Chemistry of gold(I, III) complexes with organic ligands as potential MOCVD precursors for fabrication of thin metallic films and nanoparticles

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Chemistry of gold(I, III) complexes with organic ligands as potential MOCVD precursors for fabrication of thin metallic films and nanoparticles

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Abstract

The present review deals with the chemistry of complexes of gold(I) and gold(III) with organic ligands. Compounds classified according to the type of coordinating ligands and donor atoms are considered from the point of view of their potential application as precursors in the MOCVD process, which attract considerable scientific interest. This method has undeniable advantages over other technologies (precision multi-parameter monitoring in order to control the properties of the obtained coatings, high utilization of precursors, simple equipment design, etc.) and can be used to produce thin films and gold nanoparticles with desired characteristics on different types of surfaces of complex geometries for various engineering applications. The following main results published to date are summarized and analyzed in this review: (a) chemical approaches to synthesis, structural characteristics and properties of the main classes of organic compounds of gold (I, III), (b) thermal stability of gold compounds in solid state, (c) temperature-dependent measurements of vapor pressure used for the characterization of gold compound volatility, (d) thermolysis processes of gold complex vapor on heated substrates, (e) examples of modern high-precision applications of gold precursors in MOCVD technique of metallic layers and nanoparticles. Mechanisms and growth processes of gold films and nanoparticles, their composition, structure, and characteristics are also considered.

Keywords: gold(I) complexes; gold(III) complexes; volatile precursors; gold layers; gold nanoparticles; MO CVD; ALD

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1. Introduction

Interest in the chemistry of volatile compounds of gold is associated, primarily, with the growing demand for Metal Organic Chemical Vapor Deposition (MOCVD) precursors used in the process of growing gold thin films and nanoparticles. Due to their low resistivity and high corrosion stability thin films and nanomaterials of gold find numerous valuable applications as in anticorrosion coatings [1], films in optical and microelectronic devices [2-10], protective layers for inner surfaces of microwave waveguide resonators [11, 12], electrical contacts and interconnects and layers in solar batteries [13]. Furthermore, they find application in electrochemical and biomedical applications [14], in the areas of organic synthesis and catalysis [15,16], photophysics, photochemistry [17-19] and in chemotherapy [20].

In the last two decades, nanotechnology started to take advantage of various forms of CVD for the preparation of various composite nanomaterials, such as AuNP/semiconductor oxides [21], AuNP/titania composites [22], AuNP/transition metal composites [23], SiO_2 sandwiched AuNP arrays [24], AuNP-doped vanadium dioxide thin films [25], titanium dioxide/tin dioxide nanocomposites [26], and AuNP/organic semiconductors [27]. Gold nanoparticles deposited on materials with developed surface (TiO_2, Fe_2O_3 and Al_2O_3) exhibit a high catalytic activity in various chemical processes and are used as active component in the matrix of catalytic systems for the photocatalytic production of hydrogen from ethanol, reactions of propylene epoxidation, conversion of ethanol to formaldehyde, hydrogenation of unsaturated hydrocarbons, oxidation of hydrocarbon and CO at low temperatures [28-31]. In addition, recently, gold-based nanostructured materials have been the object of intense research in medicine [32]. Gold nanoparticles with tunable plasmon resonance are widely used in modern biotechnology for the photothermolysis of cancer cells [33] as well as in combination with carbon nanomaterial [34] and organic and oxide semiconductors as chemical sensors and biosensors [35-39]. Moreover, in recent years they become to be used in new generation of nanoparticle-doped optical fibers [40].

Modern trends in the development of high-tech industries constantly increase the requirements to the size, composition and structure of film nanomaterials and nanoparticles. Along with the physical gas-phase methods (molecular beam epitaxy, pulsed laser deposition, cathodic, magnetron, high frequency spray deposition), methods of electrochemical deposition [41], sol-gel [42], photochemical deposition [43] MOCVD is one of the fastest developing methods used for the above-mentioned high-tech applications MOCVD and its variants (for example, Atomic Layer Deposition (ALD), pulsed MOCVD and thermal MOCVD at low and atmospheric pressure, photo-enhanced MOCVD, etc.) have all the necessary capabilities to control the processes of growth of coatings with the specified composition and structure on objects of different geometry [44, 45].

The main stages involved in the MOCVD process are the transport of precursor vapor in the deposition zone followed by the activated decomposition on the surface, leading to the formation of the functional layer. MOCVD method is characterized by a relatively low energy cost, precision multi-parameter monitoring in order to control characteristics of the coating and dispersion of nanoparticles, and high utilization of the precursor. Furthermore, the method allows us to obtain coatings of different composition and surface morphology and structure, adjust coating thickness, change the deposition rate, deposit layers and nanoparticles onto substrates with any shape and onto materials of different nature (metals, semiconductors, non-conductive materials, polymers), and to create novel film materials by varying the composition of the coating during its growth. MOCVD method allows the users to control precisely the concentration of precursor vapors and, subsequently, to control the growth process of nanoparticles and layers with predetermined composition and structure. The method excludes the use of solvents, which are a source of contaminants and unwanted impurities. The range of thickness for the various layers obtained in this method may vary from nanometers to tens of microns.

The chemistry of precursors plays a key role in the deposition process, since both experimental parameters and construction of some units of MOCVD installations are determined by the physicochemical properties of the used volatile precursors. The main requirements to MOCVD precursors are their volatility, i.e. their ability to transport to the gaseous phase without decomposition under reduced or atmospheric pressure and moderate temperatures, and thermal stability in the condensed and gaseous phases. The most volatile precursors are molecular crystals, however the molecular structure of the compound is essential but not a sufficient condition to transfer it to the gaseous phase at low temperatures. Some complexes with molecular structure can be polymers (oligomers), and they can include not only organic but also other ligands and have low volatility and stability. The compound is volatile when the energy of intermolecular interactions (van der Waals, electrostatic and dipole interaction between monomer molecules in the molecular crystal) is much smaller than the energy of intramolecular bonding. Thus, the volatility and the thermal stability of the compounds are determined primarily by their structural characteristics and electronic structure.

In addition, the precursors should meet the following criteria:

- vapors should decompose completely under the experimental conditions, and decomposition products must be gaseous, with the exception of the coating material;
- precursor vapors and thermal decomposition products should be inert to the materials of the substrate and installation;
- compounds must be non-toxic or low-toxic, stable in air and stable in storage;

- availability of the initial reagents and high yield in the precursors synthesis.

Thus, for the correct choice of the MOCVD precursor it is necessary first of all to have full data on its volatility, thermal behavior and stability.

