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The Oxidation-reduction Reactions of Gold Complexes

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The review deals with reactions involving oxidative addition to both organogold compounds and to gold complexes without Au-C bonds. Furthermore, the review includes reactions involving the reductive elimination of alkyl groups from tervalent gold complexes.
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I. INTRODUCTION

The oxidation addition reactions constitute one of the types of reactions characteristic of organometallic σ-compounds of transition metals. The most familiar reagents capable of oxidative addition are halogens, alkyl halides, and alkyl disulphides. However, the range of these compounds is being continually expanded. Oxidative addition is nowadays regarded as one of the stages in the protolysis of certain organometallic compounds by hydrogen halides.

Despite the fact that the oxidative addition reactions are known for derivatives of many metals, their characteristics are by no means clear. The most convenient objects for the investigation of these reactions are compounds of gold and platinum group metals. This is due to the fairly high stability of the organometallic σ-derivatives of these elements and also the simplicity with which the stereochemistry of the process can be followed.

This review is devoted to reactions of organogold compounds of the oxidative addition type. The reductive elimination processes can be logically related to the former reactions and are also considered in the present review.

Apart from its general theoretical importance, the study of reactions involving oxidative addition to gold(I) complexes is also important from the preparative standpoint, because gold(I) compounds are much more readily available than gold(III) compounds.

II. OXIDATIVE ADDITION REACTIONS

1. Reactions Involving Oxidative Addition to Complex Salts LAuX

When phosphine[1-5] and arsine complexes[3] of univalent gold halides react in polychlorohydrocarbons with an excess of the halogen of the same type as in the halide, gold trihalide complexes are formed in high yields:

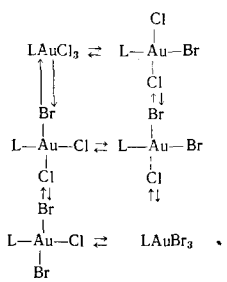
$$R_3PAuX + X_2 \rightarrow R_3PAuX_3 ;$$
$$X = Cl, Br, \text{or } I;\ R = Et,\ Ph,\ \text{cyclo-}C_6H_{11},\ \text{or } C_5H_5FeC_5H_4;$$
$$Ph_3AsAuCl + Cl_2 \rightarrow Ph_3AsAuCl_4 .$$

A mixture of ethanol and tetrahydrofuran can also be used as the solvent[3]. The infrared spectra of the complexes have been investigated[6].

The same product is formed in the reactions of Et_3PAuBr with iodine and of Et_3PAuI with bromine in equimolar amounts. This result was initially explained by the high mobility of the halogens in $Et_3PAuBrI_2$ and Et_3PAuBr_2I and by the formation of the more stable of the above two compounds in both reactions[1]. However, later investigations by NMR showed[7,8] that the process involves the formation of a mixture of all possible complexes of the type $LAuX_aY_{3-a}$ with an approximately statistical distribution of the halogens X and Y. Thus, for the reaction

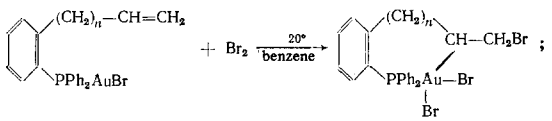
$$Et_3PAuBr + Cl_2 \xrightarrow[3\ h]{25^\circ} Et_3PAuBr_{3-a}Cl_a ;$$
$$a = 0,\ 1,\ 2,\ 3 .$$

the following equilibrium states have been discovered[8]:



Deviations for the statistical distribution of the halogen atoms in this reaction have been observed only for complexes with a large amount of bromine—$LAuClBr_2$ and $LAuBr_3$.[8] The behaviour of the univalent gold in this reaction is analogous to that of the isoelectronic platinum(II) complexes Br_aCl_{4-a}. $.PtL_2$, for which a statistical distribution of halogen atoms has also been observed[9].

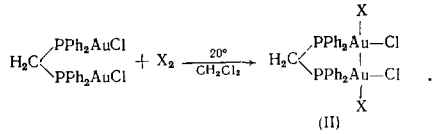
When the phosphine complexes of AuBr in which the ligand contains C=C double bonds are treated with bromine, organic derivatives of tervalent gold are formed as a result of the addition of gold to the double bond[10]:



$n = 0$ or 1. (I)

The structure of the resulting yellow crystalline compounds (I) has been determined by X-ray diffraction[10]. In both compounds (I) the gold atom has the square planar environment characteristic of gold(III). The five-membered ring in compound (I) ($n = 0$) has the envelope conformation, while the six-membered ring in compound (I) ($n = 1$) has the twist-boat conformation. The Au–C bond in compounds (I) persists also in solutions (according to ^1H NMR data).[10]

