Translated from *Uspekhi Khimii*, 438-466 (1982) U.D.C. 547.13

Organic Complexes of Univalent Gold

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Studies on the synthesis and reactivities of gold(I) complexes σ-linked to alkyl, aryl, unsaturated, and carbonyl-containing ligands, π-complexes with olefins and acetylenes, anionic, ylid, and carbene complexes, and also gold complexes with a bridging carbon atom derived from an organic group are examined.
The bibliography includes 167 references.

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I. INTRODUCTION

The chemistry of organic complexes of univalent gold has developed extremely vigorously in recent years. The first stable organometallic derivatives of univalent gold of the type RAuL, where L is a ligand containing phosphorus, arsenic, nitrogen, or sulphur, were obtained in 1959; in the first decade research developed mainly on the synthesis of such compounds by traditional methods—using organolithium, organosodium, or organomagnesium compounds. However, in the 1970's there was a qualitative change in the nature of the studies. New types of organic complexes of univalent gold were discovered: π-olefin, π-acetylene, carbene, anionic, and ylid complexes, as well as gold complexes with a bridging carbon atom. Fundamentally new methods of synthesis of organogold compounds were developed and hitherto unknown agents for the introduction of gold were discovered, which made it possible to obtain a wide range of alkyl and aryl complexes of gold(I) with different substituents, including functional groups, in the organic moiety. Furthermore, there has been a growth of interest in the study of the mechanisms of the reactions of organic derivatives of gold, which was aroused primarily by the more extensive utilisation of noble metals and their compounds as catalysts as well as their applications in medicine and radioelectronics.

Several reviews have now been published, most of these dealing with data on the organic complexes of both univalent and tervalent gold[1-5]. Puddephatt's monograph[6], containing extensive information about organic derivatives of gold in different valence states, was published in 1978. However, hitherto there has been no single review on organic complexes of univalent gold.

This review is devoted to the chemistry of such complexes. The data have been arranged systematically in terms of different types of organic complexes of gold(I).

II. σ-COMPLEXES OF THE TYPE RAuL

1. σ-Alkyl and σ-Aryl Complexes of Gold(I)

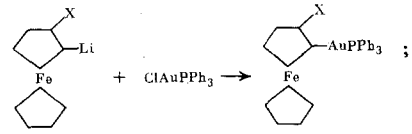
Historically the first and largest class of organic complexes of univalent gold comprises linear σ-alkyl and σ-aryl complexes of the type RAuL. Phosphines are usually employed as the stabilising ligand L;[7] very few examples of complexes with phosphites[8], arsines[9], and isonitriles[10] are known.

(a) Methods of Synthesis

The first phosphine complexes of alkyl- and aryl-gold were obtained in 1959 from complex gold halides and organolithium and organomagnesium compounds. For a long time, this was the only procedure for synthesising compounds of this type[7, 11-13]:

$$PhCH_2MgCl + ClAuPPh_3 \rightarrow PhCH_2AuPPh_3 .$$

Lithium derivatives of aromatic π-complexes (ferrocene and cymantrene) give rise to high yields of organogold σ-complexes on treatment with triphenylphosphine complexes of gold halides[14-16]:



X = H, Cl, OMe, CH_2NMe_2 .

Organogold complexes with ligands such as diphenylferrocenyl- and triphenylferrocenyl-phosphines have been obtained via organolithium and organomagnesium compounds. The diphenylferrocenylphosphine complex of gold bromide reacts with organolithium and organomagnesium compounds like its triphenylphosphine analogue[17]:

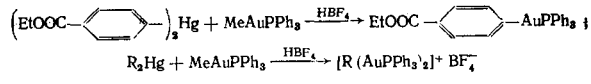
$$BrAuPPh_2C_5H_4FeC_5H_5 \xrightarrow{MeMgI} MeAuPPh_2C_5H_4FeC_5H_5 ;$$
$$BrAuPPh_2C_5H_4FeC_5H_5 \xrightarrow{p\text{-}MeC_6H_4Li} p\text{-}MeC_6H_4AuPPh_2C_5H_4FeC_5H_5 .$$

The triphenylphosphine complex of gold bromide reacts with methylmagnesium iodide, but does not react with aryl- and alkenyl-lithium and organomagnesium compounds[17]:

$$BrAuP(C_5H_4FeC_5H_5)_3 + MeMgI \rightarrow MeAuP(C_5H_4FeC_5H_5)_3 .$$

A preparative method of synthesis of organogold complexes with a wide range of organic groups via organomercury derivatives was proposed in 1978.[18-21] When organomercury compounds R_2Hg are acted upon by a phosphine complex of

methylgold $MeAuPR'_3$ in the presence of HBF_4, either mononuclear or dinuclear organogold complexes are formed depending on the groups R and R' and the reaction conditions[21,22]:



$$R_2Hg + MeAuPPh_3 \xrightarrow{HBF_4} [R(AuPPh_3)_2]^+ BF_4^-$$

where R = ferrocenyl, β-naphthyl, α-thienyl, styryl, cymantrenyl, tolyl, or phenyl.

The dinuclear organogold complexes can be converted into mononuclear complexes readily by treatment with nucleophiles[21,22]:

$$[R(AuPPh_3)_2]^+ BF_4^- \xrightarrow{Cl^-} RAuPPh_3 + ClAuPPh_3 .$$

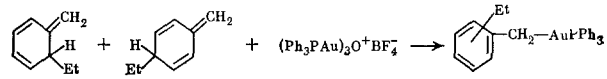
The synthesis of organomonogold complexes from the dinuclear complexes is of significant preparative importance, because a wide variety of dinuclear complexes are obtained in high yields from organomercury derivatives or by inserting gold into ferrocenes (see below).

Perhalogenoaryl derivatives of gold(I) are formed when phosphine complexes of univalent gold salts react with organic derivatives of tervalent thallium[23,24]:

$$(C_6F_5)_2TlBr + MeCOOAuPPh_3 \rightarrow C_6F_5AuPPh_3 + (C_6F_5)TlBr(OCOMe) .$$

Apart from the methods of synthesis of σ-complexes of gold enumerated above, based on the use of various organometallic derivatives or on the gold insertion reaction, single examples of the preparation of complexes of alkyl- and aryl-gold by other methods have been described.

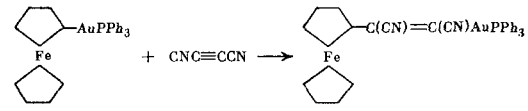
Isomeric trienes, generated from *o*- and *p*-ethyltoluenes, react with tris(triphenylphosphinegold)oxonium tetrafluoroborate via the aromatising metallation mechanism[25] with formation of a benzyl derivative of gold[26]:



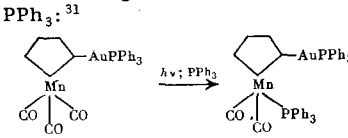
When the triphenylphosphine complex of gold pentafluorobenzoate is heated, it is decarboxylated and pentafluorophenylgold is formed[27,28]:

$$C_6F_5COOAuPPh_3 \xrightarrow{120^\circ} C_6F_5AuPPh_3 + CO_2 .$$

Other organogold compounds have been obtained from the ferrocenyl, cymantrenyl, and methyl derivatives of gold[30-32]. Thus when ferrocenyl(triphenylphosphine)gold is treated with the dinitrile of acetylenedicarboxylic acid, the acid is inserted in the Au–C bond and an organogold derivative of ferrocenyldicyanoethylene is formed[30]:



When cymantrenylgold is treated with triphenylphosphine or is exposed to ultraviolet light, one of the CO groups is substituted by PPh_3:[31]



Fluorinated alkenes react with phosphine complexes of methylgold under ultraviolet irradiation with insertion of the fluoroalkyl group in the Au–C bond[28,29]:

$$CF_2=CF_2 + MeAuPPh_3 \xrightarrow{h\nu} MeCF_2-CF_2AuPPh_3 .$$

On treatment with CF_3I, the methyl group in the phosphine complex of methylgold is exchanged for the trifluoromethyl group[32]:

$$MeAuPPh_3 + CF_3I \rightarrow CF_3AuPPh_3 + MeI .$$

Diazomethane reacts with the triphenylphosphine complex of gold chloride with insertion of methylene in the gold–chlorine bond and the formation of the chloromethyl derivative of gold[33]:

$$ClAuPPh_3 + CH_2N_2 \rightarrow ClCH_2AuPPh_3 .$$

Aromatic isonitriles react with $ClAuPPh_3$ in alcohol in the presence of alkali to form organic σ-derivatives of gold[34-36]:

$$ClAuPPh_3 + ArNC + ROH \xrightarrow{KOH} Ph_3PAu-C(OR)=NAr .$$

The same complexes have been obtained by the exchange reaction between gold chloride and organosilver compounds[37]:

$$Ph_3PAuCl + Ag-C(OEt)=NC_6H_4CH_3 \rightarrow AgCl + Ph_3PAu-C(OEt)=NC_6H_4CH_3 .$$

The phosphine complexes of arylgold have been isolated after adding phosphine to oligomeric aromatic complexes of the type $(XArAu)_n$.[38]

(b) Properties

The phosphine σ-complexes of organometallic derivatives of univalent gold are solids, which are readily soluble in benzene, chloroform, methylene chloride, and tetrahydrofuran. The complexes are monomeric in solutions, are diamagnetic, and have a linear structure[7,38,39]. The dipole moments of the alkyl and aryl derivatives of the phosphine complexes are lower than those of the corresponding halogeno-complexes: $MeAuPEt_3$ (5.5 D), $MeAuPPh_3$ (5.6 D), $C_6F_5AuPEt_3$ (6.2 D), and $ClAuPEt_3$ (8.4 D); this indicates a low polarity of the Au–C bond[6,7,40,41].