The development of MOCVD methods and chemistry of precursor for deposition of Ir, Ru, Rh, Pd, Pt, Os coatings have been the subject of several reviews [46-53], however reviews summarizing data on chemistry of gold complexes with organic ligands as precursors for deposition of Au films and nanoparticles are only sporadic and were written more than 10 years ago. A review article written by A. Grodzicki in 2005 [54] was devoted to gold(I) carboxylates and its complexes with tertiary phosphines as a new class of CVD precursors. The authors analyzed thermal decomposition and mass spectrometry data, described decomposition mechanisms of the vapor transport in the gaseous phase and layers growth processes and discussed the effect of the precursor molecular structure on the quality of the deposited metal coatings. Since 2005 over 70 articles have been published with key emphasis on the characterization of new gold precursors, and have provided a brief description of the deposition and application of gold thin films and nanoparticles. Therefore, there has been insufficient information available to interested readers summarizing the main classes of volatile compounds of gold. It can be stressed that the most classical approaches to the synthesis of gold complexes with organic ligand were suggested more than 40 years ago, however they still remain valid and are used by chemists for the synthesis of volatile gold precursors.

In this review, we are providing an overview of a wide range of data concerning existing classes of gold complexes. After illustrating the synthesis of the main classes of gold precursors and investigating their thermal properties, main emphasis will be placed on the systematic analysis of the influence of their molecular structure and properties on the growth of gold films and nanoparticles. Such an up-to-date analysis of the literature in combination with the enduring knowledge of synthetic chemistry of the main classes of gold complexes with organic ligands will allow to us to make recommendations on the choice of precursors and concrete variant of MOCVD process for the deposition of gold thin layers and its nanoparticles with required structure and properties. The present review will provide detailed analysis of both the results of the earlier work related mainly to the chemistry of gold complexes and the most significant data describing the use of MOCVD for preparation of metal coatings and gold nanoparticles for high-tech applications.

Currently a number of volatile compounds of gold used as precursors in MOCVD processes for the production of gold coatings are known; among them are, inorganic, organometallic, intracomplex (chelate complexes with {O,O} coordination center – beta-diketonates and carboxylates; with {S,S} coordination center – dithiocarbamates and dithiophosphinate; with {O,N} coordination center – iminoketonate, oxychinolinates) and mixed (multiligand) compounds. However, only a limited number of precursors are used for the deposition of gold films and nanoparticles. The problem of the use of gold precursors in MOCVD remains unsolved due to their low stability, difficulties of synthesis and storage. In addition, the lack of data on the thermal behavior of volatile gold complexes makes the choice of experimental parameters of gold films deposition for the purposeful change of their properties difficult and, therefore, hinders their practical application. In this regard, the current review also includes the available data on gas-phase reactions, mechanisms of thermolysis of the precursor vapor on the heated surface with the description of the temperature ranges of these processes and the gas products forming as a result of dissociation and fragmentation of the ligands in the gaseous phase.

2. Main classes of compounds of gold with organic ligands

In this chapter, the main classes of gold(I, III) compounds with organic ligands will be discussed. Gold chelates will be classified according to the type of coordinated ligands and donor atoms.

2.1. Gold(I) complexes with organic ligands

Gold(I) complexes with organic ligands have linear coordination. Four main classes of the compounds recognized according to the type of coordinated ligands, will be considered below.

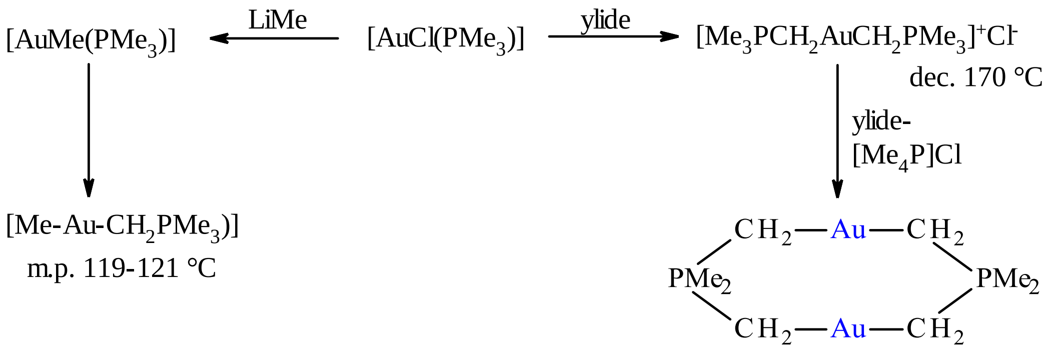
2.1.1. Dialkyl- and diarylsubstituted complexes of gold(I)

The simplest dialkylsubstituted complexes of gold(I) were synthesized by interaction with methyllithium MeLi, e.g. according to the reaction [55]:

$$[\mathrm{AuMe(PPh_3)}] + \mathrm{MeLi} \longrightarrow \mathrm{Li^+[AuMe_2]^-} + \mathrm{PPh_3}$$

The complex was isolated only in the case of coordination with pentamethyl diethylenetriamine (PMDT, $Me_2NCH_2CH_2N(Me)CH_2CH_2NMe_2$) with the formation of more stable compound $[Li(PMDT)][AuMe_2]$ melting at 120–123°C, in which gold atom has linear coordination [56].

Some stable gold(I) complexes were obtained according to the reaction involving trimethylphosphineylide $Me_3P{=}CH_2$ and similar ylide compounds [57, 58]:



Synthesis of several types of ylide gold(I) complexes is described in the literature [57, 58], among them the simplest [$MeAuCH_2PMe_3$] with the melting point of 120°C. Ylide dialkyl derivatives obtained in crystalline state were stable in air and in the presence of moisture. The compounds can be kept at room temperature under natural light environment and they can sublime in vacuum without noticeable decomposition. The introduction of more bulky substituents leads to an increase in the compounds stability. The related compounds have high volatility and thermal stability, and therefore can be successfully used as precursors in MOCVD processes.

2.1.2. Complexes [RAuL]

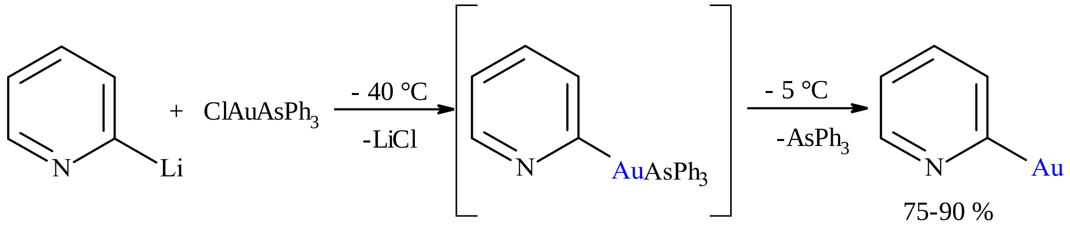
A number of gold(I) complexes of the general formula [RAuL] (where L is a stabilizing ligand, as a rule, tertiary phosphine) are known in the literature. The first compounds were obtained in 1959 via the reaction of gold halogenides with alkyl- or aryllithium [59, 60]:

$$[AuCl(PR'_3)] + RLi \longrightarrow [AuR(PR'_3)] + LiCl$$

$$R = Me, Ph; R' = Et, Ph$$

The chemistry of this class of gold compounds has been described in details by Schmidbaur *et al.* [61]. It was revealed that the most of these compounds, e.g. with R=Me, C_6F_5, CF_3 and L=PMe_3, PEt_3, PMe_2Ph, $PMePh_2$, $AsPh_3$, PPh_3 etc. exhibit both chemical and thermal stability.