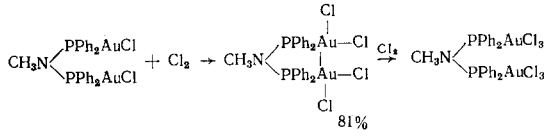
The reaction with halogens of AuCl complexes containing bidentate phosphine ligands and in which two gold atoms are in close proximity in space can lead to the formation of gold compounds with a formal oxidation state +2. Thus the reaction of equimolar amounts of a halogen and the complex of AuCl with bis(diphenylphosphino)methane leads to the formation of compound (I):[11]



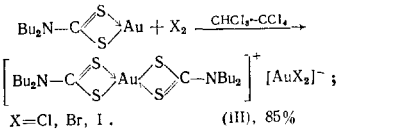
(II)

$Me_2C(PPh_2AuCl)_2$ reacts analogously with chlorine and bromine. The reaction involving $H_2C(PPh_2AuI)_2$ with iodine leads to an unstable complex $H_2C(PPh_2AuI)_2.I_2$, which readily loses iodine *in vacuo* or on recrystallisation. Infrared, ^{197}Au Mössbauer, and X-ray electron spectroscopic data have shown that the oxidation state of the gold in complexes (II) is intermediate between +1 and +3.[11]

When compound (II) is treated with an excess of a halogen, the tervalent gold complexes $H_2C(PPh_2AuClX_2)_2$ are formed. Analogous reactions have been performed for another bisphosphine complex[12]:



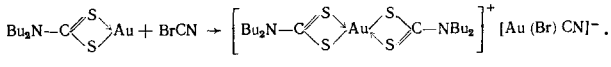
The reactions of halogens with other gold salts have been much less thoroughly investigated. When gold butylthiocarbamate is treated with halogens, the products are either the tervalent gold compound $Bu_2NCS_2AuBr_2$ [13,14] or salt-like complexes containing both Au(I) and Au(III):[15]



X=Cl, Br, I. (III), 85%

The structure of the bromide (III) has been established by X-ray diffraction (the tervalent gold atom has a square planar environment)[15].

An analogous compound has been obtained on treatment with bromocyanogen[15]:



The reactions of arsine and phosphine complexes of gold salts with tervalent thallium compounds have been studied in greater detail. Thus, when triphenylphosphinegold chloride and $TlCl_3$ are refluxed in chloroform, a gold trichloride complex is formed in 95% yield[16]:

$$Ph_3PAuCl + TlCl_3 \rightarrow Ph_3PAuCl_3 + TlCl\ .$$

The reaction of LAuX with bis(pentafluorophenyl)thallium halides in benzene leads to bis(pentafluorophenyl)gold halides[17–20]:

$$LAuX + (C_6F_5)_2TlZ \rightarrow (C_6F_5)_2Au(X)L + TlZ\ ;$$
$$L=PPh_3,\ AsPh_3;\ X=Cl,\ Br,\ I;\ Z=Br,\ I\ ;$$
$$[-CH_2PPh_2AuCl]_2 + (C_6F_5)_2TlBr \rightarrow [-CH_2PPh_2Au(C_6F_5)_2Cl]_2\ .$$

It has been established for bis(pentafluorophenyl)gold chloride that the C_6F_5 groups are in the *cis*-positions relative to one another[17]. The isonitrile complex of AuCl reacts analogously[21]:

$$PhNCAuCl + (C_6F_5)_2TlBr \xrightarrow[benzene]{80°;1.5\ h} PhNCAu(C_6F_5)_2Cl + TlBr\ .$$

The reaction of t-BuNCAuCl yields a mixture of products which are difficult to separate[21].

Pentachlorophenylthallium(III) compounds can function as oxidants in relation to gold complexes, but in this case a complex of univalent gold is formed together with the gold-(III) compound:

$$Ph_3PAuCl + (C_6Cl_5)_2TlCl \xrightarrow{-TlCl} (C_6Cl_5)_2Au(Cl)PPh_3 + C_6Cl_5AuPPh_3\ .$$

This result has been explained by the lower oxidising capacity of $(C_6Cl_5)_2TlCl$ compared with that of pentafluorophenyl derivatives of thallium[22].

