Journal of Organometallic Chemistry, 474 (1994) 1–21

Invited Review

Some aspects of the organometallic chemistry of univalent gold

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(Received December 2, 1993)

Contents

1. Introduction

The investigation of organic derivatives of univalent gold has been carried out in Moscow State University, Nesmeyanov Institute of Organoelement Compounds and Institute of Common and Inorganic Chemistry for more than 20 years. Since most of the results were published in Russian journals which are not readily available for foreign colleagues, it seems reasonable to review these results which appear in more than one hundred articles.

This review deals with the preparation, structure and reactions of mono- and poly-nuclear organic complexes of univalent gold mainly involving gold–carbon bonds. Complexes with Au–N, Au–O and Au–S bonds are also considered.

2. Preparation of complexes RAuPR'$_3$

Organic complexes of gold, RAuPR'$_3$, can be prepared by different synthetic routes. Organometallic derivatives of lithium and magnesium are the common starting materials. The exchange reaction between organomercury compounds and gold(I) complexes has provided many possibilities, and another synthetic method is direct auration of organic compounds by gold-containing oxonium salts, which were first prepared in 1974 [1,2].

The organogold complexes which will be discussed in this review are presented in Table 1. The structures of these complexes were established by spectroscopic methods and in several cases by X-ray analysis.

2.1. Syntheses through organo-lithium and -magnesium compounds

This traditional approach was used for the preparation of alkyl, alkenyl, alkynyl, cyclopropyl, cyclopentadienyl, benzyl and allyl derivatives of univalent gold. Ferrocenyl and cymantrenyl complexes also can be prepared by this route.

$$RLi + R'_3PAuCl \longrightarrow R'_3PAuR$$

Not only phosphine complexes of gold halides may

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0022-328X/94/$7.00
SSDI 0022-328X(93)24342-3

TABLE 1. σ-Organogold complexes prepared by methods A–D (L = PPh_3, L′ = PFc_3, L″ = PPh_2Fc, Fc = ferrocenyl)

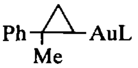
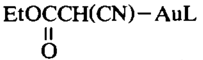
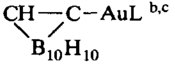
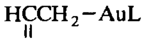
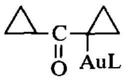
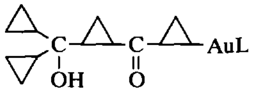
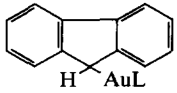
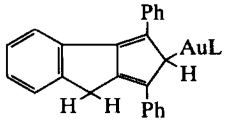
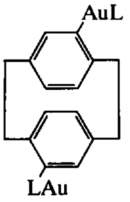
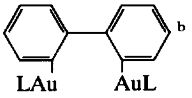
N	Compound	Method	Yield (%)	Reference
1	^{n}Bu–AuL	A	86	3, 4
2	Me–AuL′	A	95	5
3	Me–AuL″	A	100	5
4	$PhCH_2$–AuL	A, C	85	6
5	$EtC_6H_4CH_2$–AuL [a]	D	25	7
6		A	57	8
7		A	28	8
8	$ClCH_2$–AuL	D	80	9
9	Cl_3C–AuL	C	56	10
10	$NCCH_2$–AuL	A	61	11
11	$Cl_2C(CN)$–AuL [b]	C	71	11
12	 $\mathrm{EtO}\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}\mathrm{CH(CN)-AuL}$ [c]	C	94	12
13	$(NC)_2C(AuPPh_3)_2$ [b]	C	97	12
14	 [b,c]	C	98	13
15	Et_2NCOCH_2–AuL	C	61	14
16	 [b]	A	33	14, 15
17		A	89	14, 15
18	CH_3COCH_2–AuL	C, D	100	16–20
19	$CH_3CH_2COCH_2$–AuL	C	33	19, 20
20	$PhCOCH_2$–AuL	C	35	19, 20
21	$FcCOCH_2$–AuL	C	5	19, 20
22	$(MeCO)_2CH$–AuL [c]	C	60	19, 20
23	 $\mathrm{H}\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}\mathrm{CH_2-AuL}$	C	85	19–21
24		C	70	22
25		C	60	22
26		A	70	23
27		A	53	23
28	CH_2=CH–AuL	A	90	6
29	CH_2=$CHCH_2$–AuL	A	80	24
30	CH_2=C(Me)CH_2–AuL	A	51	24
31	PhCH=CH–AuL	A, B	90	25, 26
32	PhCH=CH–AuL′	B	89	26
33	Ph_2C=CH–AuL	A	61	27
34	PhCH=C(COOMe)–AuL	B	82	28, 29
35	PhCH=C(COOMe)–AuL′	B	93	29
36	4-F-$C_6H_4C\equiv C$–AuL	A	85	30, 31
37	C_5H_5–AuL [c]	C	85	32, 33
38	$C_5H_4(AuL)_2$ [b]	C	98	33
39	C_5Ph_4H–AuL [b]	A, C	83	32, 33
40	$C_5Ph_4(AuL)_2$	C	90	33
41	 [b]	A, C	80	34

TABLE 1 (continued)

N	Compound	Method	Yield (%)	Reference
42		C	100	35
43	Ph–AuL [c]	D	89	36
44	$\text{4-Me-C}_6\text{H}_4\text{-AuL}$	A	98	37
45	$\text{4-Me-C}_6\text{H}_4\text{-AuL}''$	A	76	5
46	$\text{4-Me-C}_6\text{H}_4\text{-AuL}'$	D	87	5
47	$\text{4-MeO-C}_6\text{H}_4\text{-AuL}$	A	98	38
48	$\text{4-H}_2\text{N-C}_6\text{H}_4\text{-AuL}$	B	85	28
49	$\text{4-Cl-C}_6\text{H}_4\text{-AuL}$	B	91	28
50	$\text{4-Br-C}_6\text{H}_4\text{-AuL}$	A	60	36
51	$\text{2-I-C}_6\text{H}_4\text{-AuL}$	B	82	28
52	$\text{2-I-C}_6\text{H}_4\text{-AuL}'$	B	97	5
53	$\text{4-EtOCO-C}_6\text{H}_4\text{-AuL}$	B	79	28
54	$\text{3-EtOCO-C}_6\text{H}_4\text{-AuL}$	B	82	28
55	$\text{2,3,5,6-Me}_4\text{C}_6\text{H-AuL}$	B	87	28
56	$\text{3-F-C}_6\text{H}_4\text{-AuL}'$	D	86	5
57		A	46	39
58	 [b]	A	46	40
59	$\beta\text{-C}_{10}\text{H}_7\text{-AuL}$	B	89	28
60	Fc–AuL	A–C	85	41–44
61	$\text{C}_5\text{H}_5\text{FeC}_5\text{H}_3\text{(Cl)-AuL-2}$	A	71	45
62	$\text{C}_5\text{H}_5\text{FeC}_5\text{H}_3\text{(OMe)-AuL-2}$	A, C	65	43, 45
63	$\text{C}_5\text{H}_5\text{FeC}_5\text{H}_3\text{(CH}_2\text{NMe}_2\text{)-AuL-2}$	A	50	45
64	$\text{C}_5\text{H}_5\text{FeC}_5\text{H}_3\text{(COMe)-AuL-2}$	C	68	43
65	$\text{C}_5\text{H}_5\text{FeC}_5\text{H}_3\text{(NO}_2\text{)-AuL-2}$	C	25	43
66	$\text{FeC}_{10}\text{H}_8\text{(Me)-AuL}$ [a]	C	65	43
67	$\text{FeC}_{10}\text{H}_8\text{(Ph)-AuL}$ [a]	C	80	43
68	$\text{FeC}_{10}\text{H}_8\text{(C}_6\text{H}_4\text{NO}_2\text{-}p\text{)-AuL}$ [a]	C	45	43
69	$\text{Fe(C}_5\text{H}_4\text{-AuL)}_2$	A	41	45
70	$\text{LAu-C}_5\text{H}_4\text{FeC}_5\text{H}_3\text{(CH}_2\text{OEt)-AuL-2}$	B	81	46
71	$\text{ClC}_5\text{H}_4\text{FeC}_5\text{H}_4\text{-AuL}$	B	92	28, 47
72	$\text{BrC}_5\text{H}_4\text{FeC}_5\text{H}_4\text{-AuL}$	B	83	28, 47
73	$\text{MeOC}_5\text{H}_4\text{FeC}_5\text{H}_4\text{-AuL}$	B	76	28, 47
74	$\text{MeOCOC}_5\text{H}_4\text{FeC}_5\text{H}_4\text{-AuL}$	B	80	28, 47
75	Fc–C(CN)=C(CN)–AuL [a]	D	76	48
76	$\text{(OC)}_3\text{MnC}_5\text{H}_4\text{-AuL}$	A	73	49
77	$\text{(PPh}_3\text{)(CO)}_2\text{MnC}_5\text{H}_4\text{-AuL}$	D	80	50

[a] Mixture of isomers. [b] X-ray data are available. [c] Compound has been prepared earlier by another method.

be used in these reactions; sometimes the tris(triphenylphosphinegold)oxonium salts are more convenient [4].

It is important to note the low stability of allyl, benzyl and cyclopropyl derivatives of univalent gold, and special techniques are necessary for isolating these compounds from reaction mixtures.

2.2. Syntheses based upon organomercury compounds

Organogold complexes usually react with mercury salts producing organomercury compounds, that is transmetallation occurs with cleavage of the Au–C bond [51]. However, under certain conditions the reverse reaction takes place, *i.e.* it is possible to synthesize organogold compounds starting from organomercury compounds.

Phosphine complexes of methylgold react with organomercury derivatives R_2Hg in the presence of fluoroboric acid by substitution of mercury for gold, where R can be aryl, alkenyl, ferrocenyl, cymantrenyl and heterocyclyl. Gold complexes of two different types are formed depending on the nature of R and of the phosphine.

$$\begin{tikzcd} & R(AuPR'_3)_2{}^+BF_4{}^- \\ R_2Hg \arrow[ru, "CH_3AuPR'_3 + HBF_4"] \arrow[rd] & \\ & RAuPR'_3 \end{tikzcd}$$

Derivatives of diaryl- and distyryl-mercury with electron-withdrawing substituents in the organic moiety react to form mononuclear organogold compounds, $RAuPPh_3$.

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

$R = X - C_6H_4(X = p\text{-}, m\text{-}COOEt, o\text{-}I)$,

Ph–CH=C(COOMe)

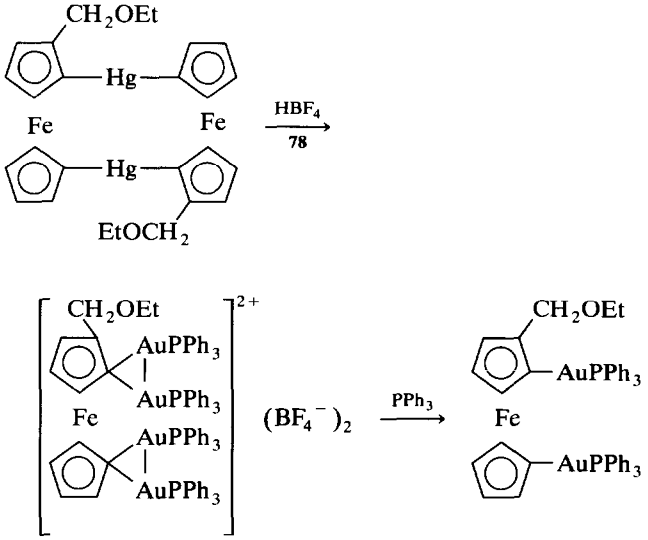
Ferrocenyl derivatives of mercury containing both electron-withdrawing and -releasing substituents, aryl derivatives with electron-releasing substituents, and distyryl- and dithienyl-mercury give binuclear cationic complexes.