The main approach to the preparation of these complexes is substitution of halogen derivatives [XAuL] (X = Cl, Br) to aliphatic or aromatic radicals; e.g. the complex [$AuCl(AsPh_3)$] reacts with 2-pyridyllithium at –40°C with the formation of 2-pyridylgold:



2-pyridylgold starts to decompose at 120°C and then it melts at 150°C with the complete decomposition to metal gold and for this reason it is potentially applicable for the manufacture of pure gold films at medium temperatures. Introduction of alkyl groups into pyridine ring leads to a substantial increase of the complexes stability.

As has been noted by Puddephatt *et al*. [62] the complexes [RAu(CNR')] (R, R' = Alk, Ar) can be used as MOCVD precursors. All the compounds were obtained according to the following reaction:

$$[AuX(SMe)_2] + RLi(RMgX) + L \xrightarrow[Et_2O]{-78\ ^\circ C,\ N_2} [AuR(L)]$$

$$X = Cl, Br$$

[MeAu(CNMe)] is the most stable volatile complex from this series, which melts with decomposition at 95°C and can sublime in vacuum and kept at low temperature for long time. Puddephatt *et al*. indicate [62] that in contrast to alkylphosphine, Au(I) coordinates isocyanide ligand to a greater extent than Au(III). For that very reason, the preparation of this complex with Au(III) has not been a success. The complex [MeAu(CNEt)] is less stable than its methyl analogue and decomposes even at 0°C. As the size of a substituent (R') grows, the complexes stability increases in the following order: *i*-Pr < *t*-Bu < Cy < Ph [62].

Several approaches to the synthesis of [LAu(β-diketonate)] complexes (where L = PPh_3, PPh_2Et, PEt_3, $AsPh_3$ etc.) have been described by Vicente and Chicote [63]. The Au atom in the related complexes bounds with a β-diketonate ligand via σ-bond Au–γC (Fig. 1).

Fig. 1.

So, the [RAuL] complexes are well-studied class of compounds; some of them are used as MOCVD precursors, however some drawbacks of [RAuL] complexes should be pointed out. Among these drawbacks, the presence of phosphorous and arsenic in the elemental composition of the molecule is undesirable in the processes of coating deposition. Moreover, both initial reagents and thermolysis products of these compounds contain toxic phosphorous- and arsenic-containing substances.

2.1.3. Alkynyl, vynil and olefinic complexes of gold(I)

The chemistry of alkynyl complexes of gold(I) was described in several publications [57, 64, 65]. Alkynyl complexes of Au(I) generally possess relatively high thermal stability (decomposition temperatures are more than 100°C) with a tendency to form alkynyl metal polymers. Fluorosubstituted derivatives differ by its improved stability compared to their unsubstituted analogues. The corresponding alkynyls of lithium, potassium and free alkynyl are usually used for the synthesis of the related compounds.

First reports regarding gold(I) olefinic complexes have appeared in 1964 when the light-sensitive [Au_2Cl_2(cod)] (cod = C_8H_{12}) complex rapidly decompose upon heating has been obtained [66]. Along with these compounds, complexes with cyclohexene, cyclopentene, cyclooctene, cyclodecene, pentandiene, norbornadiene, cyclododecatriene and some other cyclic alkenes were synthesized [67-69]. All these compounds are light-sensitive, unstable and decompose even at low temperatures.

By this means, only some alkenyl and alkynyl-substituted gold(I) complexes were used in MOCVD processes. Introduction of methyl or trifluoromethyl groups as a second substituent makes these compounds potentially suitable for MOCVD technology. The main drawbacks of these complexes are their ability to form polymers and as a consequence their low volatility. As for olefinic complexes, their instability as well as the difficulty associated with their synthesis procedure makes them unsuitable for application as MOCVD precursors.

2.1.4. Gold(I) complexes stabilized by N, O or S atoms

The synthesis of [(RO)(R'N=)CAu]$_3$ (R = Me, Me_2CH; R' = Me, Et, CH_2Ph, C_6H_{11}, *n*-MeC_6H_4) was described by Minghetti [70] according to the following reaction:

$$[\mathrm{AuCl(SMe_2)}] + \mathrm{RNC} + \mathrm{R'OH} + \mathrm{KOH} \longrightarrow \mathrm{AuC(OR')=NR} + \mathrm{KCl} + \mathrm{H_2O} + \mathrm{Me_2S}$$

The compounds are thermally stable in the condensed phase, decompose in the temperature range from 150 to 210°C depending on the radical type and do not change under ambient conditions [70]. Pyridine, benzothiazole or benzoimidazol derivatives can serve as donor ligands in these complexes (compounds **1-3**, Fig. 2) [71].

Fig. 2.

Complexes **1** and **2** (Fig. 2) undergo thermolysis at 167 and 298ºC, respectively, with the formation of dimers of the organic ligand and metallic gold [71]. Compound **3** loses easily trimethylsilyl chloride and transfers to the corresponding oligomer which decomposes at 210°C [71] (Fig. 2). Stabilization of (triphenylphosphine)gold by azide, 1,2,3- and 1,2,4-triazole ligands leads to the formation of complexes (Fig. 2) with stability against heating and light [72]. TG/DTA analysis of these derivatives showed that the weight loss was not observed up to decomposition temperature of 195–198°C [72].

A wide range of the compounds with the formula [Au(PR_3)(OSiR'$_3$)] (R, R' = Alk, Ar) exhibiting stability to exposure to light, air and humidity were obtained [73]. The unstable complex AuN($SiMe_3$)$_2$(PMe_3) (T_m= 35–37°C) was formed on stabilization of the alkylsilyl group in the Au(I) complexes by nitrogen atom [74, 75]. At the same time $PMe_3AuOSiMe_3$ (T_m = 79–

80°C) is more tolerant to temperatures, able to transfer to the gaseous phase and decomposed at temperatures above 190ºC with the formation of $(Me_3Si)_2O$, Me_3PO, PMe_3 and gold mirror [74]. Its analogue $AuN(SiMe_3)_2)(PEt_3)$ was synthesized via the reaction with $Li(N(SiMe_3)_2$ and was recently used as a precursor in ALD processes [76]. It is worth mentioning that the precursor decomposition products are toxic and highly flammable, which makes it difficult to use such complexes as MOCVD precursors.