When Ph_3PAuCl reacts with a fully substituted organic compound of thallium(III), oxidation is not observed at all and only a gold(I) compound is formed[23]:

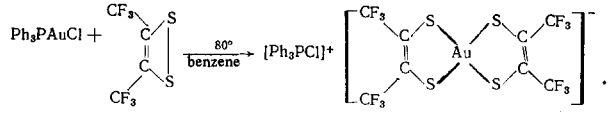
$$Ph_3PAuCl + (C_6HCl_4)_3Tl \xrightarrow{CHCl_3} Ph_3PAuC_6HCl_4\ .$$

In contrast to complexes of univalent gold halides, the triphenylphosphine complexes of gold(I) nitrate, perchlorate, acetate, and thiocyanate react with perfluorophenylthallium compounds to form only univalent gold derivatives[19]:

$$Ph_3PAuZ + (C_6H_5)_3TlX \rightarrow Ph_3PAuC_6F_5\ ;$$
$$Z=NO_3,\ ClO_4,\ CH_3COO,\ SCN,\ X=Br,\ I\ .$$

The causes of the difference between the reactivities of gold halides and those of other gold(I) salts are not discussed in the literature, but the differences agree satisfactorily with the greater ease of reductive elimination in the compounds $LAuR_2Z$ for $Z = NO_3$ or ClO_4 compared with Z = halogen (see below).

The reaction of triphenylphosphinegold chloride with the disulphide $(CF_3)_2C_2S_2$ has been described[24]. During the reaction, the phosphine ligand is displaced and an anionic complex of tervalent gold is formed, its structure having been established by X-ray diffraction[25]:



The gold atom in the anion of this complex has a square planar coordination and the S...S distances are 3.23 Å.

2. Reactions Involving Oxidative Addition to the Aurates $M^+[Au(X)Y]^-$

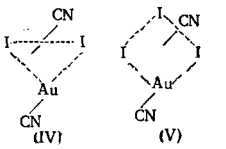
When a slight excess of halogens is allowed to act on potassium dicyanoaurate in H_2O-CH_3OH, tervalent gold aurates are formed[26–29]:

$$K[Au(CN)_2] + X_2 \rightarrow trans\text{-}K[Au(CN)_2X_2]\ ;$$
$$X=Cl,\ Br,\ I\ .$$

The infrared spectra of the compounds obtained have been studied in detail[27,28] and it has been shown that the reaction involves *trans*-addition.

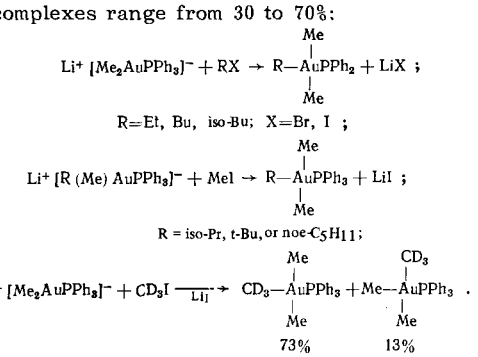
It has been observed that the addition of iodine is greatly accelerated in the presence of the iodide ion[30]. This effect has been explained by the preferential *trans*-disposition of iodine atoms in the transition state of the reaction with I_3^-

compared with the addition of I_2 [cf. the transition states (IV) and (V)]:

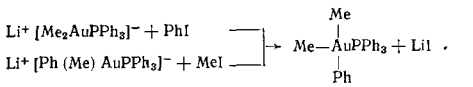


(IV) (V)

Oxidative addition products have been obtained by treating with alkyl bromides or iodides the dialkylaurates(I), which are readily obtained when phosphine complexes of alkylgold-(I) are acted upon by alkyl-lithium compounds. In the resulting tervalent gold compounds two methyl groups are in the *trans*-positions relative to one another[31,32]. The yields of gold(III) complexes range from 30 to 70%:



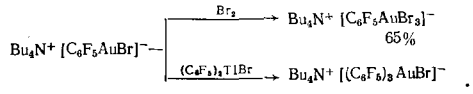
If the phenyl group is present in the gold(III) compound obtained, then the compound has the *cis*-configuration[31,32]:



When equimolar amounts of bromine and lithium dimethylaurate react, a mixture of methyl derivatives of univalent and tervalent gold is formed, probably as a result of the following reactions[32]:

$$Li^+[Me_2AuPPh_3]^- + Br_2 \rightarrow Me_2Au(Br)PPh_3 + LiBr\ ;$$
$$Li^+[Me_2AuPPh_3]^- + Me_2Au(Br)PPh_3 \rightarrow Me_3AuPPh_3 + MeAuPPh_3 + LiBr\ .$$