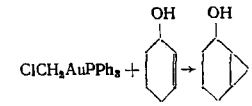
The majority of the phosphine complexes of the type RAuL readily decompose on heating in the solid state and particularly in solutions. The ferrocenylphosphine complexes have the highest thermal stability[17]. The triphenylphosphine complex of methylgold decomposes on heating to 100 °C with formation of ethane, metallic gold, and triphenylphosphine:

$$2MeAuPPh_3 \xrightarrow{100^\circ} C_2H_6 + 2Au + 2PPh_3 ,$$

while heating of ethylgold gives rise to n-butane. It has been shown that the rate of reaction is independent of the presence of oxygen and is retarded after the addition of triphenylphosphine. It has been suggested that the first stage involves the dissociation of the complex with formation of the free phosphine and methylgold, which reacts further with the initial complex[41,42]:

$$MeAuPPh_3 \rightleftarrows MeAu + PPh_3 ;$$
$$MeAu + MeAuPPh_3 \rightarrow C_2H_6 + 2Au + PPh_3 .$$

The triphenylcomplex of chloromethylgold readily decomposes on heating of its benzene solution[33]. If the decomposition is carried out in the presence of 3-cyclohexenol, then the intermediate carbenoid species adds to the double bond with formation of bicyclo[4,1,0]-2-heptanol:



Many organic complexes of gold are sensitive to light. The intermediate formation of methyl radicals has been detected in the photolysis of $MeAuPPh_3$ in deuterochloroform, giving rise

to a set of products: MeD, C_2H_6, $MeCDCl_2$, etc.:[43]

$$MeAuPPh_3 \xrightarrow{h\nu} [MeAuPPh_3]^S \rightarrow [MeAuPPh_3]^T \xrightarrow{CDCl_3} \rightarrow ClAuPPh_3 + Me^{\cdot} + {}^{\cdot}CDCl_2 .$$

The reactivity of organogold complexes is analogous to that of organomercury compounds, but the organogold derivatives are chemically more active and the range of their reactions is much wider. The reactions of complexes of alkyl- and arylgold with a wide variety of reagents, grouped in accordance with several types, are presented below.

A. Reactions with Dissociation of the Au–C Bond

Reactions with protic acids. Protic acids readily cleave the Au–C bond in alkyl and aryl complexes of gold. Thus methyl-,[7] phenyl-,[44] ferrocenyl-,[14] and cymantrenyl-gold[15] react with hydrogen halides, carboxylic acids, and hydrocyanic acid. It has been noted that the triethylphosphine complex of phenylgold is resistant to the action of an aqueous ethanol solution of hydrogen chloride[7]:

$$MeAuPPh_3 + HCl \rightarrow ClAuPPh_3 ,$$
$$PhAuPPh_3 + CH_3COOH \rightarrow CH_3COOAuPPh_3 ,$$
$$C_5H_5FeC_5H_4AuPPh_3 + HCN \rightarrow NCAuPPh_3 .$$

The reaction of aromatic complexes of gold with HBF_4 is specific, giving rise to dinuclear cationic complexes of gold (see below).

The reactions of phosphine complexes of methylgold with benzenethiol[45] and benzeneselenol[46] give rise to methane and gold mercaptide or selenide. The formation of the methyl radical has been detected in the reaction mixture by EPR:

$$MeAuPMe_3 + PhSH \rightarrow PhSAuPMe_3 + CH_4 ,$$
$$MeAuPMe_2Ph + PhSeH \rightarrow PhSeAuPMe_2Ph + CH_4 .$$

On reaction with trifluoromethylacetylene and phenylacetylene, which behave as protic acids, the corresponding gold acetylide is formed[28,29,47]:

$$MeAuPMe_2Ph + CF_3C{\equiv}CH \rightarrow CF_3C{\equiv}CAuPMe_2Ph + CH_4 .$$

Even weak protic acids, such as diphenylphosphine and diphenylarsine, cleave the Au–C bond with liberation of methane and the formation of insoluble gold-containing polymers[46].

Reactions with hydrogen halides and acid anhydrides. The reactions of ferrocenyl- and phenyl-gold with carboxylic acid anhydrides of halides entail the dissociation of the Au–C bond, but products of the electrophilic substitution of the gold atom are not formed[48].

Thus, when ferrocenylgold is treated with acetic anhydride or acetyl chloride, the products are ferrocene, biferrocenyl, a gold(I) salt, and acetaldehyde[48]. On treatment with powerful electrophiles, for example, acetylium and nitronium tetrafluoroborates, ferrocene and biferrocenyl are also obtained and a dinuclear cationic organogold complex is formed: $[R(AuPPh_3)_2]^+BF_4^-$ (see below[48]).

The reactions of phenylgold with carboxylic acid chlorides and nitronium tetrafluoroborate do not give rise to electrophilic substitution products—ketones and nitrobenzene[48]. The results can be readily explained from the standpoint of the mechanism involving one-electron transfer as the first elementary step in the above reactions.

The most convincing example of this is provided by the reaction of ferrocenyl-, phenyl-, or cymantrenyl-gold with ferrocenium tetrafluoroborate, which manifests strikingly the properties of a one-electron acceptor. In the first reaction stage the ferrocenium cation accepts an electron and is converted into ferrocene, while the organogold compound, having lost an electron, decomposes into a radical and triphenylphosphinegold tetrafluoroborate. This coordination-unsaturated compound reacts with a molecule of the initial organogold compound of triphenylphosphine when the latter is added to the reaction mixture[48]:

$$RAuPPh_3 + (C_5H_5)_2Fe^+BF_4^- \rightarrow (C_5H_5)_2Fe + [R^{\cdot}] + [Ph_3PAu^+BF_4^-]$$
$$\downarrow \qquad\qquad \downarrow PPh_3$$
$$R{-}H + R{-}R \qquad (Ph_3P)_2Au^+BF_4^- .$$

Reactions with alkyl halides. The experimental data accumulated so far suggest that many reactions of organic complexes of gold(I) involve oxidative addition with subsequent reductive elimination of the resulting gold(III) complex and the formation of new univalent gold complexes†. Only the mechanism of the reactions of phosphine complexes of alkylgold with alkyl halides has been studied in detail[32,49–54].

The interaction of alkylgold complexes with alkyl halides proceeds via oxidative addition, which is characteristic not only of organic derivatives of univalent gold but also of complexes of other transition metals[55]. The final products of the reaction of methyl iodide with the triphenylphosphine complex of methylgold are ethane and the triphenylphosphine complex of gold iodide:

$$MeAuPPh_3 + MeI \rightarrow C_2H_6 + IAuPPh_3 .$$

It has been established experimentally that the reaction proceeds via the following mechanism:

$$MeAuPPh_3 + MeI \rightarrow Me_2AuIPPh_3 ,$$
$$Me_2AuIPPh_3 + MeAuPPh_3 \rightarrow Me_3AuPPh_3 + IAuPPh_3 ,$$
$$Me_3AuPPh_3 \rightarrow C_2H_6 + MeAuPPh_3 .$$

The initial stage of the reaction involves the oxidative addition of methyl iodide to the univalent gold atom. The dimethylgold iodide formed then reacts rapidly with the complex of the initial methylgold, giving rise to a complex of trimethylgold, which undergoes reductive elimination under the reaction conditions with formation of ethane and a gold iodide complex[49–52].

The mechanism proposed has been confirmed by the reactions of other derivatives of alkylgold. Thus the final products of the reaction of triphenylphosphine complexes of ethylgold with methyl iodide are a gold iodide complex and butane[51]:

$$EtAuPPh_3 + MeI \rightarrow (Me)(Et)AuIPPh_3 \rightarrow (Me)(Et)_2AuPPh_3 + IAuPPh_3$$
$$\rightarrow MeAuPPh_3 + C_4H_{10} .$$

When trimethyl- and dimethylphenyl-phosphine complexes of methylgold are used, only the product of the oxidative addition of methyl iodide, namely Me_2AuIL, was isolated from the reaction mixture[53,54]. The complexes of methylgold also react with CF_3I; the nature of the final reaction products depends, as for methyl iodide, on the nature of the ligand[32]. In the case of the trimethylphosphine complex a tervalent gold compound was isolated, while transalkylation takes place in the reaction involving the triphenylphosphine complex. The reaction with the methyldiphenylphosphine ligand gives rise to a mixture of trifluoromethyl derivatives of univalent and tervalent gold[32]:

$$MeAuL + CF_3I \rightarrow \begin{cases} \xrightarrow{L=PPh_3} CF_3AuL + MeI \\ \xrightarrow{L=PMe_3} (CF_3)Me_2AuL + IAuL . \end{cases}$$

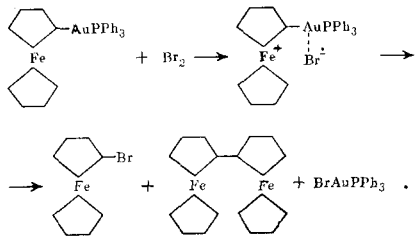
The triphenylarsine complex of pentachlorophenylgold reacts with MeI to form an oxidative addition product[9].

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† The data on this question have been described in detail in Dyadchenko's review (see the next review in this issue).

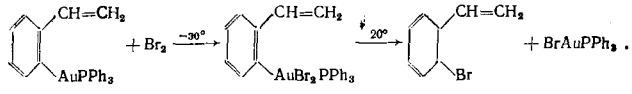
Presumably other reactions, and in particular the reactions of gold(I) complexes with metal halides and salts, proceed analogously, since in some instances the intermediate oxidative addition products have been isolated.

Reactions with halogens. The reactions with bromine and chlorine have been studied in detail in relation to the organogold derivatives of the ferrocene, cymantrene, and benzene series[14,15,44,56,57]. Together with the halogenoderivatives of aromatic systems, compounds of the type RH or R–R are formed in this reaction. For the ferrocenyl compounds of gold, the ratio of bromoferrocene and biferrocenyl varies as a function of the rate and order of mixing of the reactants. When bromine is added rapidly to ferrocenylgold, *mainly bromoferrocene is formed, while under the conditions of a slow addition there is an appreciable increase of* the amount of biferrocenyl. The reaction of ferrocenylgold with bromine and chlorine proceeds specifically also in another respect; at low temperatures in organic solvents an unstable product of the addition of the halogen molecule to the organogold compound is formed initially[56,57]:



It may be that the intermediate complex of ferrocenylgold with a halogen molecule has the structure of a ferrocenium salt, in which the radical-anion is coordinated to the gold atom. This is confirmed indirectly by the finding that in the case of the less reactive organomercury derivatives of ferrocene, a complex of this type has been isolated and investigated[58].