A number of thio- and selenocyano-complexes of Au(I) with the formula [LAuSCN] were studied by Schneider *et al*. [77]; in dependence on the type of stabilizing ligand L they can exhibit various properties. Introduction of trialkylphosphine into the complexes $[R_3P{=}SAuX]$ (R = Alk, Ar; X = Cl, Br, CN) allow to increase their stability [78]. The data on the complexes $[R_3PAuSC(O)CX_3]$, $[R_3PAuOC(O)CX_3]$ (X = Cl, F, H) [79], $[R_3PAuSS(O)_2R']$ [80], $[R_3PAuS(O)_2R']$ and $[R_3PAuOS(O)_2R']$ [81] (R, R' = Alk, Ph), which decompose at temperatures below 100°C, are also available in the literature.

Ketenide complexes of Au(I) can be synthesized via the following reaction [82, 83]:

$$2[AuClL] + CH_2{=}C{=}O + 2Et_3N \longrightarrow Au_2(C{=}C{=}O)L + L + 2[Et_3NH]^+Cl^-$$

The authors used 2,6-dimetylpyridine as L, but the structural formula of the above-mentioned ketenides is unknown. The $Au_2(C{=}C{=}O)L$ complex easily loses the ligand with the formation of $Au_2(C{=}C{=}O)$ and explodes upon heating above 100°C. However if the controlled thermal decomposition was carried out on a glass surface heated to 100°C, a compact metal gold film was formed, which was further used in the process of catalytic propylene oxidation [82].

Stabilization of the gold complexes by donor atoms as N, O and S should give stable compounds, however the analysis of the literature data has shown the relative compounds are characterized by rather “poor” chemistry and decompose even at relatively low temperatures along with their inability to sublime without decomposition. This appears to be connected with the features of chemistry of gold(I), whereas gold(III), on the contrary, exhibits affinity to N, O, S-donor ligands. Trialkyl- and triarylphosphines are used for the additional stabilization of the class of compounds under consideration. Grodzicki *et al*. in their review [54] have considered gold(I) complexes with carboxylates and tertiary phosphines of the general formula $[Au(OOCR)(PR'_3)]$ where R’ = Me, Et, Ph, ^{p}tol and $R{=}CH_3$, $C(CH_3)_3$, $CHCl_2$, CF_3, C_3F_7, C_6F_{13}, C_7F_{15}, C_9F_{19}, C_6F_5, $C_6F_5CH_2$, $CH(CH_3)NHC(O)C_6H_5$, $CH_2NHC(O)CH_3$, $CH_2NHC(O)C_6H_5$ as alternative organometallic CVD precursors. Compounds were prepared in a metathetical reaction of (phosphine)gold(I) halide and silver carboxylates:

$$[AuCl(PR_3)] + AgOOCR \longrightarrow [Au(OOCR)(PR_3)] + AgCl.$$

Using structural studies these species were shown to be monomers or dimers depending on the steric effects of the tertiary phosphine and carboxylate substituents.

Recently new ALD precursor dimeric gold(I) tert-butyl-imino-2,2-dimethylpyrrolidinate was prepared by Coyle *et al.* [84] by salt metathesis of lithium tert-butyl-imino-2,2-dimethylpyrrolidinate and a gold chloride salt providing good yield (Fig. 3). This compound is soluble in aromatic or chlorinated solvents and stable in air up to 170°C; it decomposes at the temperature of 300 °C as determined by CVD experiments.

Fig. 3.

Two precursors, Au(HMDS)(NHC) (HMDS = hexamethyldisilazide, NHC = 1,3-diisopropylimidazolidin-2-ylidene) and Au(HMDS)(PMe_3) (compounds **1-2**, Fig. 4) were obtained using similar procedure [84] by salt metathesis of metal chloride and lithiated hexamethyldisilazide with a good yield [85]. They were successfully used for the self-seeded growth of gold plates and wires with high aspect ratio by MOCVD, however it is necessary to point out that the compounds were sensitive to moisture. According to TGA data the complexes start to sublime with decomposition at 100 and 80 ^{o}C, respectively.

Fig. 4.

Whilst on the subject of organic complexes of gold(I) in general, trialkylphosphinylide derivatives (dialkyl-substituted gold complexes) should be particularly emphasized. These complexes have demonstrated sufficiently good thermal stability together with their high volatility. [RAuL] (L = PR_3, CNR; R = Alk) complexes can also be considered as promising MOCVD precursors, however information on thermal behavior of these compounds both in gaseous phase and in condensed state is lacking. The presence of phospine groups in the molecules and the fact that some alkylphospines are toxic may restrict the application of these compounds in CVD processes. Iminopyrrolidinates and carboxylates of gold(I) could also be promising precursors, however the necessity to synthesize them in nitrogen atmosphere using dry boxes makes both synthetic procedure and the preparation technology of gold films and nanoparticles quite difficult. It is also necessary to note the lack of information about thermal behavior of the complexes considered above both in solid and in gaseous phases.

2.2. Gold(III) complexes with organic ligands

Gold(III) complexes with organic ligands are more varied class of compounds than complexes of gold(I). This appears to be due to the larger variety of ligands coordinating Au(III) as well as the higher stability of organic complexes of gold(III). By convention, gold(III) chelates can be divided into four groups according to the number of alkyl and aryl substituents in the coordination sphere of the central metal.

2.2.1. Tetraalkyl- and tetraaryl-substituted complexes

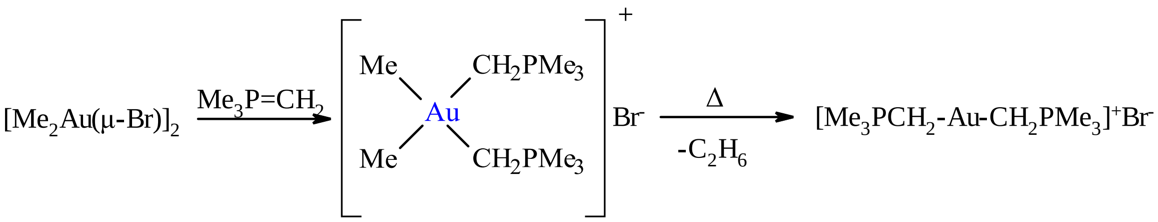
The chemistry of tetraalkyl- and tetraaryl-substituted gold(III) compounds has been described in details by Schmidbaur *et al.* [61]. The simplest complex of this type was synthesized according to the following reaction:

$$[AuMe_3(PPh_3)] + LiMe \longrightarrow Li[AuMe_4] + PPh_3$$

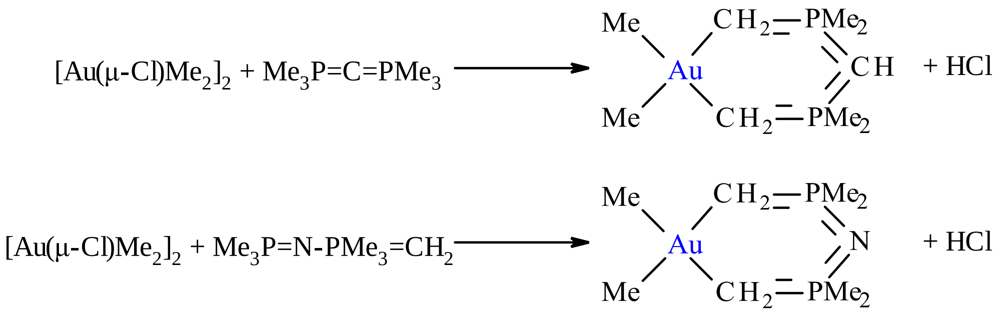
Interestingly compound $Li[AuMe_4]$ was shown to be stable for long time in ether solution at room temperature and in air ambient [56], whereas trimethylgold(III) in ether decomposes even at –40°C. Rice *et al.* [56] assumed that gold(III) complexes with even number of alkyl groups should be more stable than those with odd number of organic radicals. Upon solvation of lithium ion by the PMDT ligand, the complex $[Li(PMDT)][AuMe_4]$ which melts with decomposition at 86–88°C was isolated [56].

Tetraarylsubstituted complexes of gold(III) are also known [61, 86], e.g. pentaphenyl gold(III) stabilized by tetrabutylammonia $[Bu_4N][Au(C_6F_5)_4]$ are also stable and melts without decomposition at 240°C, but it loses two C_6F_5 radicals with the formation of $[Bu_4N][Au(C_6F_5)_2]$ upon further heating.

The use of ylides as ligands allows obtaining a number of gold complexes containing four Au–C bonds [58, 61, 87]. In the reaction of $[Me_3Au(PMe_3)]$ with $Me_3P{=}CH_2$ the corresponding ylide $[Me_3Au^{-}{-}CH_2P^{+}Me_3]$ (T_m=111–112ºC) form, which is stable in air and in the presence of moisture, is obtained [87]. Moreover, it sublimes in vacuum and decomposes in inert atmosphere at 185°C. Schmidbaur *et al.* [87] have noticed unusual thermal stability of the above mentioned ylide complex since other known compounds containing AuR_4^- fragments do not exist above room temperature. Ylides and their derivatives which can lose ethane molecule may also be obtained from dimethylgold(III) halogenides [87]:



In a similar manner trimethylgold(III) complexes of reactive sulfonium and sulfonium ylides [$Me_3Au^{-}–CH_2S^{+}(O)Me_2$] and [$Me_3Au^{-}–CH_2S^{+}Me_2$] which are capable of reacting with PMe_2Ph, giving [$Me_3Au(PMe_2Ph)$] can be obtained from [$Me_3Au(PR_3)$] [88]. Bidentate ylide derivatives were synthesized via the reaction of dimethylgold(III) chloride with $Me_3P{=}C{=}PMe_3$ and $Me_3P{=}N–PMe_2{=}CH_2$ [88]:



Both products are isostructural and have close sublimation temperatures in vacuum (115 and 100°C, respectively, at 10^{-4} Torr) and decompose at temperatures above 250°C [88]. The high stability of these compounds can be explained by the formation of the stable six-centered π-system.

Another example to obtain tetraalkyl-coordinated complex of gold(III) was demonstrated via the reactions of methyllithium with halogenated derivatives of dimer ylides (Fig. 5) [89]:

Fig. 5.

Compound **2** (Fig. 5) in crystalline state is thermally stable and decomposes only at 153°C. It is worth mentioning that ylide complexes of gold easily undergo transformations, which allows compounds with various substituents and functional groups to be obtained [89].

By this means among tetraalkyl-substituted complexes of gold(III) ylide derivatives should be particularly emphasized. Some of them are distinguished for their high thermal stability and volatility and are good enough for MOCVD processes, however the properties of ylides have not been adequately studied and still require further investigation. The main drawback in this instance is the low stability and high cost of ylide precursors.

2.2.2. Trialkyl- and triarylsubstituted complexes of gold(III)

As has been discussed earlier, gold(III) complexes triple-substituted by organic ligands have less stability compared to their twice- and tetra-substituted analogues. More stable complexes can be obtained at low temperatures in the case of coordination of trialkylgold with ligands containing donor atoms of group V in the periodic table (N, P or As, etc.) [75]. The synthesis and some properties of [R_3AuL] complexes have been described in a book chapter [61]. The melting point and thermal stability of these complexes can vary over a wide temperature range depending on the type of stabilizing ligands and organic radicals. The main classes of [R_3AuL] complexes which have potential application as MOCVD precursors will be considered below in more details.

2.2.2.1. Gold(III) compounds stabilized by P atoms

Trialkyl- and triphenylphosphines are good stabilizers of trimethylgold(III) [90]. Me_3AuPMe_3 compound decomposes even at room temperature, whereas Me_3AuPPh_3 is quite stable and decomposes at 120°C [60]. The products of pyrolysis of Me_3AuPPh_3B in vacuum were studied by Coates *et al.* [60]; among those products are ethane (95%), a precipitate containing PPh_3 and gold metal. Obviously, the stability of gold(III) complexes stabilized by PR_3 ligand grows with increasing the inductive effect of R, viz. in the order $PMe_3 < PMe_2Ph < PMePh_2 < PPh_3$ when the nature of Au–C bond is the same [60, 91]. The most stable $R_3AuPR'_3$ complexes are those with R' = Ph, however the nature of R substituents should also be taken into account. A series of RMe_2AuPPh_3, where R = Et, *n*-Pr, *iso*-Pr, *tert*-Bu, *neo*-C_5H_{11}, *n*-Bu, Ph, σ-C_5H_5 and CD_3 was also synthesized and studied [71]. The compounds decompose in the range from 77 to 142°C.

Fluorosubstituted derivatives of trialkylgold are of particular interest. Trifluoromethyl derivatives of the complexes ($(CF_3)_3AuL$) stabilized by phosphorous atom are stable against moisture and air and can be easily purified by vacuum sublimation (e.g. in the case when L = PMe_3) [92]; some of those derivatives are considered as promising precursors for MOCVD of film materials [93]. Generally speaking, the approaches used for the synthesis of trialkylderivatives of gold(III) through alkyllithium in substitution reactions can be used for the preparation of fluorosubstituted complexes [94]. Sanner *et al*. [95] suggested a new method for the synthesis of fluorosubstituted gold trimethylphosphinate $(CF_3)_3AuPMe_3$, which was purified by sublimation in vacuum at 75°C. With the use of stabilizing PPh_3 group the thermally stable triarylgold complex $(C_6F_5)_3AuPPh_3$ was obtained which was also tolerant to moisture and air. When an attempt was made to sublime the compound without addition of stabilizing PPh_3 fragment the formation of decafluorobiphenyl and gold metal was observed. This fact confirms once again the applicability of triarylphosphorous for the stabilization of gold(III) complexes, however stabilization by triarylphosphorous leads to the decrease of the compounds volatility.