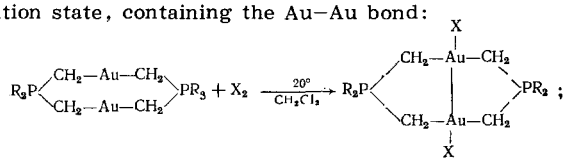
In contrast to dimethylaurate, the mixed complex (VI) is converted into gold(III) compounds in high yields on treatment with bromine or bis(pentafluorophenyl)thallium bromide[33]:



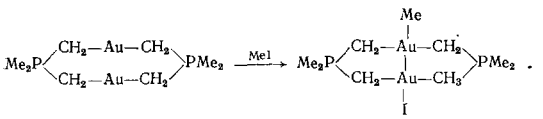
(VI) 90%

Thus the oxidative addition of univalent gold to aurates constitutes a convenient and promising method of synthesising organic derivatives of tervalent gold.

Reactions involving the oxidative addition of halogens[34–36] and methyl iodide[36] have also been achieved for close analogues of dialkylaurates—the ylid complexes of gold. The spatial proximity of the gold atoms in these dinuclear complexes and their structural rigidity permit in this instance the formation of gold compounds (VII), with a formal +2 oxidation state, containing the Au–Au bond:



R = Me, or Et, X = Cl, Br, or I, (VII), 36—85%

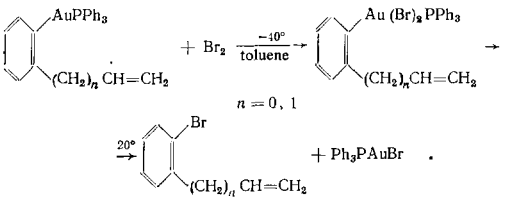


When gold(II) complexes are acted upon by an excess of halogen or MeI, they are converted into tervalent gold compounds.

The presence of the transannular Au–Au bond in compound (VII) has been demonstrated by an X-ray diffraction study of compound (VII, X = Cl), in which the distance between the gold atoms is 2.597 Å.[34] In the initial ylid complex of univalent gold the Au...Au distance is 3.023 Å.[37]

3. Reactions Involving Oxidative Addition to the Polyhalogenoaryl Compounds $C_6X_nH_{5-n}AuL$

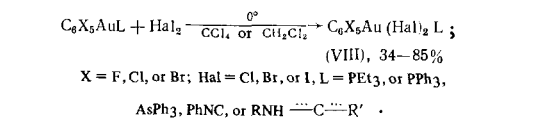
The Au–C bond in the aryl and the similar ferrocenyl organogold compounds $RAuPR'_3$ is readily ruptured by halogens with formation of $R'_3PAuHal$.[38–41] Unstable oxidative addition products have been detected only in the reaction of *o*-vinylphenyl- and *o*-allylphenyl-(triphenylphosphine)gold with bromine[42]:



However, the gold(III) complexes have been fairly poorly characterised.

On the other hand, the polyhalogenoaryl compounds of gold(I) are readily converted into gold(III) complexes on treatment with halogens, thallium trichloride, and methyl iodide.

The reaction with halogens[16,20,21,43–46] leads to the formation of the corresponding dihalides (VIII):



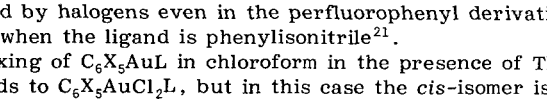
(VIII), 34—85%

X = F, Cl, or Br; Hal = Cl, Br, or I, L = PEt_3, or PPh_3, $AsPh_3$, PhNC, or RNH—C—R'.

The *trans*-configuration of the coordination environment of gold has been demonstrated for the dichloride (VIII).[21,44–46] The *trans*-dihalides (VIII) are readily converted into the *cis*-isomers on heating[16,45,46].

The formation of the products of the cleavage of the C–Au bond on treatment with halogens has been observed only for the perfluorophenyl compounds[16,43–45]. The proportions of the products of the oxidative addition and of the cleavage of the C–Au bond depend on the nature of both the halogen and of the stabilising ligand L. For $C_6F_5AuPPh_3$, the amount of the oxidative addition product increases in the sequence Cl < Br < I, while the opposite sequence holds for $C_6F_5AuAsPh_3$: I < Br < Cl.[45] However, the C–Au bond cannot be ruptured by halogens even in the perfluorophenyl derivative of gold when the ligand is phenylisonitrile[21].

Refluxing of C_6X_5AuL in chloroform in the presence of $TlCl_3$ also leads to $C_6X_5AuCl_2L$, but in this case the *cis*-isomer is formed:



L = PEt_3, PPh_3, or $AsPh_3$; X = F 16, Cl 16, 44, 46, or Br 45.

