides with XAuL ($L = PPh_3$, $AsPh_3$) lead to results which vary according to the character of X. When X is Cl, Br or I an oxidation from gold(I) to gold(III) takes place through the transference of two C_6F_5 groups, and with the simultaneous precipitation of thallous halide.

When X is C_6F_5, C_6H_5, NO_3, CH_3COO, SCN or PPh_3 substitution but not oxidation takes place, which may be followed by secondary reactions.

Reasons for this behaviour are discussed.

Introduction

Even though diorganothallium(III) halides, $XTlR_2$, are rather more stable than the mono- and triorganoderivatives, X_2TlR and TlR_3, they are still very reactive [1]. We are especially interested in those reactions which take place with halide complexes of transition and post-transition metals, and which lead to bis(pentafluorophenyl) derivatives by the transference of the two C_6F_5 groups to the starting complex, thus increasing the oxidation-number of the central metal by two [2,3].

We have shown [4] that thallous bromide is precipitated and $XAu(C_6F_5)_2L$ can be crystallized from the resulting solution when $BrTl(C_6F_5)_2$ in benzene is treated at reflux temperature with gold(I) complexes of the type XAuL (X = Cl, Br; $L = PPh_3$, $AsPh_3$) in stoichiometric amounts. Here we report the results obtained with complexes of the above-mentioned type with X = Br, I, C_6F_5, C_6H_5, NO_3, CH_3COO, SCN and the cationic complex $[Au(PPh_3)_2]ClO_4$

Results and discussion

Table 1 gives a summary of our results. Only with the compounds where X

TABLE 1

REACTIONS AND RESULTS

	Reagents		
	Au compound	Tl compound	Identified products
I	$ClAuPPh_3$	$BrTl(C_6F_5)_2$	$ClAu(C_6F_5)_2PPh_3 + TlBr$
II	$BrAuPPh_3$	$BrTl(C_6F_5)_2$	$BrAu(C_6F_5)_2PPh_3 + TlBr$
III	$IAuPPh_3$	$ITl(C_6F_5)_2$	$IAu(C_6F_5)_2PPh_3 + TlI$
IV	$ClAuAsPh_3$	$BrTl(C_6F_5)_2$	$ClAu(C_6F_5)_2AsPh_3 + TlBr$
V	$BrAuAsPh_3$	$BrTl(C_6F_5)_2$	$BrAu(C_6F_5)_2AsPh_3 + TlBr$
VI	$IAuAsPh_3$	$ITl(C_6F_5)_2$	$IAu(C_6F_5)_2AsPh_3 + TlI$
VII	$C_6F_5AuPPh_3$	$BrTl(C_6F_5)_2$	No reaction
VIIIa	$C_6H_5AuPPh_3$	$BrTl(C_6F_5)_2$	$C_6F_5AuPPh_3 + BrTl(C_6H_5)_2 + BrTl(C_6F_5)_2$
VIIIb	$2\ C_6H_5AuPPh_3$	$BrTl(C_6F_5)_2$	$2\ C_6F_5AuPPh_3 + BrTl(C_6H_5)_2$
IX	NO_3AuPPh_3	$BrTl(C_6F_5)_2$	$C_6F_5AuPPh_3 + NO_3Tl(C_6F_5)_2 + TlBr$
X	$CH_3COOAuPPh_3$	$BrTl(C_6F_5)_2$	$C_6F_5AuPPh_3 + CH_3COOTl(C_6F_5)_2 + TlBr$
XI	$SCNAuPPh_3$	$BrTl(C_6F_5)_2$	$C_6F_5AuPPh_3 + SCNTl(C_6F_5)_2 + TlBr$
XII	$[Au(PPh_3)_2]ClO_4$	$BrTl(C_6F_5)_2$	$C_6F_5AuPPh_3 + PPh_3 + TlClO_4$

is a halogen does the reaction lead to the formation of a gold(III) complex by the transfer of two C_6F_5 groups to the gold and the precipitation of thallous halide, as in the above-mentioned cases [4].

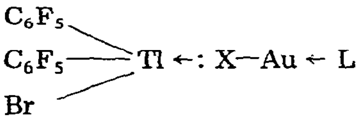
We have used $ITl(C_6F_5)_2$ instead of the bromo derivative to oxidise the $IAuAsPh_3$ because the former is a more effective oxidant, which makes it possible to operate at lower temperatures and with shorter reaction times; secondary reactions can thus be avoided, notably in the substitution of Br for I in the Au^{III} complex [4].

In the remaining systems(VII—XII) either no reaction took place and the unchanged starting products could be collected (VII), or quite different end products were obtained. In VIIIa and VIIIb, which started from the same gold and thallium compounds, but in different stoichiometric proportions, and interchange of C_6H_5 for C_6F_5 took place. With a 1/1 molar ratio three products were obtained, while with a 2/1 molar ratio there were only two products because there was enough C_6H_5 for a complete interchange.