Accordingly, despite of the low stability of trialkylsubstituted compounds compared to di- and tetraalkylsubstituted agalogues some complexes stabilized by phosphorous atom exhibit high thermal stability in solid state. The simplest methyl and trifluoromethyl complexes from this class are considered by a number of research groups as promising MOCVD precursors.

2.2.2.2. Gold(III) compounds stabilized by N atoms

Chemistry of gold(III) complexes with nitrogen-containing ligands has been described in details by Cinellu *et al*. [96 and refs. therein]. The literature analysis has shown that in the case of a number of N-donor compounds, viz. aniline, dimethylaniline, n-phenyldiamine, piperidine, ethylamine, dimethylamine and glyoxime, the attempts made to stabilize trimethylgold(III) has failed. The synthesis of complexes stabilized by substituted amine group in the composition of one of the ligands were also described [97], however such compounds decompose within several hours in air and in the presence of light. Accordingly, complexes of trialkylgold(III) stabilized by nitrogen atom have low thermal stability and cannot be used as precursors for deposition of Au coatings by MOCVD.

2.2.3. Dialkyl- and diarylsubstituted complexes of gold(III)

It is well known that dimethylsubstituted derivatives of gold organic compounds are more stable in crystalline state than those of diethylsubstituted analogues, whereas di-*n*-propyl and di-*n*-butyl derivatives are liquids at normal conditions [61]. The difference in their physico-chemical properties appears to be connected with the different inductive effect of aliphatic radicals and their size, which in turn influence the energy of crystal lattice formation. The complexes of dialkyl- and diarylgold(III) will be considered below in accordance with the type of stabilizing donor atom, classified according to the groups of the periodic system.

2.2.3.1. Haloid and pseudohaloid compounds (group VII)

Diethylgold(III) bromide was the first synthesized compound from this class [98]. It was shown that it exists as a dimer, as shown in Fig. 6.

Fig. 6.

Complexes containing other alkyl groups are usually synthesized by addition of gold(III) halogenides to Grignard reagents in ether solution [61], as described by the following equation:

$$[Au_2Br_6] + 4MeMgBr \longrightarrow [Au_2Me_4(\mu\text{-}Br)_2] + 4MgBr_2$$

To prevent hydrolysis the anhydrous gold(III) halogenides or the complexes $[AuCl_3(Py)]$ or $[AuBr_2(Py)_2]$ stabilized by pyridine are used.

Organolithium compounds are rarely used because they undergo further reactions forming tri- and tetraalkylsubstituted compounds of gold, however in some cases in the reactions with halogenides or acids, the latter can form complexes of dialkylgold(III). Almost all haloid and pseudohaloid gold(III) complexes have low melting points and decompose even at low temperatures. There are three main structural types of pseudohaloid dialkylgold(III) compounds [61, 94, 99, 100]. The first one includes azides and cyanates, which form bridged dimers where gold atoms are connected via nitrogen atoms, as shown in Fig. 7.

Fig. 7.

The second type includes thiocyanates and selenocyanates of dimethylgold(III) having dimer structure, but gold is connected via sulfur or selenium atoms, respectively [61, 94, 101, 102] (Fig. 8).

Fig. 8.

There are also tetramer structures because cyanides form only linear bonds as shown in Fig. 9.

Fig. 9.

Cyanides of dimethylgold(III) quickly decompose upon heating with the formation of the mixed complex of Au(I) and Au(III) of the general formula $R_2AuCN{\cdot}AuCN$ as an intermediate [99]. The further decomposition processes can be represented as follows:

$$2R_2AuCN \longrightarrow R_2Au_2(CN)_2 + R\text{-}R \longrightarrow 2AuCN + 2R\text{-}R$$

Using $[Et_2Au(\mu\text{-}Br)]_2$ as an initial reagent a number of gold complexes having similar dimer structures were synthesized. As a result of interaction with the corresponding silver salts the complexes containing azide, acetate, trifluoromethanesulphate brige fragments were obtained [99, 103-105]. Preparation of diphenylphosphate, phenylphosphate and phenylarsenate derivatives was also described [94].

Thermochemical and physical properties of R_2AuX (R = Et, *n*-Pr, *iso*-Pr, *n*-Bu, *iso*-Bu, *n*-Am, C_6H_{11}, $PhCH_2$, Ph and X = Cl, Br, CN) compounds widely vary in dependence on the type of radical and stabilizing ligand. It is necessary to mention that cyanides are more stable than halogenides of the corresponding dialkyl gold(III) derivatives [94]. $[Me_2AuBr]_2$ and $[Me_2AuCl]_2$ can be obtained via the reaction of $[Me_2AuI]_2$ with silver nitrate in water solution with the subsequent addition of KBr or KCl, respectively, with the yield of 80–90% [105]. IR and Raman spectra of $[Me_2Au(\mu\text{-}X)]_2$ and $[Me_2AuX_2]^-$ (X = Cl, Br, I) are very similar; the Au–X bond covalency increases in the order Cl < Br < I [105].

Dialkylgold(III) halogenides are usually used as initial reagents for the synthesis of other dialkylgold(III) derivatives, which are stabilized by various mono- and bidentate ligands.

2.2.3.2. Compounds stabilized by atoms of group VI elements

The complex of dimethylgold(III), *cis*-$[Me_2Au(OH_2)_2]^+$, with water exists in water solution as dimer; it has short life time in water solution before it undergoes hydrolysis [75]. Dimethylgold(III) hydroxide $[Me_2Au(OH)]_4$ with unique tetramer structure (Fig. 10) was obtained in solid state in organic solvents [106].

Fig. 10.

The formation of tetramer structure was quite unexpected because most of dimethylgold(III) compounds have dimer structures. Dimethylgold(III) acetate $[Me_2AuOAc]_2$ (compound **1,** Fig. 11) which was obtained by addition of silver acetate to dimethylgold(III) bromide also exists as a dimer [103].

Fig. 11.

The use of dimethylgold(III) iodide instead of bromide gives rise in the yield of $[Me_2AuOAc]_2$ to 93% [103]. Complex **1** (Fig. 11) starts to melt at 97–97.5°C and decomposes at 170°C [103, 104]. Three carboxylate complexes of dimethylgold(III), viz. trifluoroacetate $[Me_2Au(OOCF_3)]_2$, pivalate $[Me_2Au(OPiv)]_2$ and benzoate $[Me_2Au(OBz)]_2$ (Fig. 12), were synthesized using a similar procedure starting from dimethylgold(III) iodide obtained with the yield of 60% [104].

Fig. 12.