The complexes of ethyl- and phenyl-gold do not give rise to gold(III) compounds under these conditions[16]:

$$RAuPPh_3 + TlCl_3 \rightarrow Ph_3PAuCl + TlCl\ ;\quad R = Et, \text{ or } Ph.$$

The reaction of pentachlorophenyl(triphenylarsine)gold with methyl iodide[44], leading to a mixture of isomeric gold(III) complexes, has been achieved:

$$C_6Cl_5AuAsPh_3 + MeI \rightarrow \underset{60\%}{C_6Cl_5\,(Me)\,Au\,(I)\,AsPh_3}\ .$$

$C_6F_5AuAsPh_3$ also reacts with methyl iodide, but the products of this reaction have not been determined[44].

Thus reactions involving oxidative addition to polyhalogenoaryl compounds of univalent gold constitute a convenient method of synthesising the corresponding gold(III) complexes.

4. Reactions Involving Oxidative Addition to the Alkyl Complexes RAuL

The reactions of methylgold complexes with MeI and CF_3I have been studied in fair detail. The first studies on this problem showed that the reaction of methyl(triphenylphosphine)gold with methyl iodide in benzene or in MeI at 20 to 25 °C leads to ethane and a gold iodide complex[47,48]:

$$MeAuPPh_3 + MeI \rightarrow C_2H_6 + Ph_3PAuI;$$
$$[-CH_2P(Ph)_2AuMe]_2 + MeI \rightarrow [-CH_2P(Ph)_2AuI]_2 + C_2H_6\ .$$

Methyl iodide reacts analogously with silicon-containing derivatives of univalent gold[47]:

$$Ph_3PAuCH_2SiMe_3 + MeI \rightarrow Ph_3PAuI + Me_3SiEt\ ;$$
$$Ph_3PAuOSiMe_3 + MeI \rightarrow Ph_3PAuI + MeOSiMe_3\ .$$

NMR study of the interaction of methyl iodide with phosphine complexes of methylgold[48,49] as well as kinetic data[50] have shown that the reaction is a multistage process, the first two stages [(1) and (2)] being rapid:

$$MeAuL + MeI \rightarrow Me_2Au\,(I)\,L\ ; \quad (1)$$
$$Me_2Au\,(I)\,L + MeAuL \rightleftarrows Me_3AuL + LAuI\ ;\quad L=PMe_3,\ PMe_2Ph,\ PMePh_2 \text{ or } PPh_3. \quad (2)$$

Reaction (2), which leads to a complex of trimethylgold, is analogous to the exchange of methyl groups between platinum and gold compounds[7]:

$$cis\text{-}Pt(Me)_2L_2 + LAuBr \rightleftarrows trans\text{-}PtBr(Me)L_2 + MeAuL\ .$$

The subsequent fate of the Me_3AuL formed in reaction (2) depends greatly on the nature of the ligand L. For L = PPh_3, reductive elimination of ethane and subsequent interaction of $MeAuPPh_3$ with methyl iodide take place:

$$Me_3AuL \rightarrow C_2H_6 + MeAuL\ . \quad (3)$$

The overall result is thus the formation of methane and of a gold iodide complex.

However, the triphenylphosphine complex of trimethylgold can be isolated with a high yield when the reaction is carried out at 0 °C:[48]

$$MeAuPPh_3 + MeI \xrightarrow[0°,\ 6\ days]{\text{in soln. in MeI}} \underset{87\%}{Me_3AuPPh_3} + Ph_3PAuI\ .$$

The complexes of trimethylgold with ligands such as PMe_3 and PMe_2Ph are more stable than Me_3AuPPh_3 and equilibrium (2) shifts towards the formation of the oxidative addition product via the reaction of MeAuL with an excess of methyl iodide [reaction (1)]. Thus a complex of dimethylgold iodide has been obtained in a high yield from the trimethylphosphine complex[49]:

$$MeAuPMe_3 + MeI \xrightarrow[20°,\ 3\ weeks]{\text{in soln in MeI}} cis\text{-}Me_2Au\,(I)\,PMe_3\ .$$

When L = $PMePh_2$, a mixture of products is formed as a result of reactions (1)–(3).[50]

The mechanism of the interaction of methyl iodide with methylgold complexes discussed above is consistent with the higher rate of formation of butane compared with the rates of formation of ethane and propane on interaction of MeI with an ethylgold complex[48]:

$$EtAuPPh_3 + MeI \rightarrow C_4H_{10} + C_3H_7 + C_2H_6 + Ph_3PAuI\ .$$

However, the cause of the decomposition of the trialkylgold complex [reaction (3)] is not clear, since it is known that the complex Me_3AuPPh_3 is fairly stable at 20–25 °C.[51] It may be that the elimination of ethane is in this instance catalysed by methyl iodide[48].