However, one cannot rule out the possibility that the substitution of the $AuPPh_3$ group by bromine or chlorine in the aromatic series involves the oxidative addition of the halogen to the gold atom with subsequent reductive disproportionation of the resulting tervalent gold compound. The possibility of reaction via this mechanism is confirmed by the finding that, in the reaction of *o*-vinylphenylgold with bromine at –30 °C, the product of the addition of the halogen to gold was isolated. At room temperature reductive elimination takes place with formation of gold bromine and *o*-bromostyrene[59]:



Perhalogenoaryl complexes of gold react either with cleavage of the Au–C bond or with its retention and the formation of aryl halide complexes of tervalent gold, depending on the nature of the halogen and the initial complex[9,10,60–64]. Thus the arsine complex of pentafluorophenylgold reacts with chlorine to form only the oxidative addition product; reaction with bromine involves partial cleavage of the Au–C bond in addition to the above reaction, while the reaction with iodine entails the complete cleavage of the Au–C bond[9];

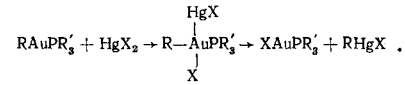
$$C_6F_5AuAsPh_3 + I_2 \rightarrow C_6F_5I + IAuAsPh_3 .$$

The isonitrile complexes of perhalogenoarylgold[62] and the triphenylarsine complex of pentachlorophenylgold react with halogens to form only the oxidative addition products[9].

Reactions with metal salts and organometallic compounds. Organic complexes of gold react with metal salts usually with cleavage of the Au–C bond, but sometimes they proceed with retention of this bond and the formation of the products of the oxidative addition to the gold atom. The reaction of the phosphine complexes of alkyl- and aryl-gold with mercury salts has been studied in greatest detail. Under mild conditions, mercury(II) chloride reacts with methyl-, ethyl-,[65] phenyl-,[44] benzyl-, ferrocenyl-, and cymantrenyl-gold[2], giving rise to high yields of the products of the cleavage of the gold–carbon bond.

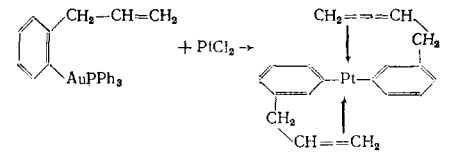
This reaction has served as a model for the investigation of the mechanism of electrophilic substitution at a saturated carbon atom. It has been shown[65] that, for the majority of alkyl complexes of gold, the reaction proceeds via an S_N2 mechanism. Mercury(II) reacts via an S_N1 mechanism in polar solvents with complexes of alkylgold having powerful electron-accepting substituents.

Before the publication of the study of Gregory and Ingold[65], data on the mechanism of substitution in organometallic compounds were obtained mainly in relation to organomercury compounds. However, later a mechanism of the "oxidative addition–reductive elimination" type was proposed as an alternative[49]:



It is known that adducts corresponding to an intermediate of this type have been obtained for phosphine complexes of iridium[61]. On the basis of the experimental data available at present, it is impossible to make a choice between these two mechanisms.

Both platinum halides[59] and platinum and palladium halide complexes[67] react with complexes of the type of RAuL in which a gold atom is substituted for platinum or palladium:



The complexes of methylgold react with tervalent gold halides and their complexes to form a univalent gold halide and an alkyl derivative of tervalent gold[50,52,54,67]. The reaction involves the transfer of the methyl group from the Au(I) atom to the Au(III) atom[52,68]:

$$2MeAuPMe_2Ph + Br_2AuPMe_2Ph \rightarrow 2BrAuPMe_2Ph + Me_2BrAuPMe_2Ph .$$

In the triphenylphosphine complexes of ethyl- and phenylgold, the Au–C bond is cleaved by $TiCl_3$,[60] while perhalogenoaryl derivatives of gold(I) react with thallium halides via the oxidative addition mechanism with formationof perhalogenoaryl derivatives of gold(III):[9,60,62–64,67]

$$C_6Cl_5AuAsPh_3 + TlCl_3 \rightarrow cis\text{-}C_6Cl_5AuCl_2AsPh_3 + TlCl .$$

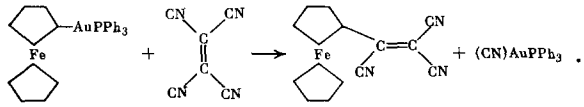
When chloromethylgold is treated with KI and NaCN, chlorine substitution products are not formed. The reaction of chloromethylgold with KI gives a high yield of triphenylphosphinegold iodide, while the reaction with NaCN gives rise to methyltriphenylphosphonium dicyanoaurate[33]. The formation of the latter salt is probably associated with the fact that, when chloromethylgold reacts with NaCN, the CN^- anions are coordinated to the gold atom with ejection of a chloride ion and the stabilisation of the intermediate species as a result of the abstraction of a proton from the solvent

with subsequent migration of the methyl cation, leading to the formation of a phosphonium salt:

$$ClCH_2AuPPh_3 \xrightarrow{2CN^-} \left[Ph_3PAu(CN)-CH_2-CN \right]^- \xrightarrow{H_2O} [Ph_3PCH_3]^+[Au(CN)_2]^- .$$

The triphenylphosphine complex of phenylgold exchanges the phenyl group for the perfluorophenyl group on treatment with $(C_6F_5)_2TlAr$.[24]

Other reactions. The reactions of phosphine complexes of ferrocenyl- and phenyl-gold with tetracyanoethylene (TCE) at room temperature proceed in different ways. In the reaction of ferrocenylgold one of the CN groups is substituted by the ferrocenyl residue, while in the reaction of phenylgold two $AuPPh_3$ groups add to the double bond of TCE:[2,29]



The phosphine complexes of methylgold react with hexafluoroacetone to form a product of addition of the carbonyl group, containing two $AuPPh_3$ groups[27,28]:

$$MeAuPPH_3 + (CF_3)_2C{=}O \rightarrow C_2H_6 + Ph_3PAu{-}O{-}C(CF_3)_2{-}AuPPh_3 .$$

The reaction with hexafluoroacetone hydrate gives rise to $(CF_3)_2C(OAuPPh_3)_2$.[28]

B. Reactions with Retention of the Au–C Bond

The reactions of RAuL with retention of the gold–carbon bond but with a change in the oxidation state of gold take place when the complexes interact with alkyl halides, halogens, and metal salts (see above). The reactions involving the substitution of the ligand L by another less strongly bound ligand without the dissociation of the Au–C bond have been described for complexes of the type RAuL. In the arylgold compounds the Ph_3P ligand has been replaced by the more electron-donating triferrocenylphosphine ligand[17]:

$$p\text{-}CH_3C_6H_4AuPPh_3 \xrightarrow{P(C_5H_4FeC_5H_5)_3} p\text{-}CH_3C_6H_4AuP(C_5H_4FeC_5H_5)_3 .$$

Alkylphosphines are readily displaced from the complex by triphenylphosphine[68]:

$$MeAuPMe_3 + PPh_3 \rightarrow MeAuPPh_3 + PMe_3 .$$

On the basis of such exchange reactions, the series based on the electron-donating properties of the ligands in the methylgold complexes has been established[68]:

$$PPh_3 > PEt_3 > PMe_3 \geqslant AsPh_3 .$$

It has been shown that the exchange of ligands in methylgold complexes involves an associative mechanism[8,69,70]:

$$MeAuL \underset{-L'}{\overset{+L'}{\rightleftharpoons}} MeAu\begin{matrix} L' \\ L \end{matrix} \rightleftarrows MeAuL' .$$

The exchange of a monodentate ligand for a bidentate ligand has been achieved in methylgold complexes[68]:

$$MeAuPMe_3 + Me_2P{-}CH_2{-}CH_2PMe_2 \xrightarrow{-PMe_3} \begin{matrix} MeP{-}CH_2{-}CH_2{-}PMe_2 \\ \downarrow \qquad\qquad \downarrow \\ AuMe \qquad\quad AuMe \end{matrix} .$$

In the σ-linked complexes $Ph_3PAu{-}C(OR){=}NAr$ there is a nitrogen atom capable of complex formation. Complexes of this type readily give rise to picrates and also behave as unusual organometallic ligands in relation to another transition metal[71]:

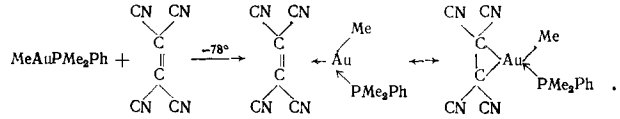
$$Ph_3PAu{-}C(OMe){=}NC_6H_4Me + Rh_2(CO)_4Cl_2 \rightarrow Ph_3PAu{-}C(OMe){=}NC_6H_4Me$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \downarrow$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad Cl{-}Rh{-}CO$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad CO$$

C. Reactions Involving Insertion in the Au–C Bond

Methylgold complexes react with fluorinated alkenes under ultraviolet irradiation with insertion of the fluoroalkyl fragment in the Au–C bond[27–29]. It may be that the reaction proceeds via the intermediate formation of a π-complex with the olefin:

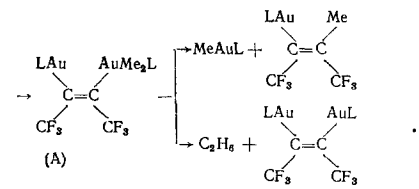
$$MeAuPPh_3 + CF_2{=}CF_2 \xrightarrow{h\nu} MeCF_2{-}CF_2AuPPh_3 .$$

The phosphine complexes of methylgold react with TCE at low temperatures to form a very unstable 1 : 1 complex[29,47]. The parameters of the infrared and ultraviolet spectra of this complex are inconsistent with the usual charge-transfer complexes of the product involving the insertion of the TCE fragment in the Au–C bond. On the basis of these spectroscopic data and by analogy with the isoelectronic phosphine complex of platinum[72], a metal-containing ring structure was attributed to the tetracyanoethylene complex of methylgold:



The reactions with alkynes sometimes lead only to the product of the insertion of the alkyne in the carbon–metal bond; in most instances a mixture of products is formed[28]. In the reaction of phosphine complexes of methylgold with hexafluorobut-2-yne under ultraviolet irradiation or on heating, a product (A), incorporating a *cis*-bridged C_4F_6 fragment and two gold atoms in different oxidation states, is formed initially[27,47,73,74]. ^1H NMR, Mössbauer spectroscopic, and X-ray spectroscopic data, confirming the proposed structure, are available for this product with L = PMe_3:[47,73,75]

$$MeAuL + CF_3C{\equiv}CCF_3 \xrightarrow{h\nu}$$



In the presence of an excess of hexafluorobut-2-yne the intermediate (A) can decompose in a manner which depends on the nature of the ligand and the solvent: either with elimination of MeAuL and the formation of the product of the insertion of the $CF_3C{=}CCF_3$ group in the Au–C bond or with reductive elimination at the Au(III) centre and formation of ethane and $(AuL)CF_3C{=}CCF_3(AuL)$. In both cases the *cis*-derivatives of hexafluorobut-2-ene are formed.