Similarly to $[Me_2AuOAc]_2$ the structures of dimethylgold(III) carboxylates are built from neutral bimetal molecules $[(CH_3)_2Au(OOCR)]_2$ (R = CF_3, *t*-Bu, Ph), in which the bridged carboxylate groups form two pentamerous chelate cycles; gold atom has square planar coordination. It was shown [104] that the change of terminal substituents in ligands has a minimal impact on geometrical characteristics of the coordination center. At the same time, except for $[Me_2AuOAc]_2$, introduction of more bulky substituent leads to an increase of the Au…Au distance between adjacent molecules. These compounds have good solubility in many organic solvents, stable at room temperature within several weeks; the melting points of the complexes with R = CF_3, *t*-Bu and Ph are 102-103, 75-76 and 186-187 °C, respectively [103, 104]. They were successfully employed in MOCVD processes.

A series of sulfur-containing complexes of dimethylgold(III) in which gold atom has a four-coordinated planar structure was also synthesized. Compound **2** (Fig. 11) has bridged structure typical for haloid and pseudohaloid complexes of dimethylgold(III). Among them the monomer **3** (Fig. 11) is the most unstable compound decomposing even at room temperature [107]. The dimer **2** (Fig. 11) is more stable and quickly decomposes when the temperature reaches 115°C. According to the observations of Komiya *et al.* [107] the most stable sulfur-containing compound is the complex **4** (Fig. 11) melting without decomposition at 168°C.

One of the most studied class of volatile compounds of dimethylgold(III) is its complexes with β-diketonates [93]. Dimethylgold(III) acetylacetonate was the first complex among this class of compounds to be investigated. Various chelate derivatives of dimethylgold(III) with β-diketone ligands (R-CX-CH_2-CY-R', where X, Y = O, O; O, NH; O, S; S, NH and R, R' = CH_3, CF_3, $C(CH_3)_3$, Ph) have been synthesized [108-112] and studied by various physico-chemical methods [108-112]. Their thermal properties and volatility have also been investigated [108-112]. The decomposition temperature of these chelates in condensed state vary from 75 to 200°C in dependence on the ligand type; in the structure of molecules gold atom has square planar coordination. Zharkova *et al.* [108] have determined the crystal structures of volatile dimethylgold(III) β-diketonates Me_2AuL [L = acetylacetonate (acac), 2,2,6,6-tetramethylheptan-3,5-dionate (thd), dibenzoylmethanate (dbm)]. It was shown that the crystals consist of monomeric molecules organized in polymeric stack connection. At the same time two crystallographically independent molecules with different orientation were determined [109] to be in the unit cell of volatile iminoketonate chelate Me_2Au(i-acac) (i-acac = $CMe_3C(NH)CHC(O)CMe_3$). Volatile dimethylgold(III) iminovinylthionates $Me_2Au(MeCSCHC(NH)Me)$ and $Me_2Au(CF_3CSCHC(NH)Me)$ with melting points 83-85°C and 76-78°C, respectively, were studied by the same group of authors [110]. Their molecular structures consist of monomeric complexes combined into polymeric stack-type connection; they are volatile and thermally [110]. Later volatile dimethylgold(III) complexes based on phenyl-containing beta-diketones and beta-iminoketone, namely, $(CH_3)_2Au$(bac) (Me_2Au(Ph-CO-CH-CO-Me)), Me_2Au(btfa) (Me_2Au(Ph-CO-CH-CO-CF_3) and Me_2Au(i-bac) (Me_2Au(Ph-CO-CH-CNH-Me) were analyzed by single-crystal XRD in Ref. [111]. It was shown that the insertion of Ph and CF_3-substituents into the ligand virtually has no influence on the square coordination core of the Au atom in these complexes. The replacement of one oxygen atom by an NH-group results in a significant increase in the thermal stability of the β-iminoketonate Me_2Au(i-bac) in inert

(Ar) and reduced (H_2) atmospheres. Chen *et al.* [113] synthesized the dimethylgold(III) complex with (Me-CS-CH_2-CS-OEt) as a ligand, which melts at 35–37°C and can be kept in ambient air for long time.

Along with the dimethylgold(III) complexes described above, β-diketonates stabilized by orto-nitrobenzene radicals are capable of undergoing transformation under the action of triphenylphosphine with the formation of the corresponding trimethylgold(III) derivative (Fig. 13) [114]:

Fig. 13.

Compound **1** (Fig. 13) exhibits higher thermal stability (T_{dec} = 205°C) compared to complex **2** (Fig. 13) (T_{dec} = 165°C) derivative [114] since the π-system of acetylacetone ligand apparently stabilizes the molecule.

Bessonov *et al.* [115] have described the preparation techniques of dimethylgold(III) complexes with 8-oxyquinoline $Me_2Au(ox)$ and 8-mercaptoquinoline $Me_2Au(tox)$ from sodium salts of the ligands and $[Me_2AuI]_2$, refined the single crystal structure of $Me_2Au(ox)$ and suggested the model of spatial crystal structure of $Me_2Au(tox)$ (Fig. 14).

Fig. 14.

Structures of dimethylgold(III) quinolinates are built from neutral $Me_2Au(L)$ (L = C_9H_6NS or C_9H_6NO) complexes. Their melting points differ insignificantly: 131-132°C for $Me_2Au(ox)$ and 133-135°C for $Me_2Au(tox)$. Both compounds are stable in air and can be used in MOCVD processes.

Among gold complexes potentially applicable for MOCVD processes, compounds containing alkyloxy groups should be noted. Kodas *et al.* [93] pointed out that such compounds could be good candidates for MOCVD of thin gold films. The first work reporting the synthesis and properties of complexes **1** and **2** (Fig. 15) has been published in 1966 [116].

Fig. 15.

Based on data on the structure and properties of the related complexes of other metals Schmidbaur *et al.* [116] have suggested the procedure of synthesis of complexes **1** and **2** (Fig. 15) and studied their properties. It is necessary to mention that the dimer **1** exhibits better thermal stability than compound **2** and undergoes thermolysis at 135°C with the formation of shining gold mirror [116]. Tris-(trimethylsiloxy)gold(III) (compound **2**, Fig. 15) is less stable and slowly decomposes even at –20°C. Complex **1** sublimes in vacuum and quite stable in dry atmosphere but sensitive to moisture [116].

Bessonov *et al.* [117] have synthesized dimethylgold salicylaldiminates $Me_2Au(Sal{=}NMe)$, $Me_2Au(Sal{=}N(i\text{-}Pr)$, $Me_2Au(Sal{=}NCy)$ and $Me_2Au(Sal{=}NPh)$ by the use of salicylaldimine with the yield from 60 to 90%. Structures of dimethylgold(III) salicylaldiminates are formed by neutral mononuclear molecules $(CH_3)_2Au(Sal{=}NR')$, where R'=Me, *i*-Pr, Cy or Ph as shown in Fig. 16.

Fig. 16.