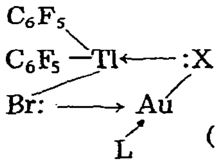
In IX, X and XI an equimolar mixture of the reactants in benzene was heated to reflux temperature. A white precipitate was obtained and $C_6F_5AuPPh_3$ could be crystallized from the solution. The solid was a mixture of thallous bromide and $XTl(C_6F_5)_2$ ($X = NO_3$, CH_3COO or SCN respectively). In the case of X = SCN the mixture could not be separated, but by analogy with the other reactions, and from the accumulated analytical data the composition may be inferred.

Finally, in XII, $C_6F_5AuPPh_3$ was again obtained, a molecule of PPh_3 being released and $TlClO_4$ precipitated.

It can be assumed that the oxidation reactions of metal complexes with bis(pentafluorophenyl)thallium(III) halide starts with the formation of a simple (A) or double (B) halogen bridge [3].



(A)



(B)

Then the transference of the two C_6F_5 groups to the transition metal atom takes place via an inner sphere mechanism. The bridge is split and thallium halide precipitates simultaneously.

Therefore the oxidation reaction is only possible if the X group attached to the gold atom in the starting compound XAuL is capable of forming a Tl : X—Au bridge. This occurs when X is a halogen but not when X lacks the necessary electron pair ($X = C_6H_5$, C_6F_5), or if the bridge-forming tendency is very poor because of the high electronegativity of the anion ($X = NO_3$, CH_3COO, SCN) whose donor atoms have such a low capacity to donate one electron pair that they cannot be expected to donate two electron pairs. In such systems there is no oxidation reaction and instead an interchange process involving the anionic substituents takes place. This is simple when the thallium compound is stable, or complex when the products are unstable and are subsequently transformed.

Thus in reaction VII an interchange between the C_6F_5 and C_6F_5 groups takes place (without any apparent reaction) and in VIIIa and VIIIb between C_6H_5 and C_6F_5, which due to stoichiometric conditions can be total or partial. When $X = NO_3$, CH_3COO or SCN we probably have an analogous primary process:

$$XAuL + BrTl(C_6F_5)_2 \rightarrow C_6F_5AuL + XBrTl(C_6F_5)$$

though it has not been possible to detect the thallium compound. This is easily understandable because of the lower stability of mono-organo derivatives of thallium(III), (vide supra), and because of the inherent instability of mixed halide derivatives. We have identified $XTl(C_6F_5)_2$ and TlBr, in small quantities, as probable products of the decomposition of the thallium compound.

Finally, the phosphine cannot act as a bridge with thallium in the case of bis(triphenylphosphine)gold(I) perchlorate and therefore no oxidation takes place.

Experimental

All the reactions were carried out similarly. Dehydrated benzene was added to an equimolar mixture of the reactants (with the exception of reaction VIIIb, where 1 mmole of $BrTl(C_6F_5)_2$ was added to 2 mmoles of $C_6H_5AuPPh_3$). The mixture was heated at reflux temperature for the quoted time. A solid precipitate was obtained, which was filtered, washed and dried, and put aside for further study. The solution was evaporated to dryness and the residue was then recrystallized from ether—hexane and dried in vacuo. Below we give the details of each preparation.

The experimental data for reactions I—IV (see Table 1) have been published elsewhere [3, 4].

Oxidation of $BrAuAsPh_3$ (V)

0.61 g (1 mmole) of $BrTl(C_6F_5)_2$ [6] were added to 0.58 g (1 mmole) of $BrAuAsPh_3$ [5] in 40 ml of benzene. The mixture was heated and stirred at reflux temperature for 2 h. $BrAu(C_6F_5)_2AsPh_3$ was obtained by recrystallizing the residue from ether—hexane. (Found: C, 38.72; H, 2.74; Au, 22.09; Br, 8.93; mol. wt. 949 (in 0.31% benzene solution). $C_{30}H_{15}AsAuBrF_{10}$ calcd.: C, 38.85; H, 1.63;

Au, 21.24; Br, 8.71%; mol. wt. 927.2. Its properties and IR spectrum coincide with those given for the same product obtained by substitution reactions [4].

Oxidation of $IAuAsPh_3$ (VI)

0.66 g (1 mmole) of $ITl(C_6F_5)_2$ [7] were added to 0.63 g (1 mmole) of $IAuAsPh_3$ [5] in 40 ml of benzene. The mixture was stirred at room temperature for 1 h. $IAu(C_6F_5)_2AsPh_3$ was obtained in the form of yellow crystals by recrystallizing the residue from ether—hexane. (Found: C, 36.84; H, 1.55; Au, 21.22; mol. wt. 969 (in 0.36% benzene solution). $C_{30}H_{15}AsAuF_{10}I$ calcd.: C, 37.37; H, 1.56; Au, 20.45%; mol. wt. 964.2.) Its properties and IR spectrum coincide with those given for the same product obtained by substitution reactions [4].