In the reaction of but-2-yne with methylgold, only $Ph_3PAuMeC{=}CMeAuPPh_3$ was isolated in a low yield[28] while the reaction with $MeOOCC{\equiv}CCOOMe$ involves decomposition to metallic gold and the formation of two products, one of which results from the insertion of acetylene in the Au–C bond, while the other is *cis*-$LAuMe_2(MeOOC)C{=}C(COOMe)Me$.[29] Ferrocenylgold reacts with acetylenedicarboxylic acid to form the product of the insertion of the alkyne in the Au–C bond (see above).

Methylgold[29] and arylgold[59,76,77] react with SO_2 at low temperatures, SO_2 being inserted in the Au–C bond with formation of gold sulphinate complexes:

$$RAuPPh_3 + SO_2 \rightarrow R-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-AuPPh_3 ;$$

$$R = Me,\ o\text{-}CH_2{=}CHC_6H_4 .$$

It has been shown that, in contrast to copper and silver sulphinate complexes in which the metal atom is linked to the oxygen atom, the gold sulphinate complexes have the Au–S bond[29,59,76,77].

2. σ-Alkenyl Complexes of Gold(I)

The σ-alkenyl complexes have been obtained by the reaction of complex gold halides with organosodium[79] or organomagnesium[13,79,80] compounds:

$$C_5H_5Na + ClAuPPh_3 \rightarrow C_5H_5AuPPh_3 ;$$
$$CH_2{=}CHMgBr + ClAuPPh_3 \rightarrow CH_2{=}CHAuPPh_3 .$$

The synthesis via organomercury derivatives is more general[22,81]. Depending on the nature of the alkenyl group and the ligand, the reaction of organomercury compounds with the methylgold complex in the presence of HBF_4 gives rise to either mononuclear organogold complexes:

$$[PhCH{=}C(COOMe)]_2Hg \xrightarrow{MeAuPPh_3;HBF_4} PhCH{=}C(COOMe)AuPPh_3$$

or to the dinuclear complexes, which can be readily converted into the mononuclear complexes by treatment with various nucleophiles:

$$(PhCH{=}CH)_2Hg \xrightarrow{MeAuPPh_3;HBF_4} [PhCH{=}CH(AuPPh_3)_2]^+BF_4^- .$$

The σ-alkenyl complexes are also formed when methylgold interacts with acetylenic compounds via the insertion of the unsaturated group in the Au–C bond (see above).

The σ-alkenyl complexes of gold are solids stable in air, which are readily soluble in chloroform, methylene chloride, and benzene; they are associated in solution in benzene. The styryl derivatives of gold are coloured yellow.

The cyclopentadienyl derivatives of gold may be expected to have either the η^5-structure, similar to that of the triphenylphosphine complex of cyclopentadienylcopper[82], or the η^1-structure, established for the cyclopentadienyl derivatives of mercury. Careful analysis of infrared and ^1H NMR spectra of the triethyl- and triphenyl-phosphine complexes of cyclopentadienyl- and methylcyclopentadienyl-gold, obtained at different temperatures, showed that, like the cyclopentadienyl derivatives of mercury, these compounds constitute an example of stereochemically non-rigid organometallic compounds with η^1-coordination of the cyclopentadienyl ligand[78,84,85].

The reactivity of the alkenyl derivatives of gold has been studied mainly in relation to vinylgold. The gold–carbon bond is readily broken by hydrogen halides, halogens, dithiocyanogen, and mercury salts. The vinyl derivative of gold is resistant to the reaction of dilute acetic and hydrochloric acids:

$$\begin{array}{ccccc} PhCOOAuPPh_3 & & & & ClAuPPh_3 \\ \uparrow PhCOOH & & & & \uparrow HCl \\ & & & & \\ NCSAuPPh_3 & \xleftarrow{(SCN)_2} & CH_2{=}CHAuPPh_3 & \xrightarrow{Hal_2} & HalAuPPh_3 \\ & & & & \\ \downarrow HgCl_2 & & & & \downarrow KMnO_4;\ Me_2CO \\ CH_2{=}CHHgCl + ClAuPPh_3 & & & & MeC(O)CH_2AuPPh_3 \end{array} ;$$

$$Hal = Cl,\ Br,\ I .$$

When an acetone solution of $KMnO_4$ was allowed to react with vinylgold, a stable product of the oxidation of the vinyl group was not isolated, gold-substituted acetone being obtained[86].

Reactions involving the cleavage of the gold–carbon bond have been used to confirm the configuration of the styryl derivatives of gold. Thus the interaction of *trans*-styrylgold with iodine in dimethylformamide (DMF) or with mercury(II) bromide yielded the *trans*-isomers of the corresponding styrene derivatives[80]:

$$trans\text{-}PhCH{=}CHAuPPh_3 \begin{cases} \xrightarrow[DMF]{I_2;CdI_2} trans\text{-}PhCH{=}CHI + IAuPPh_3 \\ \xrightarrow{HgBr_2} trans\text{-}PhCH{=}CHHgBr + BrAuPPh_3 . \end{cases}$$

trans-Styryl(triphenylphosphine)gold is unusually readily converted into the *cis*-isomer. Whereas for the mercury derivatives this transition requires a high temperature, ultraviolet irradiation, or treatment with peroxides, the transformation of *trans*-styrylgold into the *cis*-isomer takes place when its solutions are allowed to stand at room temperature or in chromatography on Al_2O_3.[80]

In order to determine the configuration of the phosphine complexes of 1-methoxycarbonyl-2-phenylvinylgold, they were protolysed[22] and *trans*-cinnamic acid and the corresponding gold chloride complexes were isolated in high yields.

3. σ-Alkynyl Complexes of Gold(I)

Gold acetylide C_2Au_2 was obtained as early as 1900; it is an explosive powder with a polymeric structure[87]. Other alkynyl complexes, for example, gold phenylacetylide, proved to be more stable. These complexes have been obtained by treating gold halides with alkali metal acetylides[88]. Gold phenylacetylide was isolated after gold ketenide had been treated with phenylacetylene[89].

A series of very stable gold phenylacetylide complexes with phosphines, arsines, amines, and isonitriles were obtained in 1962. They are formed readily from sodium phenylacetylide and gold halides in the presence of the corresponding ligand[40]:

$$PhC{\equiv}CH \xrightarrow{1)CH_3COONa;\ 2)AuBr} (PhC{\equiv}CAu)_n \xrightarrow{L} PhC{\equiv}CAuL .$$

Yet another method of synthesis of these compounds involves the reaction of an alkyne with methylgold complexes[28,29,47]:

$$MeAuL + RC{\equiv}CH \rightarrow RC{\equiv}CAuL + CH_4 ;$$
$$R = Ph,\ CF_3 .$$

Gold phenylacetylides, stabilised by n-donor ligands, are thermally stable solids, which are readily soluble in many organic solvents; they are usually monomeric in solution with exception of the amine complexes[6,40]. The amine complexes are associated via hydrogen bonds[90]. The activity of the σ-alkynyl complexes has not been studied. It is only known that gold phenylacetylide gives rise to diphenylbutadiyne in the presence of $CuCl_2$:[91]

$$2PhC{\equiv}CAu + CuCl_2 \rightarrow PhC{\equiv}C{-}C{\equiv}CPh + CuCl + 2AuCl .$$

4. Carbonyl-Containing Derivatives of Gold(I)

α-Gold-substituted ketones, gold-substituted acetaldehyde, β-dicarbonyl-gold containing complexes, and gold ketenide are now known. Gold-substituted carbonyl compounds of various types have become readily available after the discovery of a new gold-substituting agent—tris(triphenylphosphinegold)oxonium salts[92,93].

Gold-containing oxonium salts are obtained in high yields in the reaction of coordination-unsaturated cation Ph_3PAu^+ with water in an alkaline or acid medium. The Ph_3PAu^+ ion is generated in solution when triphenylphosphinegold chloride reacts with silver tetrafluoroborate[5].

The most convenient method of synthesis of tris(triphenylphosphinegold)oxonium salts is the reaction of triphenylphosphinegold halides with silver oxide and sodium tetrafluoroborate or potassium permanganate[93]:

$$Ph_3PAuX + Ag_2O \xrightarrow{NaBF_4} (Ph_3PAu)_3O^+BF_4^- \quad (Ph_3PAu)_3O^+MnO_4^- ;$$

X=Cl, Br.

X-Ray diffraction study of tris(triphenylphosphinegold)-oxonium tetrafluoroborate showed that the $(Ph_3PAu)_3O$ fragment has a pyramidal structure: the oxygen atom is displaced from the plane formed by the three gold atoms. The Au–Au distances are 3.03 and 3.215 Å, which suggests Au–Au interaction in the oxonium cation[5].