Trifluoroiodomethane reacts with MeAuL similarly to methyl iodide[49,52]. In this case, when L = PMe_3 or PMe_2Ph, the isomeric complexes (IX) are formed in high yields:

$$MeAuL + CF_3I \rightarrow Me_2Au\,(CF_3)\,L + LAuI\ ;\quad L = PMe_3,\ PMe_2Ph\ (IX). \quad (4)$$

Reaction (4) in methylene chloride leads to *trans*-(IX), while in CF_3I the product is *cis*-(IX). In other solvents (ether, acetone) a mixture of the *cis*- and *trans*-isomers is formed[49].

The triphenylphosphine complex reacts with trifluoroiodomethane differently[52]:

$$MeAuL + CF_3I \rightarrow CF_3AuL + MeI\ ;\quad L=PPh_3\ . \quad (5)$$

When L = $PMePh_2$ a mixture of products corresponding to reactions (4) and (5) is formed[52].

The inhibiting influence of a radical trapping agent (galvinoxyl) on reaction (4) has been observed and a radical mechanism of the formation of compound (IX) has been proposed on this basis[52]:

$$CF_3^{\cdot} + MeAuL \rightarrow [MeAu(CF_3)L]^{\cdot} \xrightarrow{CF_3I} Me(CF_3)Au(I)L + CF_3^{\cdot}\ ;$$
$$Me(CF_3)Au(I)L + MeAuL \rightarrow Me_2Au(CF_3)L + LAuI\ .$$

The poor reproducibility of the kinetic data has also been adduced as an argument in support of the radical reaction mechanism. However, the intermediate paramagnetic bivalent gold compound (X) was not detected and the authors[52] do not consider the radical mechanism to be the only one possible.

An unusual example of oxidative addition is provided by the reaction of hexafluorobut-2-yne with complexes of methyl- and ethyl-gold. This results in the formation of the dinuclear organogold compounds (XI), containing both univalent and tervalent gold[53]:

$$RAuL + CF_3C{\equiv}CCF_3 \xrightarrow{\text{ether}} \underset{\text{R = Me, or Et; L = PMe3, PMe2Ph, or PMePh2. (XI), 40–77\%}}{\begin{array}{c} F_3C \quad CF_3 \\ \diagdown\ \ \diagup \\ C{=}C \\ \diagup\ \ \diagdown \\ LAu \quad\ Au \\ \qquad\ \ \diagdown\ \ \diagup \\ \qquad\ \ R \quad\ L \end{array}}\ ;\ \ R \text{ in trans-positions}$$

The groups R in compounds (XI) are in the *trans*-positions relative to one another. In the case of $MeAuPMe_3$ the *cis*-isomer is formed in addition to the *trans*-isomer. On interaction with hexafluorobut-2-yne, the triphenylphosphine complex $MeAuPPh_3$ yields the dinuclear organogold compound $Ph_3PAuC(CF_3){=}C(CF_3)AuPPh_3$, which does not contain tervalent gold[54,55]. There are data indicating a radical mechanism of the reaction of hexafluorobut-2-yne with alkoxygold complexes[53].

Thiophenol[56] and selenophenol[57] react with methylgold complexes without the formation of gold(III) compounds:

$$MeAuL + PhSH \rightarrow CH_4 + PhSAuL\ ;$$
$$L=PMe_3,\ PMePh_2 \text{ or } PPh_3;$$
$$MeAuPMe_2Ph + PhSeH \rightarrow PhSeAuPMe_2Ph\ .$$

The reactions have a radical mechanism. Compounds containing the P–H and As–H bonds react analogously and polymeric products are obtained[57]:

$$MeAuPMe_2Ph + Ph_2ZH \rightarrow (AuZPh_2)_x\ ;$$
$$Z = P, \text{ or As.}$$

III. REDUCTIVE ELIMINATION FROM TERVALENT GOLD COMPOUNDS

One of the factors determining the result of the interaction of univalent gold compounds with reagents capable of oxidative addition is the thermal stability of the resulting gold(III) complex, which is directly related to the possibility of reductive elimination.