Reaction with $C_6F_5AuPPh_3$ (VII)

0.61 g (1 mmole) of $BrTl(C_6F_5)_2$ were added to 0.62 g (1 mmole) of C_6F_5-$AuPPh_3$ [3] in 30 ml of benzene. The mixture was heated at reflux temperature for 3 h. On reducing the volume to 10 ml by evaporation and then cooling the solution, $BrTl(C_6F_5)_2$ crystallized and was filtered off. The remaining solution was evaporated to dryness and the residue was recrystallized from ether—hexane. The gold complex obtained was identical with the starting compound.

Reaction with $C_6H_5AuPPh_3$ (VIII)

(a). 0.61 g (1 mmole) of $BrTl(C_6F_5)_2$ were added to 0.53 g (1 mmole) of $C_6H_5AuPPh_3$ [8] in 30 ml of benzene. The mixture was heated and stirred at reflux temperature for 3 h.

When the precipitate, obtained during the reaction was extracted with acetone a solution could be separated from an insoluble solid, which was identified as $BrTl(C_6H_5)_2$. (Found: C, 31.43; H, 2.05; Br, 19.12; Tl, 47.02; $C_{12}H_{10}BrTl$ calcd.: C, 32.87; H, 2.29; Br, 18.22; Tl, 46.60%. The solution was evaporated to dryness and the solid which was recrystallized from acetone—benzene, was shown to contain the thallium complex used as starting material.

The benzene solution was evaporated to dryness and the solid which was recrystallized from ether—hexane, was identified as $C_6F_5AuPPh_3$. (Found: C, 45.73; H, 2.28; Au, 29.31; mol. wt. 650 (in 0.46% benzene solution). m.p. 171°C. $C_{24}H_{15}AuF_5P$ calcd.: C, 46.02; H, 2.41; Au, 31.45%; mol. wt. 626.3.)

(b). When 0.61 g (1 mmole) of $BrTl(C_6F_5)_2$ was added to 1.06 g (2 mmoles) of the gold derivative and then proceeding as in (a), $C_6F_5AuPPh_3$ was extracted from the solution but the precipitate consisted only of $BrTl(C_6H_5)_2$.

Reaction with NO_3AuPPh_3 (IX)

2.47 g (4 mmoles) of $BrTl(C_6F_5)_2$ were added to 2.08 g (4 mmoles) of NO_3AuPPh_3 [9] in 50 ml of benzene. The stirred mixture was heated at reflux for one hour. The solid precipitate was filtered off and the benzene solution evaporated to dryness. The residue was recrystallized from ether—hexane and C_6F_5—$AuPPh_3$ was obtained in the form of colourless crystals. (Found: C, 45.84; H, 2.63; Au, 29.53. $C_{24}H_{15}AuF_5P$ calcd.: C, 46.02; H, 2.41; Au, 31.45%.)

The precipitate was treated with 15 ml of acetone. A very small residue of TlBr remained undissolved. After filtration a small quantity of benzene was added to the solution which was then evaporated until crystals of $NO_3Tl(C_6F_5)_2$ were formed. (Found: C, 23.20; N, 1.93; Tl, 34.34. $C_{12}F_{10}NO_3Tl$ calcd.: C, 24.00; N, 2.33; Tl, 34.20%. The properties and the IR spectrum of this complex are identical with those of a sample obtained by a different method [6].

Reaction with $CH_3COOAuPPh_3$ (X)

1.85 g (3 mmoles) of $BrTl(C_6F_5)_2$ were added to 1.55 g (3 mmoles) of $CH_3COOAuPPh_3$ [10] in 50 ml of benzene. The stirred mixture was heated at reflux temperature for 1 h and then treated in the same way as (IX). $C_6F_5AuPPh_3$ was obtained from the benzene solution, and $CH_3COOTl(C_6F_5)_2$ from the solid precipitate. Found: C, 27.93; Tl, 34.38. $C_{14}H_3F_{10}O_2Tl$ calcd.: C, 28.14; Tl, 34.20%. The properties and IR spectrum of the complex are identical to those of a sample obtained by a different method [6].

Reaction with $SCNAuPPh_3$ (XI)

The procedure was the same as for (IX) and (X), with equimolar quantities of the reagents [6, 11] used as starting materials. $C_6F_5AuPPh_3$ was obtained from the benzene solution.

The qualitative analyses and the IR spectrum of the precipitate obtained during the reaction confirmed the presence of Br, SCN, Tl and C_6F_5 but it was not possible to separate the mixture with any of the solvents we used.

Reaction with $[Ph_3PAuPPh_3]ClO_4$ (XII)

0.61 g (1 mmole) of $BrTl(C_6F_5)_2$ were added to 0.82 g (1 mmole) of $[Ph_3PAuPPh_3]ClO_4$ [9] in 50 ml of benzene. The mixture was heated at reflux temperature for two and a half hours. $TlClO_4$ was filtered off and the benzene solution was evaporated to dryness. The solid residue was recrystallized from ether—hexane and crystalline $C_6F_5AuPPh_3$ was obtained.

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