Gold-containing oxonium salts are crystalline substances, which melt with decomposition and are decomposed by halide ions. Thus treatment of a solution of a tris(triphenylphosphinegold)oxonium salt in chloroform with an aqueous NaCl solution results in a quantitative yield of triphenylphosphinegold chloride and sodium hydroxide[93]:

$$(Ph_3PAu)_3O^+BF_4^- + 3NaCl + H_2O \rightarrow 3Ph_3PAuCl + NaBF_4 + 2NaOH .$$

Gold-containing oxonium salts proved to be excellent gold-substituting agents—this is the first example of the utilisation of metal-containing oxonium salts as metallating agents. Gold-containing oxonium permanganate reacts with acetone and other ketones containing the methyl group, forming ketones substituted with gold in the methyl group[94]:

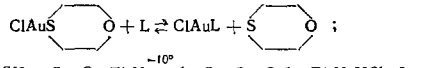
$$R{-}C(O){-}CH_3 + (Ph_3PAu)_3O^+MnO_4^- \rightarrow R{-}C(O){-}CH_2AuPPh_3 ;$$
$$R = Me, Et, Ph, C_5H_5FeC_5H_4 .$$

Gold-substituted acetone and acetylacetone have also been obtained by the reaction of triphenylphosphinegold bromide, silver oxide, and the corresponding ketone[95]:

$$Ph_3PAuX + Ag_2O \xrightarrow[Me_2CO]{X=Br} MeC(O)CH_2AuPPh_3 \quad \xrightarrow[(MeCO)_2CH_2]{X=Cl} (MeCO)_2CHAuPPh_3 .$$

The cation Ph_3PAu^+, the structural unit of many gold compounds, is a soft Lewis acid and does not usually form bonds with hard oxygen-containing anions. Thus the gold atom in gold acetylacetonate is linked to a carbon atom, while the atoms of the majority of transition metals, including copper and silver, are linked to an oxygen atom in diketonates[96]. The gold–carbon bond is also formed in gold-substituted ketones and in gold-substituted acetaldehydes[94,97]. α-Gold-substituted carbonyl compounds have also been obtained by the reaction of a gold-containing oxonium salt with enol ethers[5]. When vinyl ethers and esters are treated with oxonium tetrafluoroborate, gold-substituted acetaldehyde is formed[94,97].

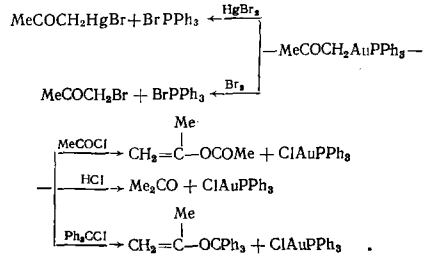
Like copper and silver, gold forms the ketenide $Au_2C{=}C{=}O$ when a gold chloride complex is treated with keten at −10 °C in acetonitrile in the presence of 2,6-dimethylpyridine (L) and triethylamine[89]:



$$ClAuL + CH_2{=}C{=}O + Et_3N \xrightarrow{-10^\circ} Au_2C{=}C{=}O{\cdot}L + Et_3N{\cdot}HCl + L .$$

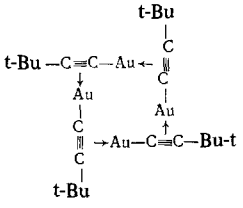
The complex gold ketenide readily loses the ligand at room temperature and gives rise to a polymeric gold ketenide, which is explosive in the solid state and is virtually insoluble in the majority of organic solvents. In the presence of aniline, gold ketinide reacts with phenylacetylene to form acetanilide and gold phenylacetylide.

The reactions of α-gold-substituted carbonyl compounds have been studied in greater detail in relation to gold-substituted acetone. Thus triethylenephosphinegold-substituted acetone reacts with electrophiles similarly to the reaction of α-mercurated carbonyl compounds, with cleavage of the metal–carbon bond and the formation of the corresponding *C*- and *O*-derivatives. The reactions involving the carbon atom proceed with acids, mercury(II) chloride, diazomethane, and bromine[5,33,98]. The reactions involving the O atom take place with carboxylic acid chlorides and chlorotriphenylmethane:



5. The Complexes $(RAu)_n$

There are few example of organic gold complexes of the type $(RAu)_n$ which exist without an outer stabilising ligand L. In such complexes the group σ-linked to the gold atom usually contains either a multiple bond or a heteroatom, which play the role of complex-forming agents in relation to another gold atom, giving rise to oligomerisation or polymerisation of the compound. Examples of such compounds are the σ-alkenyl and σ-alkynyl derivatives of gold. It has been suggested that gold t-butylacetylide exists in the form of a tetramer, for which the following structure has been proposed[1]:



The study of the infrared spectra of this and other alkynyl complexes of gold has shown that the π-coordination of the gold atom with a triple bond is extremely weak[40,88]. In oligomers this bond is readily ruptured even after the addition of a ligand having very weak electron-donating properties, for example Et_3As.[6]

An example of a compound in which intermolecular coordination involves the double bond is provided by cyclopentadienylgold, obtained when an olefin complex of gold chloride is treated with cyclopentadienylsodium or cyclopentadiene in the presence of triethylamine[78]:

$$C_5H_5Na + ClAuL \rightarrow (C_5H_5Au)_n + L + NaCl .$$

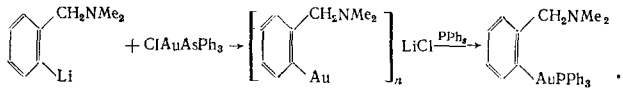
Cyclopentadienylgold is a yellow powder stable only up to −30 °C and almost insoluble in organic solvents. It has a polymeric structure. On treatment with PPh_3, its triphenylphosphine complex is readily produced[78].

Another group of complexes of the type $(RAu)_n$ includes compounds in which the σ-linked ligand contains a nitrogen atom, which functions as a complex-forming agent.

The only phenyl derivatives of gold which exists without a stabilising outer ligand, is 2-dimethylaminomethylphenyl gold[38], obtained from the mixed Au–Li cluster of arylgold:

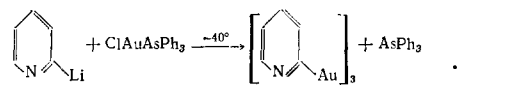
$$R_4Au_2Li_2 + Me_3SnBr \rightarrow RSnMe_3 + (RAu)_n + LiBr\ ;$$
$$R = 2\text{-}Me_2NCH_2C_6H_4\ .$$

The same compound is also formed in the reaction of the lithio-derivative of dimethylaminomethylbenzene with the triphenylarsine complex of gold chloride. Triphenylarsine was isolated in a quantitative yield and a solid residue, consisting of an LiCl–RAu mixture, was obtained, but the pure derivative of arylgold could not be isolated from this mixture. The formation of the latter was confirmed by the isolation of its stable triphenylphosphine complex after the addition of PPh_3 to the reaction mixture[38]:

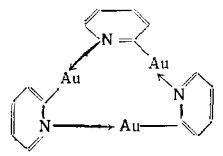


2-Dimethylaminomethylphenylgold is a colourless substance, thermally stable up to 117 °C, has a polymeric structure, and is almost insoluble in organic solvents. The group (containing a nitrogen atom) σ-linked to the gold atom plays the role of the stabilising ligand for the gold atom in another molecule.

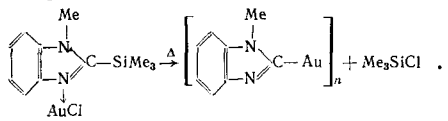
A coordination of the same type can be proposed for pyridylgold and other nitrogen-containing aromatic heterocycles. Derivatives of pyridyl- and quinolinyl-gold have been obtained via their lithio-derivatives and triphenylarsine complexes of gold chloride[99,100]:



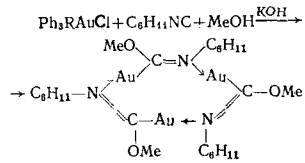
These compounds are solid, sparingly soluble polymeric substances, stable in air at room temperature, which are sensitive to the action of light. The structure of a cyclic trimer with coordination of the nitrogen atoms to the gold atoms has been proposed for pyridylgold:



Yet another example of complexes of this type is provided by the gold-containing derivatives of 1-methylbenzimidazole[101]:



The reaction of aliphatic isonitriles with gold chloride complexes in the presence of alcohol and alkali results in the formation of alkoxy(alkylamino)methylgold complexes[34–36], which are trimeric in solution and, like pyridylgold, have a planar heteroatomic ring:



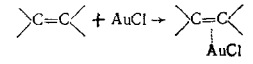
Similar cyclic trimers have been obtained from carbene complexes of gold[102] (see also Section V below).

Cyclic trimers are stable solids, do not react with CO and PPh_3 under normal conditions[36], and react with bromine and iodine via the oxidative addition mechanism, forming cyclic trimeric complexes of tervalent gold[103].

III. π-OLEFIN AND π-ACETYLENE COMPLEXES OF GOLD

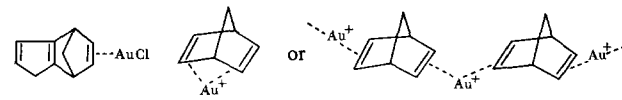
The first olefinic π-complexes of gold(I) were described by Hüttel and Dietyl[104] and Chalk[105]. Complexes of this type are intermediates in reactions involving an olefin and gold compounds as catalysts[106].

The π-complexes of gold(I) are formed at low temperatures as a result of the interaction of the olefin with gold chloride[107,108]:



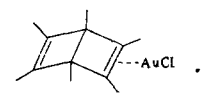
Both acyclic and cyclic olefins undergo the reaction[107–109]. The π-complexes of gold(I) are relatively unstable and readily split off the olefin ligand. Their stability increases with increase of the molecular weight of the olefin[107]. A stable complex has only been isolated for $C_{12}H_{24}$ and olefins with higher molecular weights[107]. Stable π-complexes of cyclic olefins have been isolated only for cycloheptane and compounds with larger rings[109]. The complexes with dienes and trienes are more stable than the corresponding complexes of mono-olefins[107,109,110].