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

$$[R(AuPPh_3)]_2{}^+BF_4{}^- \xrightarrow{PPh_3} RAuPPh_3$$

($R = XC_5H_4FeC_5H_4$ (X = H, Cl, Br, OMe, COOMe), YC_6H_4 (Y = H, *p*-Me, *p*-NH_2), duryl, *β*-naphthyl, *α*-thienyl, styryl, cymantrenyl)

It was proposed that the first step of the reaction is the formation of co-ordinatively unsaturated moieties R'_3PAu^+ (from $MeAuPR'_3$ and HBF_4). Further mononuclear organogold compounds $RAuPR'_3$ are formed as a result of electrophilic attack by R'_3PAu^+ on the C–Hg bond in R_2Hg, and subsequent substitution of mercury for gold. The result of the reaction depends on the ability of the compound $RAuPR'_3$ to form a stable binuclear cationic complex: the product is either $RAuPR'_3$ or the corresponding cationic complex. The gold containing oxonium salt $(Ph_3PAu)_3O^+BF_4^-$ (**78**) [46] may also serve as the source of the Ph_3PAu^+ moiety.



Accessibility of starting organomercury compounds, simplicity of the experimental work, and high yields of the desirable product – all these unequivocally establish the importance of this method for syntheses of aryl, ferrocenyl, cymantrenyl and alkenyl complexes of gold, containing different substituents in the organic moieties.

2.3. Auration by tris(triphenylphosphinegold)oxonium salts

The cation Ph_3PAu^+ is a "soft" Lewis acid and unwillingly forms bonds with "hard" oxygen containing anions. However, these coordinatively unsaturated cations react with water both in acidic and in basic medium yielding tris(triphenylphosphinegold)oxonium salts. The cations Ph_3PAu^+ are generated "*in situ*" by reaction of triphenylphosphinegold chloride and silver fluoroborate.

The most convenient method for the synthesis of gold-containing oxonium salts is the reaction of triphenylphosphinegold chloride or bromide and silver oxide in the presence of $NaBF_4$ or $KMnO_4$ [52].

$$\begin{tikzcd} & (Ph_3PAu)_3O^+BF_4^- \quad \mathbf{78} \\ Ph_3PAuX + Ag_2O \arrow[ru, "NaBF_4"] \arrow[rd, "KMnO_4"'] & \\ & (Ph_3PAu)_3O^+MnO_4^- \quad \mathbf{79} \end{tikzcd}$$

X = Cl, Br

The gold oxonium trifluoroacetate is prepared by the action of water on the triphenylphospine complex of gold trifluoroacetate [52].

X-ray structure determination of **78** revealed that the oxonium ions are dimeric, six gold atoms forming a ring in a chair conformation (Fig. 1) [52]. The Au_3O moiety has a pyramidal geometry with the O atom out of the Au plane by 0.83 Å. The distances between gold atoms indicate the existence of Au ··· Au interactions in the oxonium cation.

Gold-containing oxonium salts are readily destroyed by hydrogen chloride but they are stable towards acids whose anions do not form strong covalent bonds with the Ph_3PAu^+ cation, as well as towards alkalies and phosphines.

When the solution of gold-containing oxonium salt is treated with aqueous NaCl, triphenylphosphinegold chloride and sodium hydroxide are formed in quantitative yield. The determination of the alkali formed in this reaction represents a convenient method for the qualitative and quantitative analysis of oxonium salts.

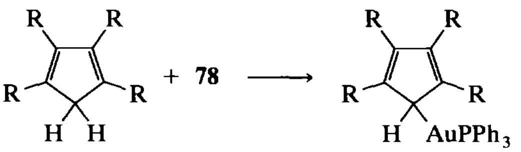
$$(Ph_3PAu)_3O^+X^- + 3\ NaCl + H_2O \longrightarrow 3\ Ph_3PAuCl + NaCl + 2\ NaOH$$

$X = BF_4,\ CF_3COO$

Tris(triphenylphosphinegold)oxonium salts reveal a unique "aurating" ability: they react under mild conditions with a variety of organic substances forming both organogold compounds and complexes in which gold is O-, N- or S-bound.

2.3.1. *Auration of cyclopentadiene and its derivatives*

The reaction of salt **78** and cyclopentadiene in the presence of base leads to a mono-substituted organogold derivative. A monoaurated compound is formed also in the reaction of tetraphenylcyclopentadiene [32,33].



R = H (**37**), Ph (**39**)

The tetraphenylcyclopentadienyl derivative **39** is non-fluxional in solution, in contrast to the non-substituted compound **37**. As X-ray analysis shows (Fig. 2) [33], the Au atom in **39** is bound to three carbon atoms of the C_5-ring, but these bonds are non-equivalent: the Au ··· C_1 distance is shorter than the Au ··· C_2 and Au ··· C_5 distances [32,33]. The Au-cyclopentadienyl co-ordination mode can be regarded as intermediate between $\sigma(\eta^1)$ and π-allyl (η^3).

An X-ray study of fluorenyl(triphenylphosphine)gold shows that the Au atom in this complex has η^1 co-ordination. Moreover, the structure of three geometrically different crystallographically independent molecules of the fluorenyl derivative in the crystal indicates limited structural non-rigidity, *i.e.* a pendular motion of the Ph_3PAu group at the sp^3-hybridized carbon atom of the fluorenyl ligand [34].

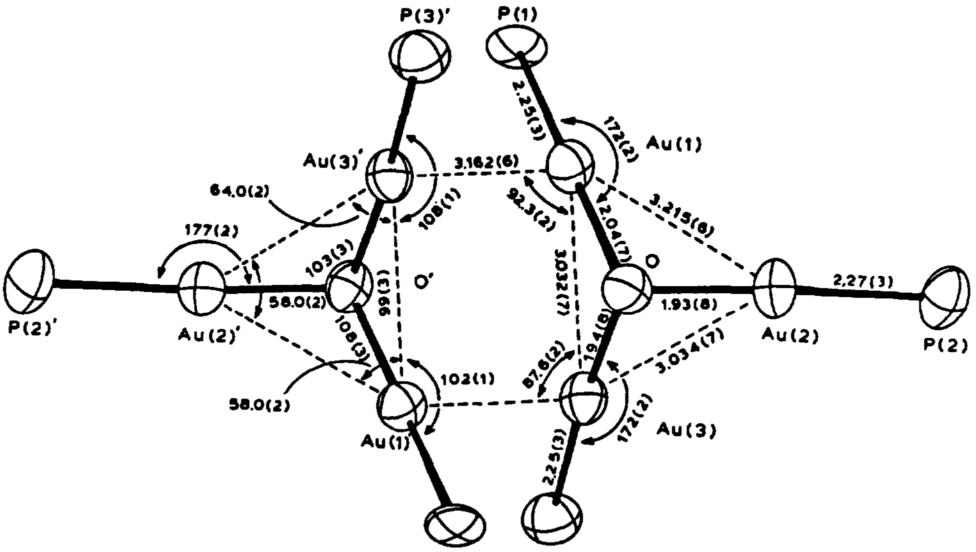


Fig. 1. Structure of $(Ph_3PAu)_3O^+$ cation (Ph substituents omitted).

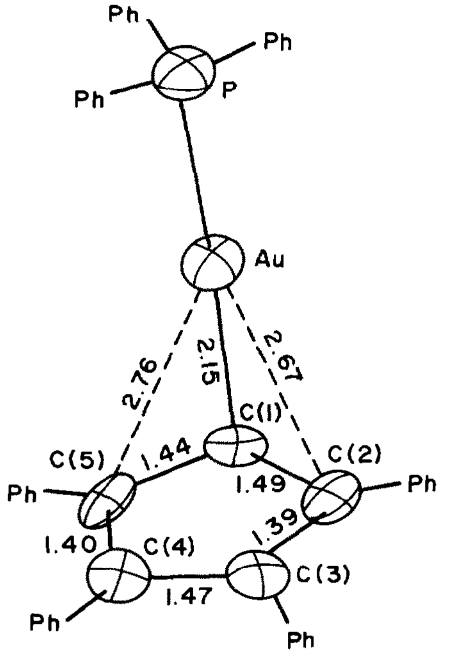


Fig. 2. Main interatomic distances in aurated tetraphenylcyclopentadiene (**39**).

If the reactions of cyclopentadienes are carried out with an excess of oxonium salt and for a longer period, so diaurated, *i.e.* binuclear, complexes are formed.

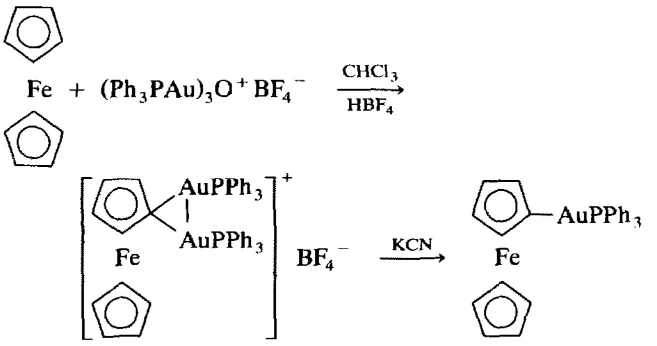
$$R_4C_5H_2 + (Ph_3PAu)_3O^+BF_4^- \longrightarrow R_4C_5(AuPPh_3)_2$$

R = H (**38**), Ph (**40**)

Compound **38** contains the carbametallacycle CAu_2. The distance between two gold atoms is 2.747 Å, *i.e.* it is shorter than in metallic gold (2.88 Å). The distribution of interatomic C–C distances in the C_5-ring reveals diene character [33].

2.3.2. *Auration of ferrocenes*

Oxonium salt **78** aurates ferrocene and substituted ferrocenes in the presence of HBF_4. In the absence of acid no reaction takes place. Auration of ferrocenes leads to the formation of binuclear cationic complexes which are readily converted in high yield into mononuclear compounds under the action of nucleophilic reagents (Cl^-, CN^-, PPh_3).



The auration of ferrocene derivatives Fc–X (X = H, Me, Ph, p-$O_2NC_6H_4$, Cl, COMe, OMe, 2-HOOC-C_6H_4CO, O_2N) gives mixtures of homo- and heteroannular derivatives in various proportions. When methoxy-, acetyl- and nitro-derivatives are aurated, homoannular 2-substituted derivatives are formed predominantly.

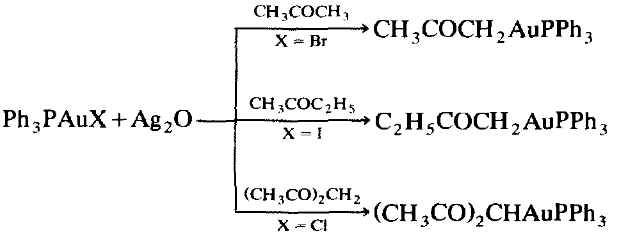
2.3.3. *α-Aurated carbonyl compounds*

Gold-containing oxonium salts aurate methyl ketones and interact with vinyl ethers and esters forming α-aurated carbonyl compounds [16–21].

$$R\text{-}CO\text{-}CH_3 + (Ph_3PAu)_3O^+MnO_4^- \longrightarrow R\text{-}CO\text{-}CH_2AuPPh_3$$

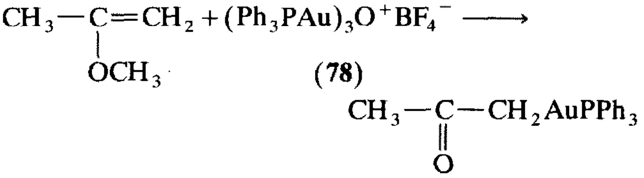
R = Me, Et, Ph, Fc

A more convenient method for preparation of aurated acetone, methylethylketone and acetylacetone is the interaction of the corresponding ketone with $Ph_3PAuHal$ and silver oxide [19].