Hitherto reductive elimination had been studied virtually only for alkylgold(III) complexes. This process, which leads to the formation of a univalent gold compound, has been known for a fairly long time for organogold compounds without stabilising ligands[58]:

$$RAuX_2 \rightarrow RX + AuX\ ;$$
$$R_3AuX \rightarrow AuX + \text{hydrocarbons.}$$

The compounds *cis*-$[Me_2AuL_2]ClO_4$ are fully stable at 20 °C in the solid state, but decompose rapidly with formation of ethane at an elevated temperature, particularly in solution (under the conditions of the study of the ^1H NMR spectrum):[59]

$$\underset{\text{(XII)}}{cis\text{-}[Me_2AuL_2]ClO_4} \xrightarrow{CHCl_3} C_2H_6 + [L_2Au]ClO_4;$$
$$L=PPh_3,\ AsPh_3,\ SbPh_3\ .$$

It is significant that methane is not formed under these conditions even in trace amounts.

A necessary condition for the ready occurrence of the reductive elimination reaction involving complexes (XII) was believed to be the presence of bulky ligands L. Thus *cis*-$[Me_2Au(PMePh_2)_2]ClO_4$ is stable under conditions where its triphenylphosphine analogue decomposes[59]. However, it was shown later that the oxidative addition reactions are facilitated while reductive elimination is hindered for alkylgold complexes and the isoelectronic platinum complexes with increase of the electron density at the metal atom[60,61].

The rate of elimination of two methyl groups in the complexes *cis*-$Me_2Au(X)L$ depends on the nature of X and increases in the sequence $Cl < CF_3COO < NO_3 < CF_3SO_3$.[62]

The reductive elimination in trialkylgold complexes has been studied in greatest detail. Thus, when the complex Me_3AuPPh_3 is heated to 120 °C in xylene, biphenyl, or in the absence of a solvent, ethane is eliminated[51]:

$$Me_3AuPPh_3 \xrightarrow[87\%]{120^\circ} C_2H_6 + MeAuPPh_3\ .$$

Further decomposition of the univalent gold complex takes place at a higher temperature.

In the presence of free triphenylphosphine, the rate of elimination of two alkyl groups from R_3AuPPh_3 diminishes. It is therefore believed[63] that the reductive elimination is preceded by the dissociation of the complex [reaction (6)]:

$$R_3AuPPh_3 \rightleftarrows R_3Au + PPh_3\ . \qquad (6)$$

Further decomposition of trialkylgold can take place both intramolecularly and intermolecularly, which has been demonstrated in the study of the thermolysis of an equimolar mixture of Me_3AuPPh_3 and $(CD_3)_3AuPPh_3$ at 80 °C.[64] In non-coordinating solvents (decalin, chlorobenzene, and dibutyl ether) the ratio of the C_2H_6, CH_3CD_3, and C_2D_6 formed is nearly statistical, which indicates the occurrence of the intermolecular elimination process, probably via a dinuclear intermediate of type (XIII):

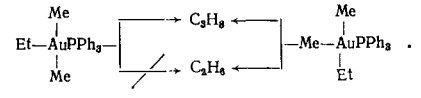
$$Me_3AuPPh_3 \rightleftarrows Me_3Au + PPh_3\ ;$$
$$Me_3Au + (CD_3)_n AuPPh_3 \rightleftarrows Me_3Au(CD_3)_n AuPPh_3\ ;$$
$$n = 1 \text{ or } 3; \qquad \text{(XIII)}$$
$$\text{(XIII)} \rightarrow MeAuPPh_3 + CD_3AuPPh_3 + C_2H_6 + C_2D_6 + CH_3CD_3\ .$$

In solvents such as dimethylformamide and dimethyl sulphoxide the cross-product CH_3CD_3 is formed only in trace amounts, which indicates intramolecular elimination. In this case the dissociation stage (6) is apparently followed by the coordination of the alkyl derivative of gold(III) to the solvent Sol:[64]

$$Me_3Au + Sol \rightleftarrows Me_3Au\cdot Sol\ ;$$
$$Me_3Au\cdot Sol \rightarrow MeAu\cdot Sol + C_2H_6, \text{ etc.}$$

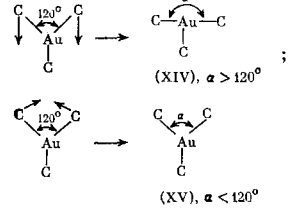
Intramolecular and intermolecular elimination pathways have also been observed in the thermolysis of $CD_3(Me)_2AuPPh_3$.[64] Apart from the nature of the solvent, the character of the process is strongly influenced also by the concentration of the gold(III) complex; with increase of concentration, the contribution of intermolecular elimination also increases.