The structure of the complexes cannot be regarded as reliably established, since there are no X-ray diffraction data and a conclusion has been reached about the structure of the complexes on the basis of infrared spectroscopic and ^1H NMR data. A structure in which gold is coordinated to one of the two double bonds has been proposed for the dicyclopentadienyl π-complex; in norbornadiene both double bonds participate in the formation of the π-complex[109]:

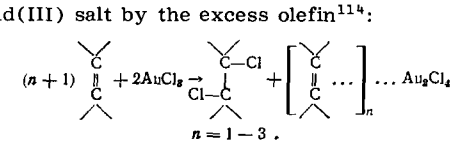


Cyclo-octatetraene reacts with AuCl at −45 °C to form an unstable complex of unknown structure, which is almost fully dissociated in ethereal solution[111].

Hexamethyl-substituted Dewar benzene reacts with AuCl to form a π-complex with coordination of the gold atom to only one of the double bonds of the diene[112]:

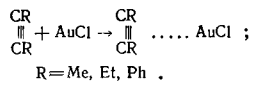


After the interaction of olefins with tervalent gold salts at low temperatures, complexes were isolated with an overall formula corresponding to the composition Au_2Cl_4.olefin.[105,108,111,113] However, the diamagnetism of these compounds as well as Mössbauer spectroscopic data show that one is dealing not with bivalent gold compounds but with a mixture of gold(I) and gold(III) derivatives formed on reduction of half of the initial gold(III) salt by the excess olefin[114]:



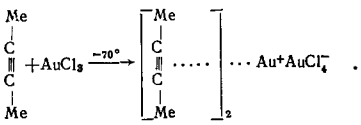
With cyclo-octatetraene (COT), a complex of the same type, having the composition COT.Au_2Cl_4, was obtained[111].

Hüttel and Forkl[115] were the first to isolate π-complexes of gold salts with alkynes. The interaction of substituted acetylenes with AuCl at low temperatures leads to the formation of relatively unstable complexes (with the exception of the toluene complex):



R=Me, Et, Ph .

Pyridine readily displaces the unsaturated ligand from these complexes, giving rise to AuCl.Py (Py = pyridine). If the same alkynes are acted upon by anhydrous $AuCl_3$ at temperatures between −30° and −70 °C, complexes having the composition $(alkyne)_2.Au_2Cl_4$ are formed. They are mixed complexes of univalent and tervalent gold, similar to those described previously for olefinic π-complexes[115,116]:



A π-complex of gold with a cyclic alkyne has been obtained recently. Cyclo-octyne reacts with AuBr to form a stable 2 : 1 π-complex: [117]



The fact that the complex has the cyclo-octyne and not the diene structure has been confirmed by its reaction with cyclone as well as infrared spectroscopic data. The diene synthesis reaction led to the isolation of the corresponding adduct[117].

IV. ANIONIC COMPLEXES OF GOLD

In the first studies on the synthesis of alkyl derivatives of gold using alkyl-lithium compounds, it was already postulated that anionic complexes of the type $(R_2Au)^-$ may be formed[40]. A detailed investigation of anionic gold complexes was begun with the studies of Tamaki and Kochi[118]. After the addition to an ethereal solution of MeAuL of an equivalent amount of methyl-lithium at a low temperature, the authors[118] were the first to detect by ^1H NMR the formation of an anionic complex of dimethylgold[118,119]:

$$MeAuL+MeLi\rightarrow[Me_2AuL]^-Li^+ .$$

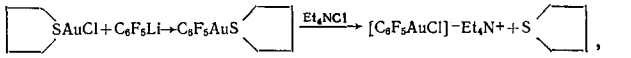
Asymmetric anionic complexes with different alkyl radicals, for example, $[(Me_3C)MeAuL]^-Li^+$, are formed also under the same conditions[118].

The attempts to isolate dialkylaurates with phosphine ligands were unsuccessful. However, it was possible to isolate and characterise a pyridine complex of the lithium salt of dimethylgold, which is unstable in air[118]:

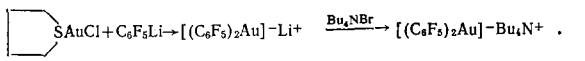
$$[Me_2AuL]^-Li^+ + Py \rightarrow [Me_2AuPy_2]^-Li^+ .$$

When the aprotic polyamine *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDT) was used as the chelating agent for the lithium ion in the reaction of methylgold with methyl-lithium, a white solid, having the composition $Li(PMDT)AuMe_2$, was isolated. It is stable in the solid state in the light and at room temperature for several months, but rapidly decomposes in protic solvents and under the influence of atmospheric moisture[120]. Spectroscopic study of this hitherto unique stable representative of dialkylanionic complexes showed that it is made up of a linear dialkyl anion and a chelate cation[120]. It has so far been impossible to replace the lithium cation in the complex and also to use other complex-forming agents for lithium.

Perhalogenoaryl anionic complexes are entirely stable in air and in the light both in the solid state and in solution. Perchloro- and perfluoro-phenyl anionic complexes of two types are known: homoligand and heteroligand. They are readily formed at low temperatures in ether from the tetrahydrothiophen complex of gold chloride and perhalogenoaryl-lithium[121–123]. When equimolar amounts of the initial reactants are employed, heteroligand anionic complexes are formed:



while in the presence of an excess of perhalogenoaryl-lithium, homoligand anionic complexes are isolated:



Dialkylaurates react with various electrophiles under milder conditions than the corresponding neutral complexes[118,124,125]. Their protolysis and their reactions with bromine and alkyl halides have been described[118,124,125].

The protolysis of lithium ethylmethyl(triphenylphosphine)-aurate takes place readily at 0 °C on treatment of its ethereal solution with hydrogen chloride[124]. The reaction resulted in the isolation of methane, ethane, and the triphenylphosphine complexes of methyl- and ethyl-gold:

$$[MeEtAuPPh_3]^-Li^+ + HCl \rightarrow CH_4 + C_2H_6 + MeAuPPh_3 + EtAuPPh_3 + LiCl .$$

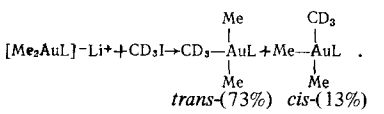
The reaction of dialkylaurates with bromine leads to a mixture of products in which the trialkylgold complex predominates[124]:

$$[Me_2AuPPh_3]^-Li^+ + Br_2 \rightarrow Me_2AuBrPPh_3 + LiBr \xrightarrow{[Me_2AuPPh_3]^-Li^+} \rightarrow Me_3AuPPh_3 + MeAuPPh_3 .$$

Under the influence of halogens and perfluoroaryl derivatives of tervalent thalium, perhalogenoaryl anionic complexes give rise to oxidative addition products[121–123]:

$$[(C_6Cl_5)_2Au]^- \xrightarrow{I_2} [(C_6Cl_5)_2AuI_2]^- .$$

The reaction of dialkylaurates with alkyl halides also proceeds via the oxidative addition mechanism[118,124,125]. The study of the stereochemistry of this reaction showed that mainly the *trans*-isomer is formed[118]:



trans-(73%) *cis*-(13%)

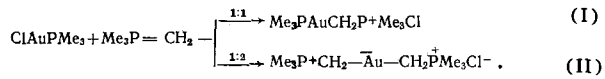
Perfluorophenylaurate reacts with bis(triphenylphosphine)-gold perchlorate, the ligand being substituted with formation of a neutral complex of perfluorophenylgold: [123]

$$[(C_6F_5)_2Au]^-Bu_4N^+ + (Ph_3P)_2Au^+ClO_4^- \rightarrow 2C_6F_5AuPPh_3 + Bu_4N^+ClO_4^- .$$

V. YLID COMPLEXES OF GOLD

The formation of extremely stable ylid complexes is characteristic of all Group IB metals[126,127]. The ylid complexes of gold, first obtained in 1973, have been investigated very vigorously in recent years. The interest in compounds of this kind is associated primarily with their unusually high thermal stability for organogold complexes. These complexes have also found applications in medicine in recent years[128].

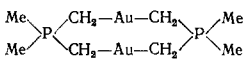
Depending on the reactant ratio, the interaction of $ClAuPMe_3$ with $Me_3P{=}CH_2$ leads to the formation of various phosphonium salts[127–130]:



(I)

(II)

In the presence of a large excess of the ylid, an eight-membered heterocyclic compound (III) with two gold atoms is obtained[127–129,131]:

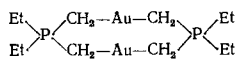


(III)

Compounds of types (I), (II), and (III) have been obtained for a series of alkylphosphines, for example for triethyl-, tributyl-, and dimethylcyclopropyl-phosphines[128,131,132] and also for triphenylphosphine ylids[130,133].

Phosphonium salts of types (I) and (II), in which the hydrogen atom of the methylene group has been substituted by the Me_3Si group, have been described[130]. As-analogues of cyclic ylid complexes have been obtained[131].

The complex

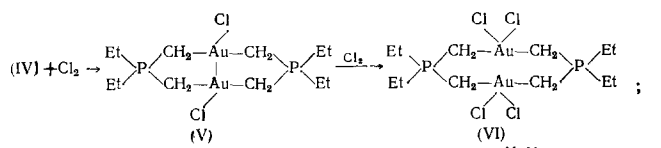


(IV)

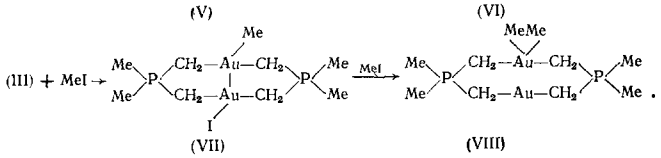
has been studied by X-ray diffraction and its Mössbauer and ESCA spectra have been investigated[134]. In complex (IV) there are two parallel linear –C–Au–C– fragments whose gold atoms hardly interact.