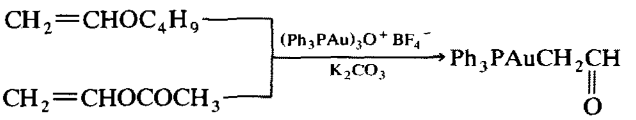
$$Ph_3PAuX + Ag_2O \xrightarrow[X = Br]{CH_3COCH_3} CH_3COCH_2AuPPh_3$$
$$Ph_3PAuX + Ag_2O \xrightarrow[X = I]{CH_3COC_2H_5} C_2H_5COCH_2AuPPh_3$$
$$Ph_3PAuX + Ag_2O \xrightarrow[X = Cl]{(CH_3CO)_2CH_2} (CH_3CO)_2CHAuPPh_3$$

Aurated acetone is obtained in high yield in the reaction of **78** and isopropenyl methyl ether.



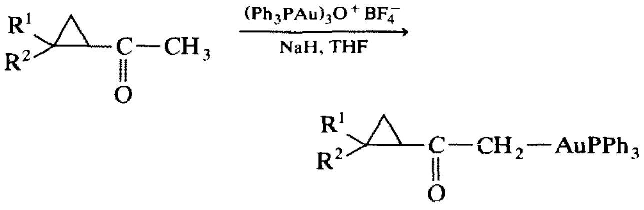
$$\underset{\displaystyle OCH_3}{CH_3-\underset{|}{C}=CH_2} + \underset{(\mathbf{78})}{(Ph_3PAu)_3O^+BF_4^-} \longrightarrow CH_3-\underset{\displaystyle O}{\underset{\|}{C}}-CH_2AuPPh_3$$

Aurated acetaldehyde is formed in the reaction of the oxonium salt with vinyl ethers and esters [19–21].



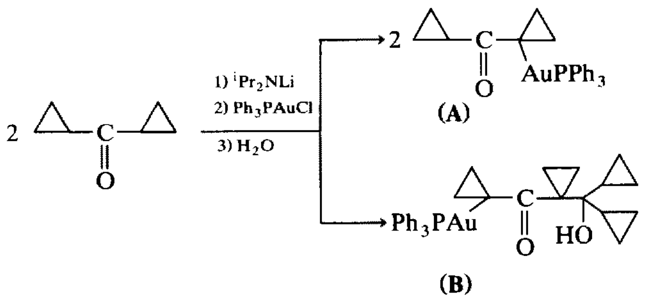
$$\left.\begin{array}{l} CH_2{=}CHOC_4H_9 \\ CH_2{=}CHOCOCH_3 \end{array}\right\} \xrightarrow[K_2CO_3]{(Ph_3PAu)_3O^+BF_4^-} Ph_3PAuCH_2\underset{\displaystyle O}{\underset{\|}{C}H}$$

In the reaction of methyl cyclopropyl ketone with the salt **78**, the three-membered ring does not cleave, and the configuration of the initial ketones remains. The Ph_3PAu moiety enters only the methyl group [22].



R^1, R^2 = H, Ph

Dicyclopropyl ketone does not react with gold oxonium salts in the presence of K_2CO_3. However, the action of lithium diisopropylamide on dicyclopropylketone with subsequent reaction with Ph_3PAuCl leads to gold-containing ketones **A** and **B** depending on the ratio of the reagents [23].



The IR spectra of α-aurated carbonyl compounds reveal an intensive absorption band at 1610–1670 cm^{-1} corresponding to vibration of the CO group. The NMR ^1H spectra display splitting of the signal of the protons of the CH_2 group joined to Ph_3PAu due to the interaction with the ^{31}P nucleus of the phosphine ligand.

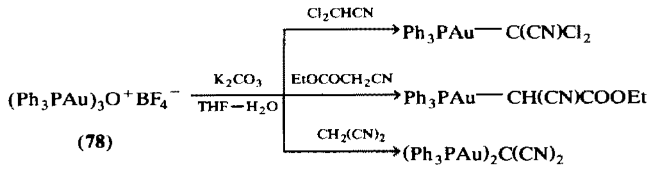
2.3.4. Auration of chloroform

Oxonium salt **78** reacts with chloroform in the presence of base forming a trichloromethyl derivative of gold, which has limited stability both in solution and in the solid state. This is the first example of metallation of chloroform by a transition metal compound [10].

$$CHCl_3 + \underset{\textbf{(78)}}{(Ph_3PAu)_3O^+BF_4^-} \longrightarrow Cl_3C{-}AuPPh_3$$

2.3.5. Auration of nitriles and amides

Oxonium salt **78** reacts in mild conditions with carboxylic acids nutriles containing electron-withdrawing substitutents; acetonitrile is not aurated under similar conditions [11]. In the reaction of **78** with malononitrile the only product is the diaurated compound [12].



The diaurated malononitrile is a binuclear complex of gold, the Au ··· Au distance being 2.912 Å which corresponds to a metal–metal bond (Fig. 3) [12].

The existence of an Au–Au bond is confirmed by the value of the Au–C–Au angle which is smaller than tetrahedral. The coordination mode of gold atoms deviates slightly from linear, which also agrees with such an interpretation. The Au–Au bond is almost perpendicular to the plane of three carbon atoms of the $C(CN)_2$ moiety. Diaurated malononitrile is the first example of a gold complex in which the sp^3-hybridized C atom is bound to two Ph_3PAu groups.

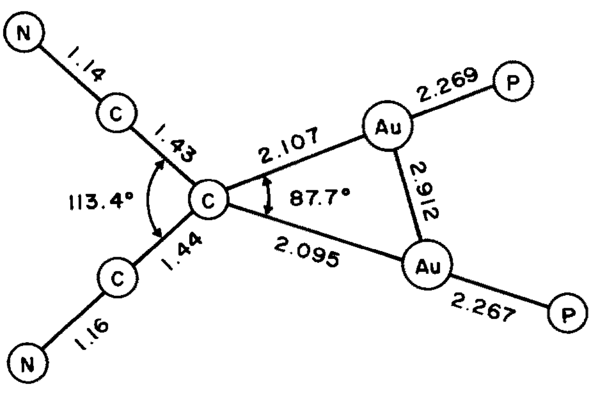
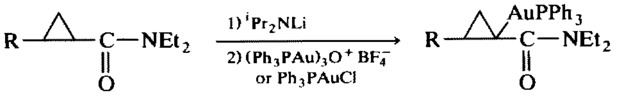


Fig. 3. Main molecular parameters of diaurated malononitrile.

The acidity of the α-hydrogen atoms in cyclopropane carboxylic acid N,N-diethylamides is not sufficient for auration of these amides by **78** to occur in the presence of NaH. However, under the action of ${}^iPr_2NLi$ the amides form Li-derivatives which react with Ph_3PAuCl or **78** forming C-aurated amides in high yield [14,15].



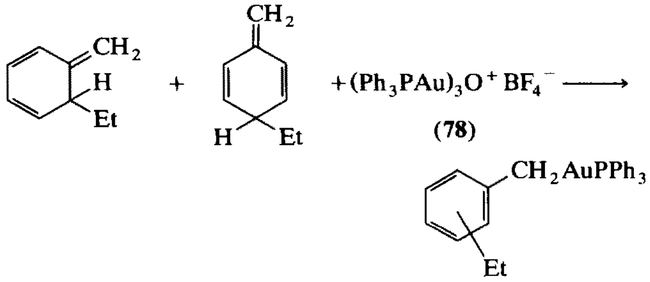
R = H, *trans*-Ph, *cis*-Ph

It is important to note that this reaction is accompanied by *cis–trans*-isomerisation.

2.4. Other syntheses

Besides the syntheses discussed in previous sections, which have been repeated many times there are single syntheses of organogold compounds by other methods. Some of these reactions which were carried out only once may be capable of wider application.

Isomeric methylenecyclohexatrienes react with oxonium salt **78** by an aromatizing metallation, forming benzyl derivatives of gold [7].



Chloromethyl gold is formed when methylene inserts into the Au–Cl bond [9].

$$\mathrm{ClAuPPh_3 + CH_2N_2 \longrightarrow ClCH_2AuPPh_3}$$

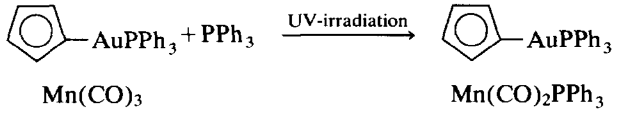
The triphenylphosphine complex of phenylgold is obtained in good yield by the reaction of sodium tetraphenylborate and $\mathrm{Ph_3PAuCl}$ [36].

$$\mathrm{Ph_3PAuCl + Ph_4B^-Na^+ \longrightarrow Ph_3PAuPh}$$

Dicyanoacetylene inserts into the Au–C bond of the ferrocenyl derivative of gold [48].

$$\mathrm{FcAuPPh_3 + NC{-}C{\equiv}C{-}CN \longrightarrow Fc(CN)C{=}C(CN)AuPPh_3}$$

The photochemical reaction of the cymantrenyl derivative of gold and triphenylphosphine leads to substitution of one of the CO groups for $\mathrm{PPh_3}$ [50].



Triferrocenylphosphine complexes are prepared by exchange of ligands (triphenylphosphine for triferrocenylphosphine). Attempts to synthesize triferrocenylphosphine complexes via organic derivatives of Li or Mg and $\mathrm{Fc_3PAuBr}$ failed [5].

$$\mathrm{Ar{-}AuPPh_3 + Fc_3P \longrightarrow Ar{-}AuPFc_3 + PPh_3}$$

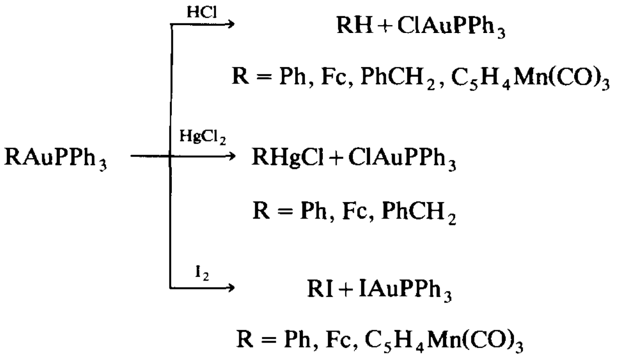
3. Reactions of organogold(I) complexes

Data on reactions of the complexes $\mathrm{RAuPR'_3}$ are reviewed according to the types of organogold compounds, since the complexes of different types reveal a certain difference in chemical behavior. Oxidative addition reactions, interaction with polycyano-compounds and reactions leading to bi- and poly-nuclear cationic complexes are reviewed in separate sections.

3.1. Derivatives of aromatic systems

For organogold derivatives of aromatic systems, *i.e.* benzene, ferrocene and cymantrene, a variety of reactions have been carried out. Among them are reactions with electrophiles cleaving the Au–C bond, insertion reactions, transformations in which the Au–C bond is retained, reactions leading to modification of the ligand environment of the gold atom, and oxidative addition reactions.