Under the conditions of intramolecular elimination, the two alkyl groups in the *cis*-positions relative to one another are split off[63,64]. Thus the thermolysis of *trans*-$Et(Me_2)AuPPh_3$ leads mainly to the formation of propane, while the decomposition of the *cis*-isomer results in the formation of ethane and propane in comparable amounts:



The relative ease of elimination depends on the nature of the alkyl group. Thus methyl groups are eliminated with greater difficulty than ethyl groups[48], which agrees with the greater strength of the bond between the metal and the primary carbon atom.

A quantum-chemical calculation on the transition state in the reaction involving reductive elimination from a trimethylgold complex has been performed[64]. In the trimethylgold formed on dissociation of Me_3AuPPh_3 the highest occupied $4e'$ orbital is doubly degenerate if Me_3Au has the C_{3h} symmetry (the C–Au–C angles are 120°). This orbital can be only half-occupied, which should lead to a distortion of the C–Au–C angles according to the Jahn–Teller theorem, removing the degeneracy thereby. T-shaped (XIV) or Y-shaped (XV) symmetry distortions are possible:

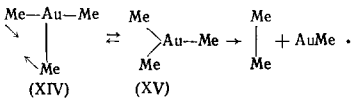


(XIV), $\alpha > 120^\circ$;

(XV), $\alpha < 120^\circ$.

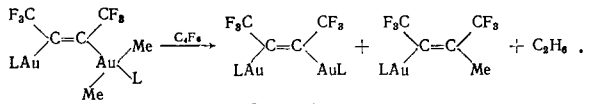
A molecular orbital calculation on the Me_3Au molecule has shown[64] that the T-shaped configuration (XIV) corresponds to the energy minimum. The vibrations of the two *cis*-Me groups towards one another lead to their spatial approach and a transition of the molecule to the Y-shaped configuration (XV), in which the coordination of the gold approaches

the linear form; under these conditions, elimination takes place:

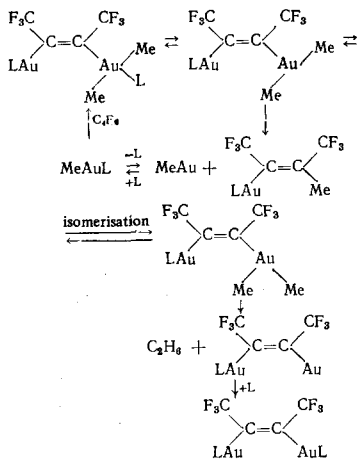


(XIV) (XV)

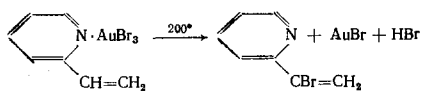
The only example of the elimination of an alkenyl group from a gold(III) complex is provided by the decomposition of the dinuclear hexafluorobutenyl derivatives (XI) catalysed by hexafluorobut-2-yne:[53]



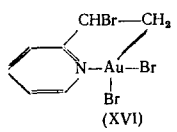
The mechanism proposed for this reaction is based on the hypothesis of the intramolecular *cis*-elimination:



A reductive elimination stage has been proposed for the thermolysis of the complex of $AuBr_3$ with 2-vinylpyridine[65]:



It has been suggested that gold adds initially to the C=C double bond with formation of the cyclic compound (XVI), from which AuBr and HBr are then split off:



(XVI)

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The data presented in the review show that the ability of a complex RAuL or the corresponding tervalent gold derivative to undergo oxidative addition or reductive elimination reaction depends greatly both on the group R and on the ligand L. However, it is at present difficult to reach an unambiguous conclusion concerning the nature of this dependence and particularly to give preference to steric or electronic factors.

The data on the oxidative addition of halogens and alkyl iodides to anionic complexes of univalent gold and to polyhalogenoaryl derivatives showed that these reactions involve in most cases *trans*-addition. However, the above conclusion cannot be extended to all types of organogold compounds, since, even within the framework of anionic complexes, there are deviations from the general rule for this class of compounds: the phenyl derivatives give rise to the *cis*-isomers. It is not clear whether this entials a change in the stereochemistry of the transition state or whether all aspects are determined by the difference between the thermodynamics of the *cis*- and *trans*-isomers of the compounds formed.

The oxidation-reduction interconversions of organometallic derivatives of univalent and tervalent gold have been little studied and, what is most important, only in isolated instances. In particular, reactions of organogold compounds with alkyl and especially aryl halides have been hardly investigated (the reaction of complexes of methylgold with methyl iodide is an exception). Despite this, one can already speak of the synthetic value of oxidative addition as a method of synthesis of organic derivatives of tervalent gold which are difficult to obtain.

Interesting results may be expected from the study of oxidative addition to zerovalent gold complexes, the first representative of which has been obtained quite recently[66].

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