The ylid complexes of gold are solid substances stable in air and in the light. The thermal stability of these complexes, some of which actually sublime and distil *in vacuo* without decomposition, is unusually high[127,129,130,132].

The ylid complexes of type (III) readily undergo oxidative addition reactions under the influence of halogens and alkyl halides[129,135]. Thus, when complex (IV) was treated with chlorine, a dinuclear cyclic complex (V) was obtained, from which a gold(III) ylid complex (VI) was formed on further treatment with chlorine. Treatment of complex (III) with methyl iodide gives rise to complexes (VII) and (VIII). Complexes (V) and (VII), in which the gold atom is in the unusual oxidation state of +2 according to Mössbauer and ESCA spectroscopic data, are of special interest[134]. According to X-ray diffraction data, the Au–Au distance in complex (V) is 2.60 Å and is the smallest in all the known organic complexes of gold[135]:

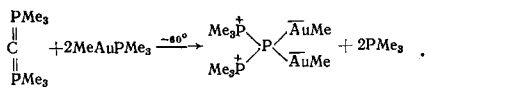


(V) (VI)



(VII) (VIII)

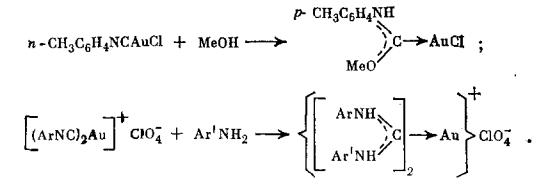
Hexamethylcarbodiphosphorane[136] reacts with two molecules of $MeAuPMe_3$ to form a complex in which the tetrahedral carbon atom is linked to two gold atoms[137]:



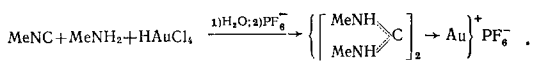
VI. CARBENE COMPLEXES OF GOLD

In 1971 two groups of investigators obtained almost simultaneously carbene complexes of gold[138,139].

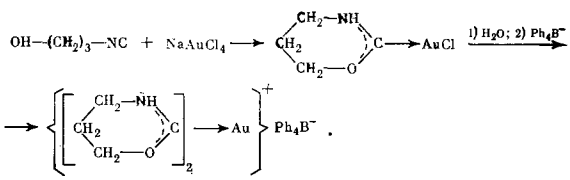
Two types of carbene complexes containing either one or two carbene ligands have been described for univalent gold. Both mono- and di-carbene complexes are formed readily from isonitrile complexes of gold in the presence of an amine or an alcohol[36,102,140–145]:



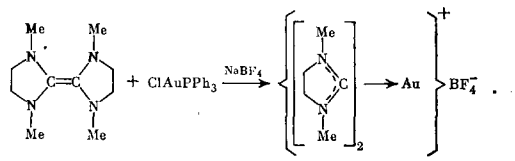
Instead of using isonitrile complexes, one can introduce into the reaction a univalent or tervalent gold salt and the isonitrile in the presence of an amine or alcohol[36,140,142]. In view of the highly nucleophilic properties of the amines, the reactions with the latter always proceed under milder conditions than with alcohols[145]:



Hydroxy-substituted isonitriles react with gold compounds to form a cyclic alkoxy(alkylamino)carbene complex[146]:

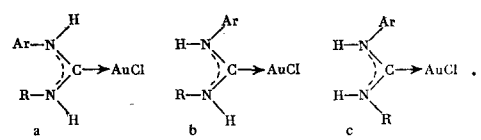


Olefins activated by electron-donating substituents are converted into carbene complexes on reaction with gold salts[147,148]:



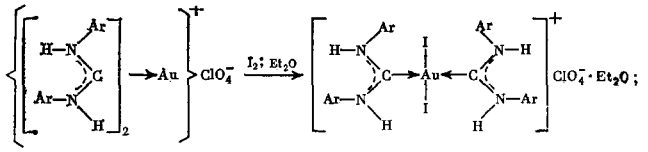
The carbene complexes of gold are white solids stable in air but sensitive to light. Some of them exhibit a luminescence of different colours and durations on irradiation with ultraviolet light[140]. This property has proved useful for the determination of the purity of the complexes. Carbene complexes with substituted tetrazoles are used in medicine as anti-inflammatory preparations[144].

Spectroscopic studies have shown that the rotation about the C–O and C–N bonds is limited, that the multiplicity of these bonds is greater than unity, and that the carbene ligand has a planar structure[142,143]. In conformity with this structure, the carbene complexes exist in the form of geometrical isomers. Among the three possible geometrical isomers a–c, isomer b predominates[142,143,145]:



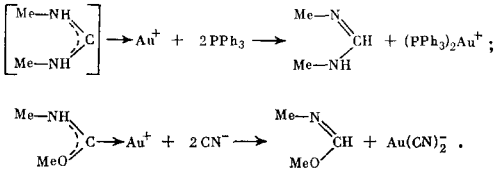
a b c

The reactivity of the carbene complexes has been little investigated. As for the majority of the organic complexes of gold, they readily undergo reactions involving oxidative addition of the halogen and ligand exchange reactions. The oxidative addition of iodine or bromine to the dicarbene complex of gold(I) leads to a dicarbene complex of gold(III):[62,140,141,149]



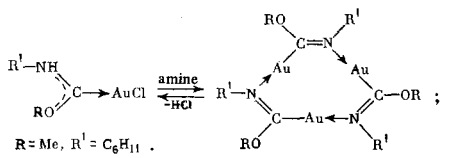
Ar = *p*-$CH_3C_6H_4$.

According to X-ray diffraction data, the tervalent gold complex is square planar with *trans*-carbene ligands[149,150]. The carbene ligand is substituted on treatment with other fairly powerful electron-donating ligands such as triphenylphosphine, cyanide, or isonitrile[140,142,145]:



It is noteworthy that the last reaction has served as a key to the explanation of the catalytic effect of added $HAuCl_4$ in reactions involving α-addition of amines to isonitriles, leading to substituted formamidines. The role of the gold salt reduces to the formation of the isonitrile complex of gold(I), which is converted into a carbene complex in which the carbene ligand is substituted by the isonitrile ligand, giving rise to a substituted formamidine and the initial isonitrile complex of gold(I).[140,142]

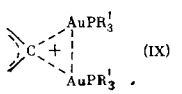
The deprotonation reaction, leading to the formation of organic σ-derivatives of gold, is specific to the carbene complexes. On treatment with bases, the deprotonation takes place with formation of cyclic trimers[36,102] (see above). This reaction is reversible and, on treatment with acid, carbene complexes are reformed from the trimer[36,102,151]:



R = Me, R' = C_6H_{11} .

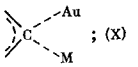
VII. ORGANOGOLD COMPOUNDS WITH A BRIDGING CARBON ATOM

Like the majority of transition metals, gold forms organometallic compounds with a metal–metal bond. The dinuclear cationic complexes $[R(AuPR'_3)_2]^+X^-$, in which the organometallic fragment (IX) of the molecule is a three-membered gold-carbon ring with an Au–Au bond and a bridging carbon atom, have been fairly thoroughly investigated[5]:



(IX)

Aryl compounds of gold in which the bridging carbon atom is linked to different metal atoms, one of which is gold and the other is zinc, copper, silver, or lithium [compounds (X)] are also known:



; (X)

M = Zn, Li, Cu, Ag .

Compounds of this type are usually dimeric and form metal–carbon macrorings—for example, triphenylgoldzinc.

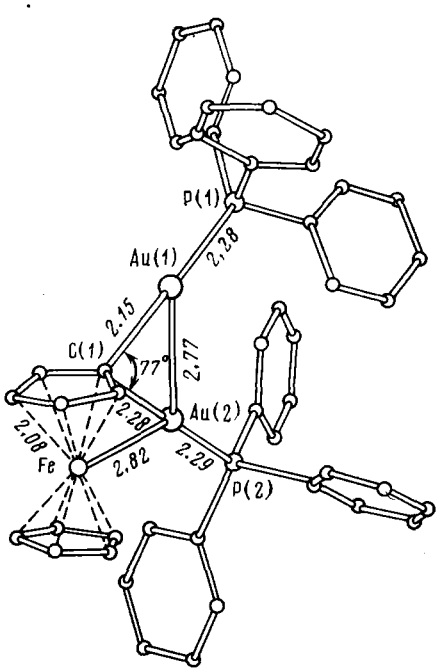
1. Homonuclear Cationic Complexes $[R(AuPR'_3)_2]^+X^-$

Dinuclear cationic complexes of type (IX) have been obtained for phenyl, ferrocenyl, cymantrenyl, and alkenyl derivatives of gold and both their structures and chemical behaviour have been studied in detail[2,5,152,153].

(a) Structure

The structures of the dinuclear cationic complexes of gold have been determined by infrared, ultraviolet, Raman, and NMR spectroscopy and also by X-ray diffraction.

The most stable ferrocenyl complex has been studied by X-ray diffraction[154,155]. It was established that the Au–Au distance in this complex (2.77 Å) is shorter than the Au–Au distance in the metal (2.88 Å), while the Au(1)–C(1)–Au(2) angle is much smaller than the tetrahedral value, which indicates the existence of a bond between the two gold atoms (see Figure). The plane of the three-membered Au(1)C(1)Au(2) ring is almost perpendicular to the plane of the cyclopentadienyl ring and the C(1) carbon atom occupies a bridging position between the two gold atoms. The interaction of C(1) with the two gold atoms must be regarded as a two-electron three-centre bond. Cluster compounds of copper and silver with a bridging ferrocenyl group have been described recently[156,157].



The structure of bis(triphenylphosphinegold)ferrocenium tetrafluoroborate.