In reactions with iodine, acids and mercury(II) chloride substitution of gold for iodine, hydrogen and mercury takes place [38,41,49,50,53].



$$\mathrm{RAuPPh_3 \xrightarrow{HCl} RH + ClAuPPh_3} \quad \mathrm{R = Ph, Fc, PhCH_2, C_5H_4Mn(CO)_3}$$

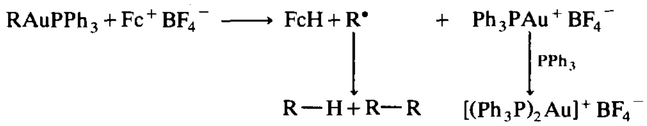
$$\mathrm{RAuPPh_3 \xrightarrow{HgCl_2} RHgCl + ClAuPPh_3} \quad \mathrm{R = Ph, Fc, PhCH_2}$$

$$\mathrm{RAuPPh_3 \xrightarrow{I_2} RI + IAuPPh_3} \quad \mathrm{R = Ph, Fc, C_5H_4Mn(CO)_3}$$

In reactions of $\mathrm{PhAuPPh_3}$ and $\mathrm{FcAuPPh_3}$ with anhydrides, acylhalides, acetyl fluoroborate and nitronium fluoroborate, the Au–C bond is also cleaved but products differ from the ones mentioned above [38,54].

$$\mathrm{FcAuPPh_3 + CH_3COCl \longrightarrow FcH + Fc{-}Fc + ClAuPPh_3 + CH_3CHO}$$

Apparently the first step of the reaction is electron transfer from the Au–C bond to the electrophilic agent, with subsequent elimination of gold salt. Radical moieties formed from the electrophile and from the organogold compound trap hydrogen or undergo other transformations. In this connection the most convincing examples are reactions of ferrocenyl and phenyl derivatives of gold with ferrocenium fluoroborate which is a typical one-electron acceptor. The ferrocenium cation accepts an electron and so is transformed into ferrocene. The organogold compound after loss of the electron disintegrates forming an organic radical and the $\mathrm{Ph_3PAu^+}$ cation. This coordinatively unsaturated cation reacts with $\mathrm{PPh_3}$ if it is added to the reaction mixture.



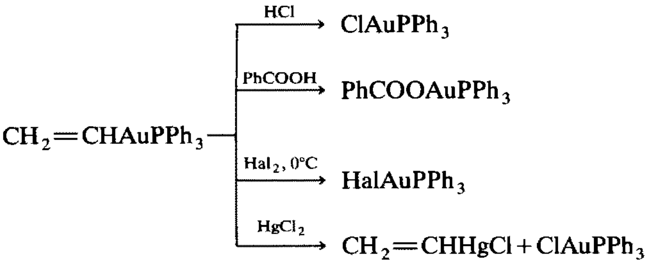
$$\mathrm{RAuPPh_3 + Fc^+BF_4^- \longrightarrow FcH + R^{\bullet} + Ph_3PAu^+BF_4^-}$$

$$\mathrm{R^{\bullet} \longrightarrow R{-}H + R{-}R} \qquad \mathrm{Ph_3PAu^+BF_4^- \xrightarrow{PPh_3} [(Ph_3P)_2Au]^+BF_4^-}$$

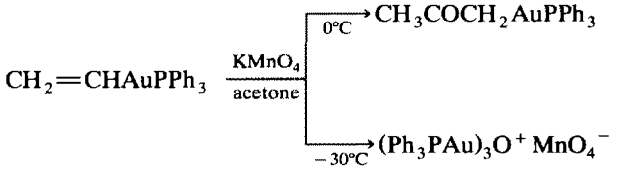
For ferrocenyl(triphenylphosphine)gold an insertion of the –C(CN)=C(CN)– fragment into the Au–C bond has been carried out (see section 2.4.). In aryl complexes of gold, the triphenylphosphine ligand is readily replaced by triferrocenylphosphine. The substitution of CO for $\mathrm{PPh_3}$ can be carried out in cymantrenyl derivative of gold (see section 2.4.).

3.2. σ-Alkenyl derivatives

In the triphenylphosphine complex of vinylgold the Au–C bond is readily cleaved under the action of a variety of electrophilic agents [17].



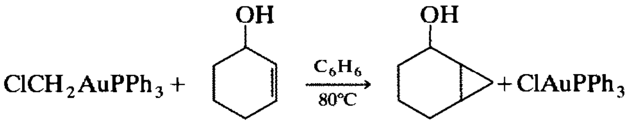
In the reaction of $KMnO_4$ with the vinyl derivative of gold in acetone solution (0°C), the product of hydroxylation of the double bond has not been detected, but unexpectedly, aurated acetone was the only stable compound of gold formed in the reaction. If the same reaction is carried out at lower temperature, the oxonium permanganate **79** is the main product [38].

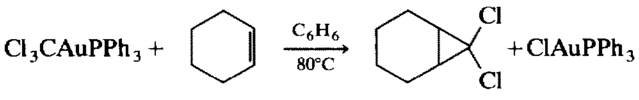


(79)

3.3. *Chloromethyl derivatives*

Chloromethylmercury derivatives are easily converted into Cl–Hg compounds with liberation of CH_2. Analogously chloromethyl compounds of gold are readily converted into Ph_3PAuCl in the presence of methylene acceptors. For example, such a transformation takes place in the presence of alkenes [9,10].





Halomethyl derivatives of tin and mercury easily undergo nucleophilic exchange of halogen. In contrast, halomethyl derivatives of gold do not react with KI or KCN to form products of nucleophilic substitution of halogen. In the reaction with KI, triphenylphosphinegold iodide is formed. The interaction of the chloromethyl compound of gold with KCN leads to the formation of methyl-triphenylphosphonium dicyanoaurate [9]. In the trichloromethyl derivative, the Au–C bond is cleaved under the action of HCl or $HgCl_2$ [10].

3.4. *Cyanomethyl derivatives*

The chemical behavior of cyanomethyl and dichlorocyanomethyl derivatives of gold is significantly different [11]. Thus aurated dichloroacetonitrile reacts with KBr forming Ph_3PAuBr. Aurated acetonitrile, on the other hand, does not undergo any transformation in these conditions.

$$Ph_3PAuC(CN)Cl_2 + KBr \xrightarrow{H_2O-CHCl_3} Ph_3PAuBr$$

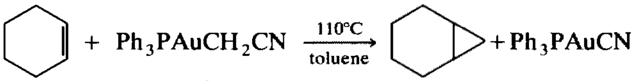
(11)

Potassium cyanide reacts with **11** forming potassium dicyanoaurate as the only gold-containing product. The analogous reaction of Ph_3PAuCH_2CN (**10**) gives a mixture of potassium and methyltriphenylphosphonium dicyanoaurates.

$$Ph_3PAuC(CN)Cl_2 + KCN \longrightarrow K[Au(CN)_2]$$

$$Ph_3PAuCH_2CN + KCN \longrightarrow K[Au(CN)_2] + [CH_3PPh_3]^+[Au(CN)_2]^-$$

Heating of **10** in the presence of cyclohexene gives the product of methylene cycloaddition and Ph_3PAuCN, but in the reaction of **11** no cyclopropanation takes place, the gold-containing products being phosphine complexes of gold cyanide and chloride.



(10)

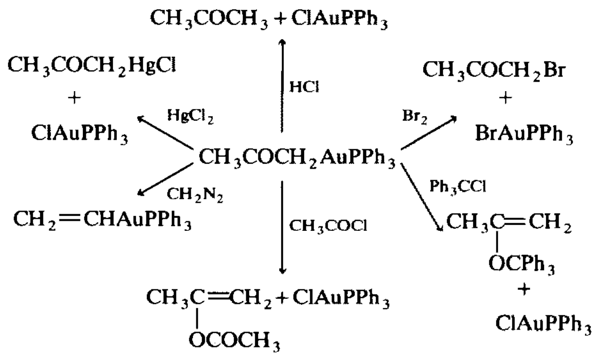
The interaction of **10** and Ph_3PAu^+ yields a cationic complex in which gold is bound to a nitrogen atom.

$$Ph_3PAuCH_2CN + [Ph_3PAu^+]BF_4^- \longrightarrow [Ph_3PAuCH_2CN{-}Au{-}PPh_3]^+BF_4^-$$

Thus the behavior of the cyanomethyl derivative of gold (**10**) resembles that of σ-organometallic compounds of gold, and the behaviour of the dichlorocyanomethyl derivative (**11**) is close to that of complexes of gold halides and cyanide.

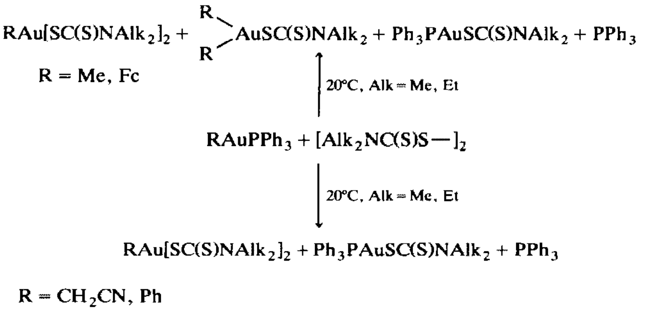
3.5. *Aurated acetone*

Acetonyl(triphenylphosphine)gold reacts with electrophilic reagents in a similar way to α-mercurated carbonyl compounds leading to cleavage of the Au–C bond and formation of C- and O-derivatives [16,20].

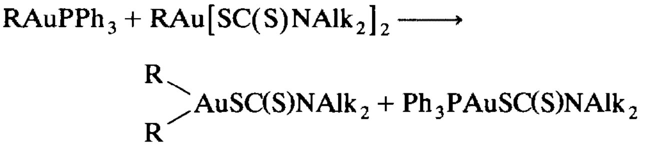


3.6. Oxidative addition reactions

Complexes $RAuPPh_3$ interact with tetraalkylthiuram disulfides by oxidative addition yielding dialkyldithiocarbamates of trivalent gold. Different products are formed in these reactions depending on the nature of R [36,55,56].



Derivatives of trivalent gold containing two organic moieties R are produced due to an interaction between the initial complex $RAuPPh_3$ and the compound of trivalent gold, $RAu[SC(S)NAlk_2]_2$, arising as a result of oxidative addition.



$$RAuPPh_3 + RAu[SC(S)NAlk_2]_2 \longrightarrow {R \atop R}{>}AuSC(S)NAlk_2 + Ph_3PAuSC(S)NAlk_2$$

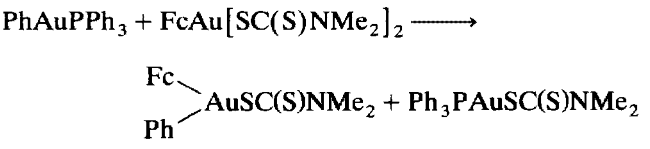
In the case of the phenyl derivative of gold, biphenyl is formed as a consequence of oxidation addition followed by an exchange reaction producing an unstable diphenyl derivative of trivalent gold, **80**, which undergoes reductive elimination.

$$PhAuPPh_3 + PhAu[SC(S)NMe_2]_2 \longrightarrow [Ph_2AuSC(S)NMe_2] \longrightarrow$$

(80)

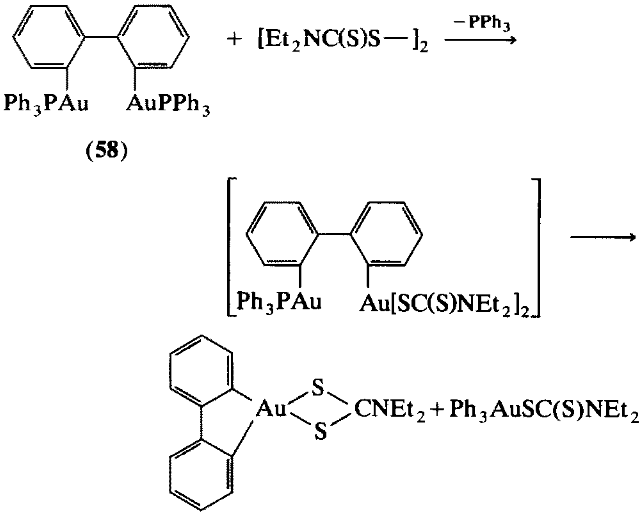
$$AuSC(S)NMe_2 + Ph_3PAuSC(S)NMe_2 + Ph-Ph$$

However methyl-phenyl and ferrocenyl-phenyl derivatives of trivalent gold proved to be quite stable.



$$PhAuPPh_3 + FcAu[SC(S)NMe_2]_2 \longrightarrow {Fc \atop Ph}{>}AuSC(S)NMe_2 + Ph_3PAuSC(S)NMe_2$$

A noteworthy result has been obtained in the reaction between tetraethylthiuram disulfide and the binuclear organogold derivative of biphenyl (**58**). The molecule of **58** has a *cisoid* conformation, and the two gold atoms are drawn together, the Au ··· Au distance being 3.025 Å [40].