The study of the ultraviolet and infrared spectra of the tolyl complex[158], the study of the *p*-fluorophenyl complex by ^{19}F NMR,[159] and the Raman spectroscopic study of the styryl complex[81] have shown that the aryl and alkenyl cationic complexes have a structure of type (IX), in which the carbon atom of the organic group occupies a bridging position between two gold atoms.

(b) Methods of Synthesis

From organogold compounds. When organogold complexes were treated with HBF_4, dinuclear complexes of type (IX) were obtained in high yields[2,5]:

$$RAuPR_3' + HBF_4 \rightarrow [R(AuPR_3')_2]^+BF_4^- + RH \ .$$

The cation R'_3PAu^+ can be conveniently generated from R'_3PAuCl on treatment with silver tetrafluoroborate.

From organomercury compounds. When organomercury derivatives R_2Hg are treated with phosphine complexes of methylgold in the presence of HBF_4, mercury is substituted by gold in a series of aryl, alkenyl, ferrocenyl, cymantrenyl, and heterocyclic organomercury compounds[21,22,160]. Depending on the group R in the initial organomercury derivative, various types of organogold complexes are formed. Thus treatment of diaryl- and distyryl-mercury derivatives with electron-accepting substituents in the group with phosphine complexes of methylgold and HBF_4 led to the isolation of only the organomonogold complexes[21]:

$$R_2Hg + MeAuPPh_3 \xrightarrow{HBF_4} RAuPPh_3 \ ;$$

R=X—C_6H_4, where X= *p*-, *m*-COOEt, *o*-I; PhCH=C(COOMe).

Cationic dinuclear complexes are formed from diferrocenylmercury derivatives having both electron-donating and electron-accepting substituents, from distyryl-, dicymantrenyl-, and dithienyl-mercury, and also from diaryl compounds of mercury having electron-donating substituents in the aromatic ring[21,22,160]:

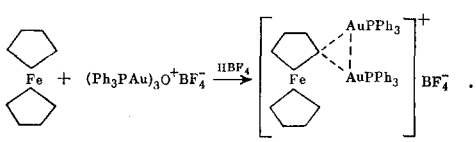
$$R_2Hg + MeAuPPh_3 \xrightarrow{HBF_4} [R(AuPPh_3)_2]^+BF_4^- \ ;$$

R=X—$C_5H_4FeC_5H_4$, where X=H; Cl; Br, OMe, COOMe; Y—C_6H_4, where Y=H, Me, NH_2.

A characteristic feature of *p*-halogenoarylmercury derivatives is that, by altering the reaction conditions, it is possible to obtain from them both dinuclear gold complexes and organomonogold compounds[21].

It is noteworthy that organogold complexes having the same geometrical configuration as the initial organomercury compound have been obtained from the *trans*-isomers of alkenyl derivatives of mercury[22,81].

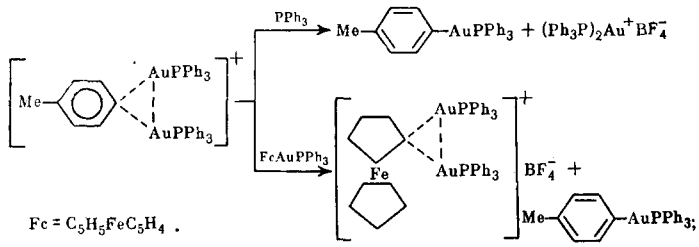
Substitution of gold in ferrocene and its derivatives. Ferrocene and its derivatives react with tris(triphenylphosphinegold)oxonium tetrafluoroborate at room temperature in the presence of HBF_4 to form dinuclear cationic complexes[161,162]:



The preferential formation of homoannular substituted compounds on substitution of gold in chloro-, bromo-, methoxy-, acetyl- and nitro-ferrocenes is apparently caused by the additional stabilisation of the cationic centre in the 1,2-isomer by the coordination of the gold atom to the substituent[162].

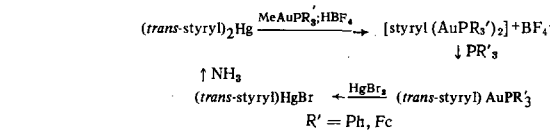
(c) Reactions

The study of the chemical behaviour of dinuclear organogold compounds has shown that reactions of two types are characteristic of these compounds—those involving only one or both $AuPR'_3$ groups. The first type involves the striking ability of the complexes $[R(AuPr'_3)_2]^+BF_4^-$ to enter into various reactions involving the transfer of the $R'_3PAu_3^+$ cation. The reaction proceeds readily under the influence of nucleophiles such as phosphines, amines, and halide ions. Another organogold compound can also fulfil the role of the nucleophile[2,5]:



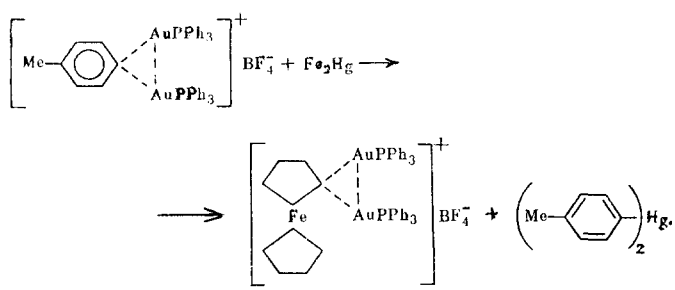
A feature of the reactions of alkenyl dinuclear complexes should be noted. Thus the dinuclear cationic complex obtained from the triphenylphosphine complex of *trans*-styrylgold generates, under the influence of triphenylphosphine or ferrocenylgold, an organomonogold compound having the same geometrical configuration as that of the initial *trans*-styrylgold[81].

A series of reactions, illustrated schematically below, have been carried out for *trans,trans*-distyrylmercury[81]:



An analogous sterochemical result has also been obtained for *trans,trans*-di(1-methoxycarbonyl-2-phenylvinyl)mercury[22].

The reactions of the cationic complexes with organometallic compounds belong to the second type. Thus the interaction of the cationic tolyl complex with diferrocenylmercury results in the formation of ditolylmercury and a dinuclear ferrocenylgold complex in high yields[2,19]:



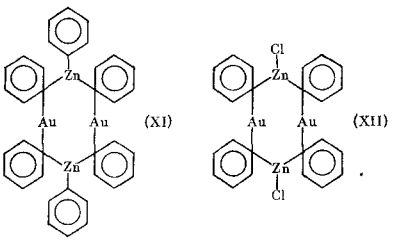
The mild reaction conditions and the high yields of products make it possible to use the dinuclear cationic complexes of gold for the synthesis of new organogold complexes with different organoelemental ligands, including gold-containing ligands.

2. Heterometallic complexes of arylgold

Heterometallic cluster complexes of arylgold of type (X) have been described by two groups of Dutch investigators.

De Graaf and coworkers[163,164] obtained aryl complexes containing gold and zinc; Van Koten and coworkers[39,165-167] investigated arylgold complexes containing also lithium, silver, or copper atoms.

Triphenylgoldzinc was isolated after treating diphenylzinc with an ethereal solution of $AuCl_3$ or AuCl(CO).[163] The compound is dimeric in benzene; since it has a dipole moment close to zero, a dimeric structure (XI) was attributed to it. ^1H and ^{13}C NMR data also agree with the dimeric structure. If diphenylzinc and AuCl(CO) react in proportions of 1 : 1, a compound having the composition $Ph_2AuZnCl$ is formed, for which structure (XII) has been proposed. Here the phenyl groups at the zinc atom have been substituted by chlorine atoms:



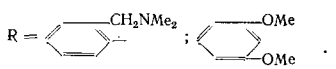
Whereas triphenylgoldzinc is extremely sensitive to atmospheric moisture, its chlorine-containing analogue is much more stable.

Analogues of compounds (XI) and (XII) have been obtained for *p*-ditolylzinc, whereas for other arylzinc derivatives with electron-donating substituents, only complexes of type (XII) have been isolated[164]. Organozinc and organogold compounds are known to form the most stable complexes with nitrogen- and phosphorus-containing ligands respectively. Accordingly, the reaction of triphenylgoldzinc with bipyridyl and tetramethylethylenediamine gives rise to complexes via the zinc atom, while the interaction with triphenylphosphine and diphos leads to phosphine complexes of phenylgold[164]:

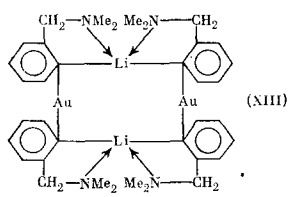
$$XI \xrightarrow{(C_5H_4N)_2} 2Ph_3AuZn\cdot(C_5H_4N)_2$$
$$XI \xrightarrow{PPh_3} 2Ph_2Zn + 2PhAuPPh_3 .$$

The triphenylphosphine complexes of arylgold or gold bromide react with aryl-lithium compounds to form mixed Au–Li clusters with bridging aryl groups[38]:

$$(RLi)_4 + BrAuPPh_3 \rightarrow R_4Au_2Li_2 ;$$

$R =$  ; .

Bis[2-(dimethylaminomethyl)phenyl]goldlithium is a dimeric compound thermally stable up to 170 °C; structure (XIII) has been proposed for it[4,38]:



This mixed Au–Li cluster has served as the starting material for the synthesis of a stable phenyl derivative of univalent gold, existing without an external stabilising ligand—(2-dimethylaminomethyl)phenylgold[38] (see above). In addition, other cluster complexes of gold have been obtained from compound (XIII). Thus the reaction of compound (XIII) with copper(II) bromide led to the isolation in a high yield of a dimeric (in benzene) cluster containing gold and copper atoms[165,166]:

$$R_4Au_2Li_2 + 2CuBr \rightarrow R_4Au_2Cu_2 + 2LiBr .$$

The reaction of compound (XIII) with $(CF_3SO_3)Cu$ and $(CF_3SO_3)Ag$ yielded new hexanuclear clusters containing gold and copper and gold and silver respectively[167]:

$$R_4Au_2Li_2 + (CF_3SO_3)M \rightarrow R_4M_2Au_2(CF_3SO_3)_2 ;$$
$$M = Cu, Ag .$$

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