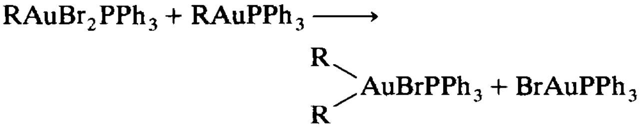
(58)

(81)

The bis-aryl derivative of gold **81** possesses a fixed cyclic structure and is quite stable in contrast to the diphenyl derivative **80** mentioned above. Reductive elimination in compound **81** is not profitable because it would lead to formation of a strained cyclobutadiene framework, and probably this is the reason for the enhanced stability.

Reactions of the complexes $RAuPPh_3$ ($R = CH_3$, CH_2CN, CH_2NO_2, $CH(CN)COOC_2H_5$, Ph, Fc) with chlorine and bromine also proceed by oxidative addition [57–59]. At low temperature (−70°C), compounds of trivalent gold ($RAuBr_2PPh_3$) are formed. Their stability depends on the nature of R. The most stable are complexes with electron-withdrawing substituents in the radical R (CN, NO_2, $COOC_2H_5$). The complexes $RAuBr_2PPh_3$ interact with $RAuPPh_3$ yielding $R_2AuBrPPh_3$ or undergo reductive elimination, especially at enhanced temperature. At room temperature, reaction of $RAuPPh_3$ with bromine gives a mixture of products arising in the following transformations.

$$RAuPPh_3 + Br_2 \longrightarrow RAuBr_2PPh_3$$



$$RAuBr_2PPh_3 + RAuPPh_3 \longrightarrow {R \atop R}{>}AuBrPPh_3 + BrAuPPh_3$$

$$RAuBr_2PPh_3 \longrightarrow RBr + BrAuPPh_3$$

$$RAuPPh_3 + Br_2 \longrightarrow RBr + BrAuPPh_3$$

The relative contribution of each of these processes depends on the nature of R and on the ratio of reagents.

In the bromides of trivalent gold discussed here, the bromine can be easily replaced by the dithiocarbamate ligand. This reaction proved to be a useful procedure for transforming unstable bromides into stable dithiocarbamate complexes, especially for phenyl and ferrocenyl derivatives [59].

$$\begin{tikzcd}
\mathrm{FcAuPPh_3 + Br_2} \arrow[r, "-70^{\circ}\mathrm{C}"] & \mathrm{FcAuBr_2PPh_3} \arrow[r, "\mathrm{FcAuPPh_3}"] \arrow[d, "\mathrm{NaSC(S)NEt_2}"'] & \mathrm{Fc_2AuBrPPh_3} \arrow[d, "\mathrm{NASC(S)NEt_2}"'] \\
& \mathrm{FcAu[SC(S)NEt_2]_2} & \mathrm{Fc_2AuSC(S)NEt_2}
\end{tikzcd}$$

3.7. Reactions with polycyano compounds

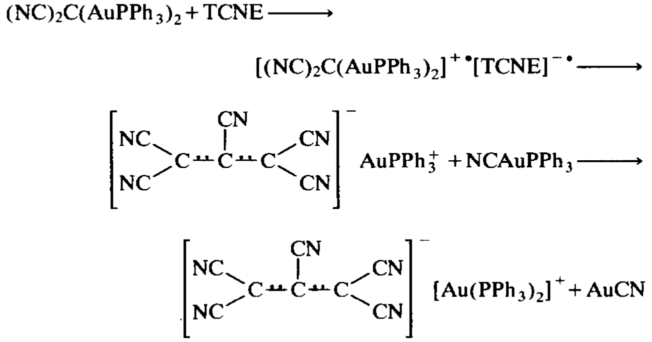
Tetracyanoethylene (TCNE) is a well-known one-electron acceptor and it is reasonable to suppose that the first step in its reactions with organogold compounds would be one electron transfer from an Au–C bond to TCNE, further transformations being dependent on the nature of the gold complex. Reactions of TCNE with organogold derivatives of ferrocene, tetraphenylcyclopentadiene, malononitrile, cyanoacetic acid ethyl ester and with oxonium salt **78** have been studied.

In the reactions of TCNE with $FcAuPPh_3$ and $C_5Ph_4HAuPPh_3$, the Au–C bond is cleaved and the phosphine complex of gold cyanide together with the corresponding tricyanovinyl derivative are produced [35,48].

$$\mathrm{RAuPPh_3 + (CN)_2C{=}C(CN)_2 \longrightarrow R{-}C(CN){=}C(CN)_2 + Ph_3PAuCN}$$

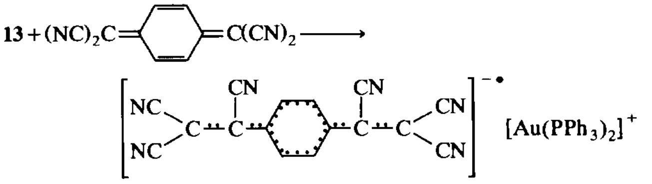
$R = Fc, C_5Ph_4CH$

No attempts have been made to identify any radical intermediates in these reactions. Arguments for radical participants in the reaction of TCNE with organogold compounds were obtained in the investigation of diaurated malononitrile **13** and the following scheme of the reaction was proposed [60].



Radical intermediates in this reaction were detected by the ESR method.

In the same manner compound **13** reacts with tetracyanoquinodimethane.



The structures of the salts were determined by spectroscopic methods and by transformation into the corresponding tetramethylammonium salts.

Thus organogold compounds in the reactions with TCNE give products which are built up of both the TCNE fragment and the organic radical from the starting organogold compound. A different result has been obtained in the reaction of the gold-containing oxonium salt **78**. TCNE or its complexes with aromatic hydrocarbons react with **78** yielding a salt containing the $[C(CN)_3]^-$ anion (**82**) [35,61].

$$\underset{(\mathbf{78})}{\mathrm{TCNE + (Ph_3PAu)_3O^+BF_4^-}} \longrightarrow \underset{(\mathbf{82})}{\mathrm{[Au(PPh_3)_2]^+[C(CN)_3]^-}} + \mathrm{AuCN}$$

The tricyanomethanide **82** is a strong electrolyte and is completely dissociated in CH_3OH–CH_3CN medium. X-ray analysis revealed that the gold atom in **82** has a linear coordination with two phosphine ligands. No additional coordination of the gold atom with the anion was observed.

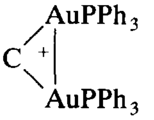
The reaction between **78** and TCNE proceeds in many steps and one of the intermediates is the relatively stable paramagnetic complex **83** which is transformed gradually in the presence of air into the stable diamagnetic salt **82** [62].

$$\underset{(\mathbf{83})}{\mathrm{[(Ph_3P)_2Au]^+[(NC)_2C{=}C(CN)_2]^{-\bullet}}}$$

X-ray analysis shows that the C–C and C≡N bonds in complex **83** are significantly shorter that the bonds in TCNE. Radical anions of **83** form infinite chains $-A^{-\bullet}-A^{-\bullet}-A^{-\bullet}-$ with strong electronic interaction, and investigation of the magnetic properties of **83** reveals that magnetic hyperexchange interactions of an antiferromagnetic type are realized in this complex [62].

4. Cationic carbametallacyclic complexes of gold including a carbon bridge

The systematic investigation of the chemical behavior of organogold complexes $RAuPR'_3$ resulted in the discovery of a new type of organogold compound. In these complexes a C-atom of organic ligand is a bridge between two directly bound Au atoms.



The depicted carbametallacyclic fragment is present not only in binuclear complexes but also in tri- and quadri-nuclear complexes of gold. The mode of binding in this fragment is regarded as a two-electron three-center bond.

4.1. Binuclear cationic complexes of gold

Binuclear cationic complexes of gold (BCC) can be prepared starting from organogold compounds $RAuPR'_3$. For the formation of BCCs it is necessary that the C atom of R which is bound to the Au atom should be sp^2- or sp-hybridized, and BCCs were prepared for aryl [5,29,37,38], alkenyl [26,27,30,65], alkynyl [67], ferrocenyl [42–44,47,63–65], cymantrenyl [66] and heterocyclic [5,29] derivatives of gold.

Attempts to prepare BCCs for alkyl organogold compounds were unsuccessful. BCCs are known also for cyclopropyl derivatives of gold in which hybridization of the C atom also differs from sp^3 [8]. To date, more than 30 BCCs have been prepared [20,44,68,69].

4.1.1. Syntheses of BCCs

BCCs are formed in reactions of organogold or organomercury compounds with the R'_3PAu^+ cation. As a counterion BF_4^- is mainly used. The first BCC was prepared in 1972 by the reaction between ferrocenyl derivative of gold and fluoroboric acid [63].

$$FcAuPPh_3 + HBF_4 \longrightarrow [Fc(AuPPh_3)_2]^+BF_4^- + FcH$$

(84)

By this method were prepared also BCCs for aryl, alkenyl and cymantrenyl derivatives of gold. As has already been said, BCCs of the ferrocene series can be prepared by auration of ferrocenes by oxonium salt **78** in the presence of HBF_4 (see section 2.3.2.).

The common route for the preparation of aromatic and alkenyl BCCs is interaction of organomercury compounds with phosphine complexes of methyl gold in the presence of HBF_4 (see section 2.2.).

4.1.2. Structure of BCCs

Structures of the complexes were determined by NMR, IR, UV, Mössbauer and Raman spectroscopy and by X-ray analysis. The structure of ferrocenyl complex $[C_5H_5FeC_5H_4(AuPPh_3)_2]^+BF_4^-$ (**84**) [44,62, 63,66] was investigated in detail.

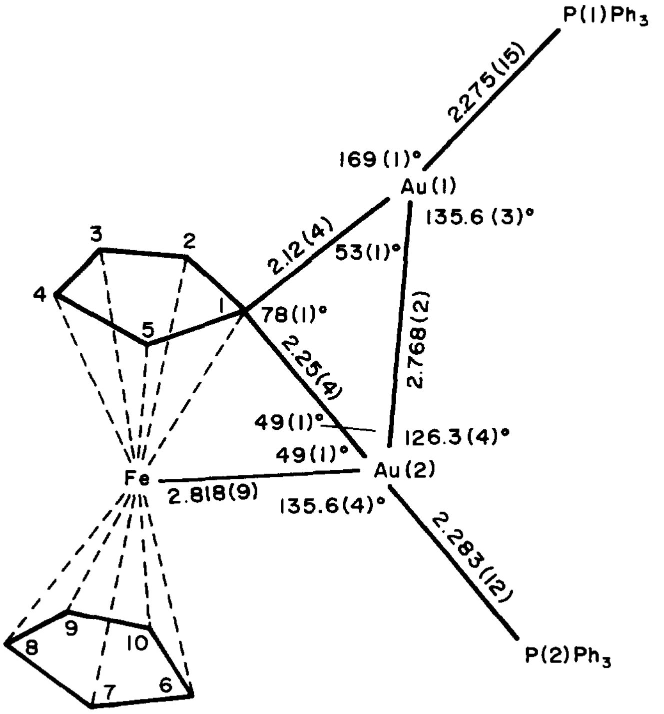


Fig. 4. Main molecular parameters of the $Fc(AuPPh_3)_2^+$ cation.

The ^1H NMR spectrum reveals a significant shift of the ferrocene protons to low field in comparison with $FcAuPPh_3$ and the spectrum of **84** has a close similarity to spectra of α-ferrocenylcarbenium ions. The UV spectrum shows a batochromic shift of the d–d transfer band of the iron atom in comparison with $FcAuPPh_3$. The appearance of the spectrum and intensities of bands in the 350–600 nm region are close to spectral parameters of ferrocenes with strong electron-withdrawing substituents.

The ^{31}P NMR spectrum of **84** has two signals corresponding to two non-equivalent phosphorus nuclei. The Mössbauer characteristics of this complex are typical for ferrocene system ($\delta = 0.77$ mm s^{-1}, $\Delta Q = 2.30$ mm s^{-1} at 80 K). An X-ray study of **84** shows that the ferrocenyl group occupies a bridging position between two gold atoms (Fig. 4) [70].

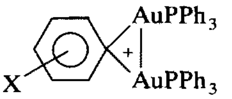
The plane of the triangle CAu_2 is approximately perpendicular to the plane of the C_5-ring. The existence of the Au–Au bond is unequivocally proved by the distance between two gold atoms, which is shorter than the interatomic distances in metallic gold (2.88 Å). It is worthy to note a surprisingly short distance between one of the gold atoms and the iron atom (2.82 Å).

Both X-ray and ^{31}P NMR data indicate the nonequivalence of the $AuPPh_3$ groups as a result of their unsymmetrical arrangement relative to the ferrocenyl moiety.

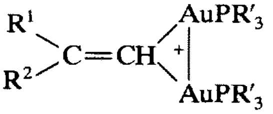
The following data are available concerning the structure of the less stable aryl BCC series [37,68].

In the ^{1}H NMR spectra of *p*-tolyl and *p*-methoxyphenyl complexes, the signals of the CH_3 group are strongly shifted to weak field. This indicates the presence of a strong electron withdrawing substituent in the benzene ring. The ^{31}P NMR spectrum of the *p*-tolyl complex has only one sharp signal due to the equivalence of the two $AuPPh_3$ groups.

The chemical shift of the fluorine nuclei in the ^{19}F NMR spectrum of $[p\text{-}FC_6H_4(AuPPh_3)_2]^+BF_4^-$ ($\delta = -16.40$ ppm) does not depend on the concentration and on the temperature in the range from -90°C to $+20$°C. The value of the chemical shift is close to ones for fluorobenzenes with electron-withdrawing substituents such as NO_2 and N_2^+ and differ strongly from the values for π-arene complexes of iron ($\delta = +21.05$ ppm) and chromium ($\delta = 21.90$ ppm). On the basis of these data it has been proposed that BCCs of the benzene series possess the same structure as BCCs of the ferrocene series, *i.e.* they have a bridging aryl group [71].

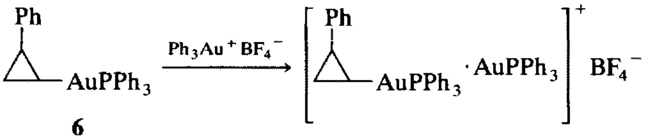


BCCs of the alkenyl and alkynyl series are powders of limited stability in the solid state and especially in solution [17,26,29]. The structures of these complexes can be discussed only by analogy with aromatic BCCs on the basis of the resemblance of methods for preparation and chemical behavior. An argument for the existence of the bridging fragment in their molecules is provided by the Raman spectrum of styryl-BCC. The shift of the absorption band of the double bond in this complex is 30 cm^{-1}, compared with the mononuclear compound. In olefin π-complexes the change of the double bond frequency in comparison with the free ligand is more significant. The same regularity was observed for phenylacetylene-BCC [67]. These facts permit the proposal that the Ph_3PAu^+ moiety is coordinated not with a double or triple bond but rather the carbametallacyclic fragment is present.

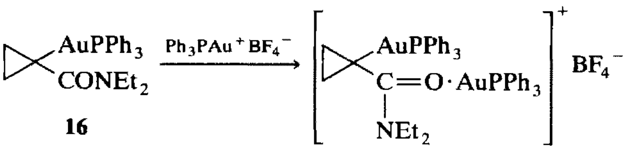


Cyclopropyl derivatives of gold are interesting in connection with the syntheses of BCCs. It is known that cyclopropanes behave in some reactions similar to alkenes and that the small ring effectively stabilizes a cationic center.

The cyclopropyl derivatives **6** and **16** form cationic complexes of significantly different stabilities [8].



(85)

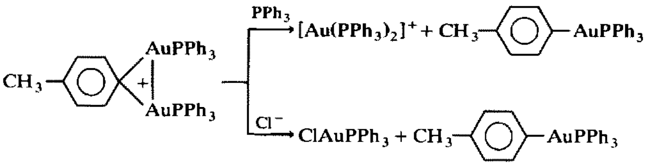


(86)

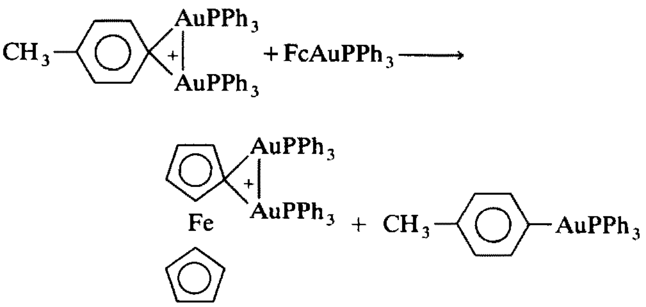
Spectral data and X-ray analysis show that the structure of complex **86** differs from those of the BCCs mentioned above. In **86** the cation, Ph_3PAu^+ is coordinated by oxygen of the diethylcarbamoyl group. No evidence for a carbametallacycle in this complex has been obtained. Complex **85** is extremely unstable and no structural data for it are available, but two possibilities may be considered: weak coordination of Ph_3PAu^+ with the phenyl ring, or a carbametallacycle characteristic for other BCCs.

4.1.3. Reactions of BCCs

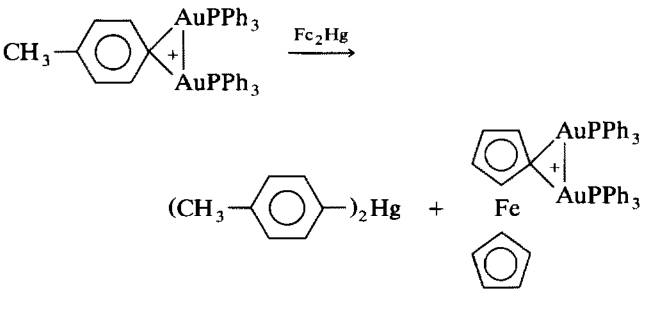
In the reactions of BCCs either or both the $AuPR'_3$ groups may be affected. The first type of reaction is transfer of R'_3PAu^+ cation to a variety of nucleophiles, resulting in regeneration of a mononuclear complex of gold. Phosphines, amines, and halide and cyanide ions [37] may serve as nucleophiles.



The R'_3PAu^+ moiety is also transferred to other mononuclear organogold derivatives [37,38].



The second type of reaction is interaction of BCCs with organomercury compounds. In these reactions two R'_3PAu groups are transferred to another organic moiety. Thus interaction between *p*-tolyl-BCC and diferrocenylmercury leads to ditolylmercury and ferrocenyl-BCC [44,64].



4.2. *Trinuclear cationic complexes of gold*

In view of the inclination of organogold compounds to form cationic complexes, it was proposed to synthesize trinuclear complexes from diaurated compounds.

Diaurated malononitrile gives the trinuclear cationic complex **87** in the reaction with $Ph_3PAu^+BF_4^-$. The same complex is formed when malononitrile reacts with the gold oxonium salt **78** in the absence of base [12].

$(NC)_2C(AuPPh_3)_2 + Ph_3PAu^+BF_4^-$

$CH_2(CN)_2 + (Ph_3PAu)_3O^+BF_4^- \longrightarrow$

$[(NC)_2C(AuPPh_3)_3]^+BF_4^-$

(87)

Trinuclear complexes were prepared also for cyclopentadienyl derivatives of gold [32,33].

$$C_5R_4H—AuPPh_3 + HBF_4 \longrightarrow$$

$$C_5R_4H_2 + [C_5R_4(AuPPh_3)_3]^+BF_4^-$$

R = Ph(**88**), H

In **88** the coordination mode of one of the gold atoms is the same as in the corresponding mononuclear compound **39** (see section 2.3.1.) (Fig. 5) [32].

Interaction between Au(1) and carbon atoms C(2) and C(5) as well as distortion of the diene system in the trinuclear complex **88** is more pronounced than in the mononuclear compound **39**. This conclusion is based on comparison of bond lengths and angles in the C(1)Au(1)C(2)C(5) fragment in both compounds. In complex **88** there is a rather rare combination of unusual structural fragments: the cationic carbametallacycle CAu_2 and η^3-coordination of univalent gold.

Another trinuclear cationic complex was prepared by interaction of o-ferrocenoylbenzoic acid and the gold oxonium salt **78** [72].

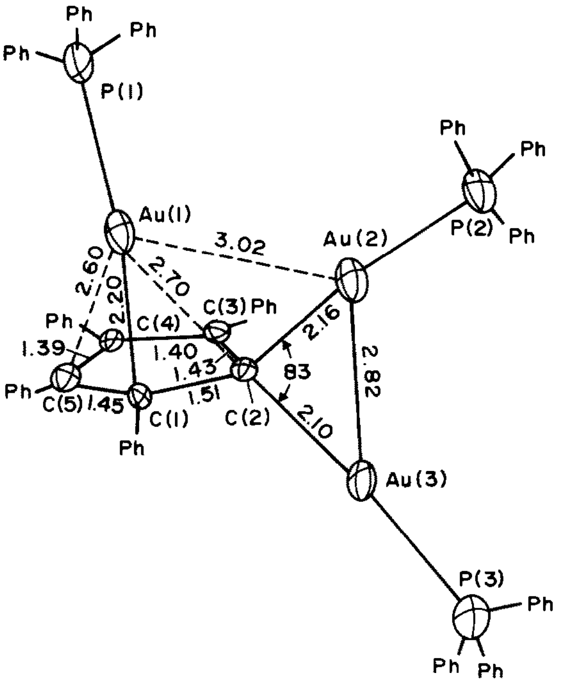
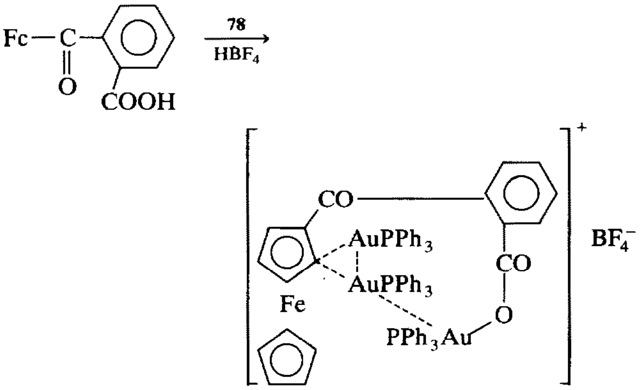


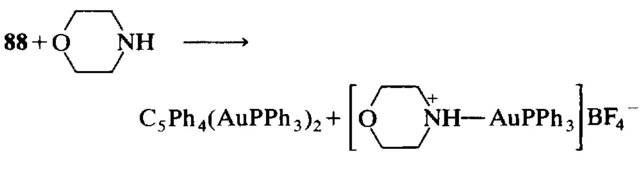
Fig. 5. Main molecular parameters of the cation $Ph_4C_5(AuPPh_3)_3^+$.



It has been proposed that one of the gold atoms of the carbametallacycle is bound also to the third gold atom resulting in a chain of three gold atoms.

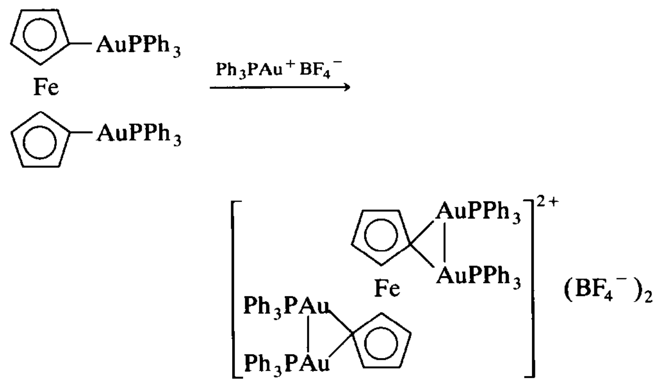
The most characteristic property of the trinuclear complexes discussed here is elimination of one of the Ph_3PAu moieties under the action of nucleophilic agents. In these reactions complexes of the Ph_3PAu^+ cation with nucleophiles and neutral binuclear compounds are always formed [32,33].

$$87 + NaCl \longrightarrow (NC)_2C(AuPPh_3)_2 + ClAuPPh_3$$



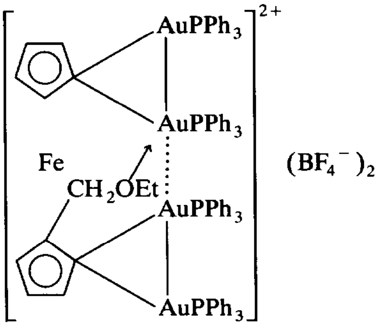
4.3. Quadrinuclear cationic complexes of gold

Only two examples of quadrinuclear dicationic complexes of the ferrocene series are known [46,73]. 1,1'-Bis(triphenylphosphinegold)ferrocene under the action of $Ph_3PAu^+BF_4^-$ forms a dicationic complex containing four gold atoms (**89**) [73].



(**89**)

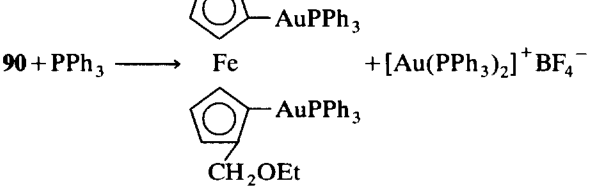
On the basis of spectral data and analysis of radial distribution functions it has been inferred that the two carbametallacyclic fragments are independent of each other [74,75]. However the mode of interatomic interactions in ferrocenyl complexes changes if a substituent (CH_2OEt) is present in the position neighbouring gold [46] and in complex **90** interaction between the two carbametallacyclic fragments takes place.



(**90**)

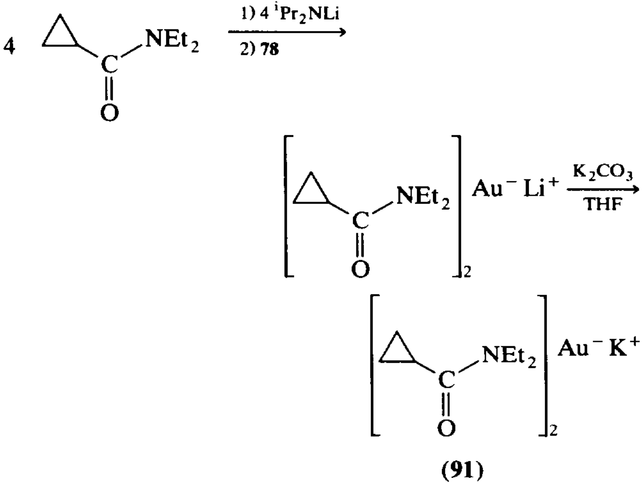
This results in the formation of a four-membered chain of gold atoms and coordination between one of the gold atoms and the oxygen atom of the ethoxymethyl group.

The chemical properties of the quadrinuclear complexes are similar to those of binuclear cationic complexes. Under the action of nucleophiles L (L = PPh_3, amine, halide ion) binuclear neutral compounds and $LAuPPh_3$ are formed.



5. Anionic gold complexes of the cyclopropane series

The gold oxonium fluoroborate (**78**) reacts with an excess of lithiated cyclopropane carboxylic acid diethylamide yielding unusually stable anionic complexes of univalent gold, (1-diethylcarbamoylcyclopyl)aurates [14,76].



(**91**)

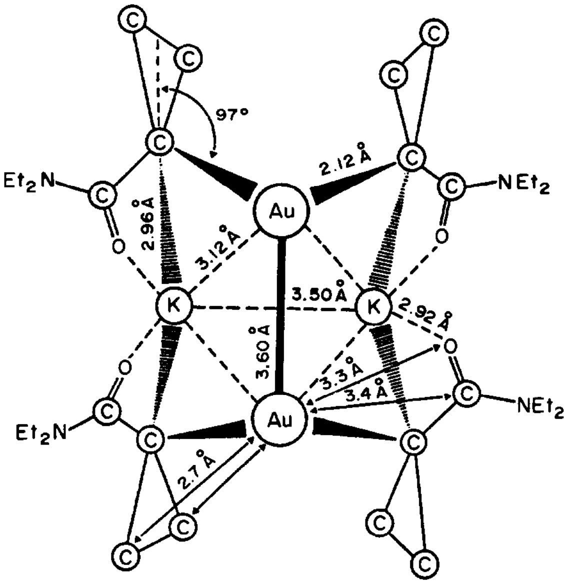
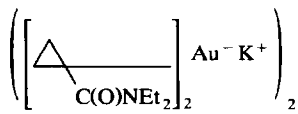


Fig. 6. Main interatomic distances in dimer



(**91**).

The properties of the Li and K salts of dicyclopropylaurates differ significantly from those of dialkylaurates which have been known for more then 20 years [77]. Thus, for example, dicyclopropylaurates are stable in air for a long time. The radial distribution functions method suggested the structure of complex **91** as shown in Fig. 6 [76].

The molecules of the K salt **91** are dimers, the Au_2K_2 fragment being a distorted tetrahedron. The cyclopropane moiety occupies a bridging position between the gold and potassium atoms. So the structure of complex **91** is reminiscent of diaryl aurates (which have a bridging aryl group [78]) but not dialkyl aurates. However the geometry of the Au_2K_2 moiety in **91** differs from that of the Au_2Li_2 fragment in diarylaurates probably because of a difference in the electronic configurations of the bridging carbon atoms of the phenyl ring and of the small cycle.

6. Complexes with Au–heteroatom bonds

As has already been said, the gold-containing oxonium salt **78** is a universal aurating agent, and it makes it possible to introduce the Ph_3PAu moiety into organic molecules forming not only Au–C bonds but also Au–heteroatom bonds.

6.1. Complexes with Au–N bonds

Treatment of oxonium fluoroborate **78** with an excess of liquid ammonia leads to the formation of aurated ammonium fluoroborate (**92**) [79]. X-ray analysis revealed that cation **92** is a distorted tetrahedron built up of four gold atoms (Fig. 7).

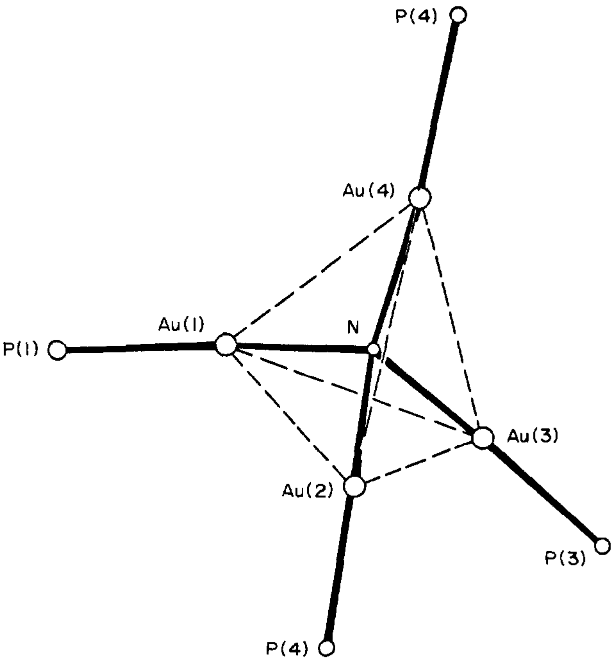


Fig. 7. Cation $(Ph_3PAu)_4N^+$ (Ph substitutents omitted). Interatomic distances: Au(1)–Au(2) 3.138, Au(1)–Au(3) 3.012, Au(1)–Au(4) 3.504, Au(2)–Au(3) 3.160, Au(2)–Au(4), 3.321, Au(3)–Au(4) 3.489, Au(1)–N 2.01, Au(2)–N 1.93, Au(3)–N 2.10, Au(4)–N 2.03 Å. Bond angles Au–N–Au 94.3–120.7°.

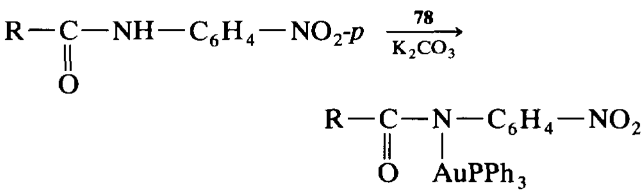
Three of the gold atoms, Au(1), Au(2) and Au(3), are drawn together to interatomic distances of 3.012–3.160 Å, which are close to those found in the aurated oxonium dimer **78**, but the Au(4) atom is distinctly further away from the three others (3.321–3.504 Å) [80]. Cation **92** may thus be considered as a small heteronuclear cluster with weak interatomic interactions.

A variety of NH-acids (amides of carboxylic and sulfonic acids, anilines) react with oxonium salt **78** in the presence of a base forming the corresponding N-aurated derivatives in high yields [14,15,81,82].

$$\mathrm{RCONH_2 + \underset{(\mathbf{78})}{(Ph_3PAu)_3O^+BF_4^-}} \xrightarrow[\mathrm{THF-H_2O}]{\mathrm{K_2CO_3}} \mathrm{RCONHAuPPh_3}$$

R = Me, ${}^tBu$, $ClCH_2$, Ph, $CH_2{=}CH$

Under these conditions acetanilide does not react with **78** but *p*-nitroacetanilide, whose NH-acidity is higher, forms the corresponding N–Au derivative [14,15,81].



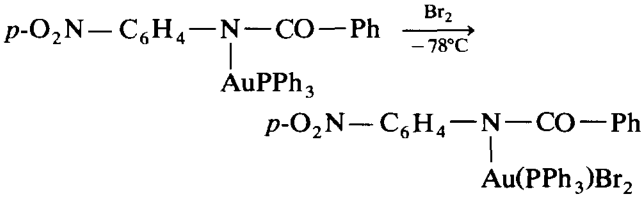
$$\mathrm{R{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}NH{-}C_6H_4{-}NO_2}\text{-}p \xrightarrow[\mathrm{K_2CO_3}]{\mathbf{78}} \mathrm{R{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}\underset{\underset{\displaystyle AuPPh_3}{|}}{N}{-}C_6H_4{-}NO_2}$$

R = Me, Ph, 2-phenylcyclopropyl

X-ray analysis revealed the agostic interactions Au ··· H in the N-aurated *p*-nitroanilides of acetic and cyclopropanecarboxylic acids [83,84].

Amides of sulfonic acids are aurated in a similar way to carboxylic acids amides.

In aurated amides the Au–N bond is easily cleaved under the action of bromine, disulfides, and aqueous solutions of HCl and NaCl. Only in the reaction with bromine at −80°C was it possible to isolate a product of oxidative addition [81].



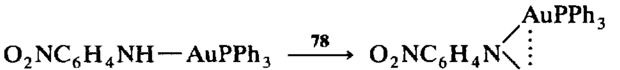
$$p\text{-}\mathrm{O_2N{-}C_6H_4{-}\underset{\underset{\displaystyle AuPPh_3}{|}}{N}{-}CO{-}Ph} \xrightarrow[-78^\circ\mathrm{C}]{\mathrm{Br_2}} p\text{-}\mathrm{O_2N{-}C_6H_4{-}\underset{\underset{\displaystyle Au(PPh_3)Br_2}{|}}{N}{-}CO{-}Ph}$$

Alkylamines and anilines with electron-releasing substituents do not react with **78** in the presence of K_2CO_3; only anilines with strong electron-withdrawing substituents give N-aurated derivatives under these conditions [82].

$$\mathrm{ArNH_2} + \mathbf{78} \xrightarrow[\mathrm{THF-H_2O}]{\mathrm{K_2CO_3}} \mathrm{ArNH{-}AuPPh_3}$$

Ar = C_6F_5, o-$O_2NC_6H_4$, p-$O_2NC_6H_4$

In *p*-nitroaniline it is possible to substitute two hydrogen atoms by gold.


(**93**)

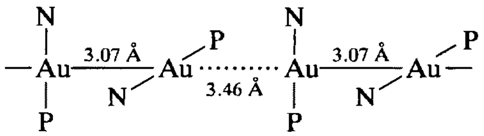
(**94**, Au · · · Au 3.03 Å)

The *p*-nitroaniline derivatives **93** and **94** react with coordinatively unsaturated cations Ph_3PAu^+ yielding bi- and tri-nuclear cationic complexes in which intramolecular Au · · · Au interaction exists.

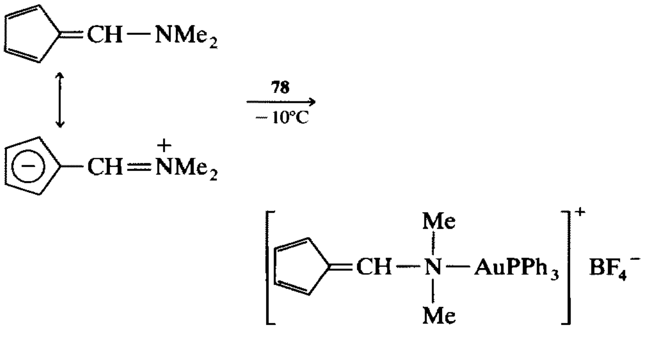
$[p\text{-}O_2NC_6H_4{-}NH(AuPPh_3)_2]^+BF_4^-$

$[p\text{-}O_2NC_6H_4{-}N(AuPPh_3)_3]^+BF_4^-$

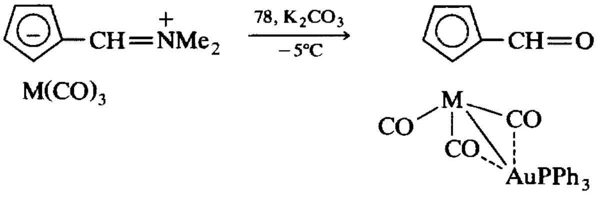
It is noteworthy that in the synthesis of monoaurated *p*-nitroaniline (**93**), two products of different color are formed depending on the method of isolation: yellow crystals or a red amorphous powder. These two substances have identical elemental compositions and ^{1}H NMR spectra but different UV and IR spectra. X-ray analysis showed the yellow crystalline solid to be N-aurated *p*-nitroaniline and that it is monomeric. The other, red amorphous substance consists of associated molecules, *i.e.* firm dimers (short contacts Au · · · Au 3.07 Å) forming chains due to secondary weak interactions between gold atoms (Au · · · Au distances being 3.46 Å) [85,86].



The ability of the Ph_3Au^+ cation to bind with the electron pair of nitrogen is realized in the reaction of **78** with 6-dimethylaminofulvene [87].



However π-complexes of this fulvene with carbonyls of Cr, Mo and W react with oxonium salt **78** otherwise: a bond between the transition metal and gold is formed and the CHO group is generated [88].



M = Cr, Mo, W

The X-ray analysis of the Mo complex has been carried out, and shows the presence of a Mo–Au bond and two bridging CO groups [88]. In the cyclopentadienyl-carbonyl heterobimetallic complexes containing gold and Cr, Mo or W, the gold-transition metal bond is readily cleaved both in the gas phase by electron irradiation and in the liquid phase by photolysis [89].

6.2. Complexes with Au–O and Au–S bonds

Complexes of gold incorporating Au–O bonds are known but not numerous. Most of these are gold salts of inorganic or organic acids, and they can be prepared from the gold oxonium **78** [90]. Here are described phenolates of univalent gold which have been prepared a few years ago.

The salt of gold oxonium **78** reacts with phenols in the presence of potassium carbonate but the result depends on the nature of the starting phenol. Phenols with electron-withdrawing substituents interact with **78** in a 3 : 1 molar ratio yielding stable triphenylphosphine complexes of gold phenolates [91].

$$\mathrm{ArOH} + \mathbf{78} \xrightarrow[\mathrm{THF-H_2O}]{\mathrm{K_2CO_3}} \mathrm{ArOAuPPh_3}$$

Ar = o-ClC_6H_4, o-BrC_6H_4, o-$O_2NC_6H_4$,

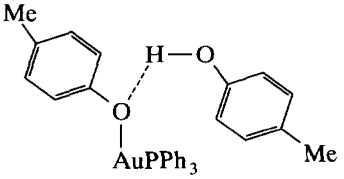
p-$O_2NC_6H_4$, C_6F_5, C_6Cl_5

Reactions of **78** with phenol, *p*-methyl- and *p*-fluoro-phenol are completed only in the presence of a three-fold excess of the corresponding phenol. The products are 1 : 1 complexes of gold phenolates with the starting phenol.

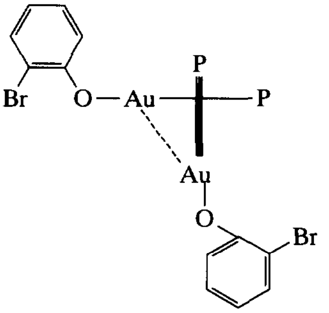
$$p\text{-R}{-}C_6H_4{-}OH + \mathbf{78} \longrightarrow p\text{-R}{-}C_6H_4{-}AuPPh_3 \cdot p\text{-R}{-}C_6H_4{-}OH$$

R = H, F, Me

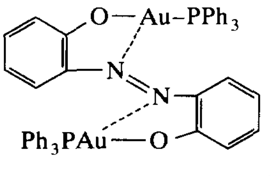
The intra- or inter-molecular interactions Au · · · Au or Au · · · heteroatom play a significant role in the stabilization of gold phenolates. In the absence of strong electron-withdrawing substituents, stabilization of the Au–O bond is achieved by intermolecular hydrogen bonds. For the complex of gold p-methylphenolate it has been shown by X-ray analysis that crystals are built up of associated pairs in which p-methylphenol is bound to the oxygen atom of gold p-methylphenolate by a hydrogen bond [92].



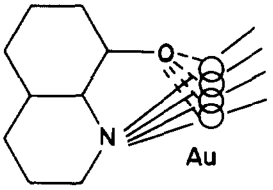
In the o-bromophenolate, the bromine and gold atoms are far from each other. In the crystal, two molecules are combined into a dimer by the intermolecular Au ··· Au interaction (the Au ··· Au distance being 3.24 Å [93]).



Intramolecular Au ··· Au interactions have been found also in diaurated 1,2-dihydroxybenzene [94]. On the other hand, in gold pentachlorophenolate the Au atom and one of the chlorine atoms are drawn together forming a 5-membered chelated ring [95]. If the chlorine atom is replaced by a more nucleophilic nitrogen atom, an enhanced secondary coordination, Au ··· heteroatom, is established. This has been shown for 2,2′-bis(triphenylphosphinegoldoxy)azobenzene [96].



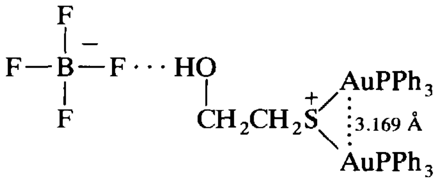
In gold 8-oxyquinolinate the formation of such a chelated ring is accompanied with structural nonrigidity of the molecule [97]. This complex crystallises in several modifications with different geometries of the chelate ring, *i.e.* the gold atom occupies different positions between the N and O atoms in different crystal modifications of the complex. The variation of geometry of the complex during the passage from one of these modifications to another can serve as a model for a migration process of the Ph_3PAu^+ cation between O and N atoms.



It is important to note that the gold atom in the complex is bound to nitrogen by a principal bond and to oxygen by a secondary bond. On the other hand, in gold 8-mercaptoquinolinate containing more the nucleophilic sulfur atom, the principal bond is Au–S and the Au–N bond is the secondary one [98].

Auration of 2-mercaptoethanol leads to the sulfonium salt **95**, the oxygen atom not being involved in coordination with gold.

$HO—CH_2CH_2—SH + \mathbf{78} \longrightarrow$



$$F_3B^-F\cdots HO-CH_2CH_2S^+(AuPPh_3)_2 \quad (Au\cdots Au\ 3.169\ \text{Å})$$

(95)

The sulfonium fragment has a pyramidal geometry, the distance between the gold atoms being short enough to confirm Au ··· Au interaction [99]. The formation of sulfonium salts of gold takes place also in reactions of thio-derivatives of ferrocene with a variety of gold complexes [100,101].

A comparison of aurating ability of gold-containing oxonium, ammonium and sulfonium salts shows that oxonium and ammonium salts are close in their reaction ability and use all Ph_3PAu moieties for auration. The sulfonium salt is significantly less effective and transfers only one Ph_3PAu group [101].

A series of exchange reactions have been carried out making it possible to evaluate relative strength of gold–heteroatom bonds. In phenolates, anilides and thiophenolates of gold, this strength increases in the order PhO < PhN ≪ PhS [82].

$$R—O—AuPPh_3 \underset{R-OH}{\overset{R-NH_2}{\rightleftarrows}} R—NH—AuPPh_3 \xrightarrow{R-SH} R—S—AuPPh_3$$

$R = p\text{-}O_2N—C_6H_4$

The electronic structure and coordination mode of gold complexes with Au–O, Au–N and Au–S bonds have been studied by NMR, IR and UV spectroscopy [30,31,85,86,102]. These investigations have revealed bonds formed by gold with a carbon atom or heteroatom to be more polar than the corresponding bonds formed by a hydrogen atom or the PhHg group [102].

7. Conclusion

The results summarized in this review demonstrate the investigation of univalent gold complexes to be indeed a "gold" contribution in organometallic and cluster chemistry. This contribution was made possible first of all by the elaboration of synthetic methods for preparation of gold complexes and especially auration reactions by gold-containing oxonium salts.

Complexes of univalent gold are excellent models for study of a wide scale of intra- and inter-molecular interactions including metal–metal bonds, chelating metallacycles and agostic metal–hydrogen interactions [103,104].

Recently in this journal a review has been published on electrochemistry of gold complexes with organic ligands [105].

In recent years, complexes of gold have been used in laser microchemistry, and laser-stimulated deposition of metallic gold on semiconductors and dielectrics has been carried out [106–108]. This shows promise for the future use of gold complexes in microelectronics.

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