Dimethylgold(III) compounds with AuS_2 coordination (Fig. 17) were described in works [94, 101, 118].

Fig. 17.

Some of the compounds shown in Fig. 17 are instable and decompose easily even at room temperature. For example, Me_2AuS_2CSEt quickly loses the CS_2 molecular fragment and transforms to the dimer $Me_2AuS_2Et_2AuMe_2$ which is stable at normal conditions, and melts without decomposition at 50°C. Attekum *et al.* [119] have studied the kinetics of decomposition under exposure to X-ray using volatile complexes $AuMe_2(S_2CNMe_2)$ and $AuBr_2(S_2CN(n\text{-}Pr)_2)$ as an example. They have shown that the decomposition rate noticeably drops as the temperature decreases. Parkhomenko *et al.* [101] have prepared one solid and two liquid complexes $[Me_2AuSCN]_2$, $Me_2AuS_2P(OMe)_2$ and $MeAuS_2P(OEt)_2$ as MOCVD precursors. The complex $[Me_2AuSCN]_2$ had a dimer molecular structure (Fig. 18).

Fig. 18.

The simple sulfuro- and selenosubstituted complexes of dialkylgold(III) can be prepared from Au(III) trialkyl derivatives [94], however the most popular method is the reaction of metathesis from dialkylgold(III) halogenides:

$$[Me_2AuBr]_2 + 2[EtOCS_2]K \longrightarrow 2KBr + 2[Me_2AuS_2COEt]$$

Monomer dithiocarbamates can also be synthesized with the use of Grignard reagents:

$$\underset{R\,=\,Alk}{[AuBr_2(S_2CNR_2)]} + 2MeMgBr \longrightarrow [AuMe_2(S_2CNR_2)] + 2MgBr_2$$

Zharkova *et al.* [119] prepared dimethylgold(III) diethyldithiocarbamate complex $Me_2AuS_2CNEt_2$ having excellent storage stability by the reaction of $[Me_2AuI]_2$ with sodium diethyldithiocarbamate. Synthesis and molecular structure (Fig. 19) of low-melting dimethylgold(III) complex with dithiophosphinate $Me_2AuS_2P(i\text{-}Bu)_2$ and its thermal properties were reported by Turgambaeva *et al.* [119].

Fig. 19.

Synthesis of two liquid dimethylgold(III) complexes with substituted dithiophosphinate of the general formula $Me_2AuS_2PX_2$ (X=OMe and OEt) as well as their thermal behavior are also reported in the literature [119]. The compounds are stable under storage, do not require special handling conditions and exhibit a good volatility and vaporization stability.

It was found that the Au–X bond in haloid compounds cleaves easily under the impact of dialkylsulfides and dialkylselenides with the formation of *cis*-$[AuR_2X(SR'_2)]$ complexes [61]:

$$[Me_2AuX]_2 + 2Me_2Se \longrightarrow 2cis\text{-}[AuMe_2X(SeMe_2)]$$

The use of $RS(CH_2)_nSR$ chelate ligands allows to obtain stable dimers (compound **1**, Fig. 20), whereas for the formation of stable bidentate monomer a counter ion is needed, e.g. a nitro-anion (compound **2**, Fig. 20) [61].

Fig. 20.

Among thiocomplexes of dimethylgold(III) (Fig. 20) the compound **2** is the most stable which melts without decomposition at 115°C, while the others are less stable and decompose below 100°C [61].

It has been shown earlier that using Au(III) complexes with β-diketones their stability increases as a result of using nitrogen as a donor atom [108-112]. By analogy, compounds with N,S-coordination (Fig. 21) exhibit higher thermal stability compared to the less stable Au(III) dithiocomplexes.

Fig. 21.

It is worthwhile mentioning that in contrast to dialkylgold(III) compounds containing S-donor ligand, their derivatives stabilized by oxygen atom are more thermally stable and can be transported to the gaseous phase without decomposition; therefore, they can be used as precursors for MOCVD processes. Dimethylgold(III) β-diketonates are often used as MOCVD precursors for deposition of gold coatings; the only one drawback is their sensitivity to light and moisture. Apart from that, the dimethylgold(III) complex with trimethyloxy-group should also be recognized as a promising precursor for MOCVD processes.

2.2.3.3. Compounds stabilized by atoms of the group V elements

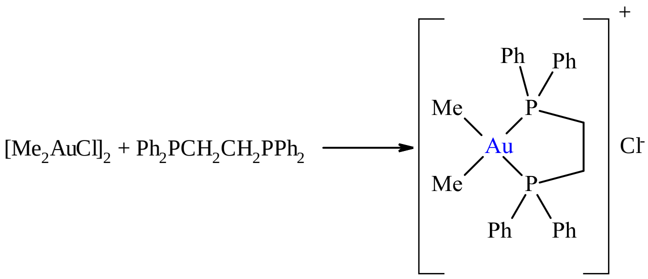
Schier and co-worker [99] have found that diethylamine and its derivatives can be good stabilizers of Au(III) complexes. For instance, ethylenediaminodimethylgold(III) iodide undergoes decomposition only at 168°C, however it exhibits lability to long-term boiling in solution. The dimer analogue $Me_2IAu–NH_2C_2H_4H_2N–AuIMe_2$ is less stable and decomposes even without heating. Stabilization of diethylaminoaurates by cyano-groups results in an increase of their stability. The majority of complexes of this type are usually obtained by the interaction of the corresponding mono- and bidentate ligands with halogenides of dialkylgold(III). However, there are some examples of the reactions with tridentate N- and P-donor ligands, but there is no information available in the literature about the formation of penta-coordinated compounds. Stocco *et al.* [120] have shown that most $[Me_2AuXL]$ complexes have a *cis*-Me_2Au fragment.

A series of auralactame complexes containing C, N, S, O donor atoms in lactame ring and organic groups in lateral substituents were synthesized Cinellu *et al.* [96 and refs. therein]. All compounds are relatively stable, have good solubility in polar solvents, but become degraded in air at room temperature, especially under the influence of natural light. Dimethylgold(III) halogenides with 2,2'-bipyridine and 1,10-phenanthroline, give the corresponding *cis*-$[AuMe_2(bipy)]^+$*cis*-$[AuMe_2Cl_2]^-$ and *cis*-$[AuMe_2(phen)]^+$*cis*-$[AuMe_2Cl_2]^-$ ions [121]. The compounds exhibit similar properties and are stable in air for up to 120°C. The other good stabilizers of dimethylgold(III) complexes are trialkylphospine and trialkylarsine:

$$[Me_2AuX]_2 + 2AsR_3 \longrightarrow 2\textit{cis}\text{-}[AuMe_2X(AsR_3)]$$

The obtained complexes are capable of undergoing further transformations, and it should be pointed out that with an excess of the ligand in reaction the ionic $[AuMe_2L_2]^+X^−$ complexes can be obtained [61, 122].

A great number of dialkyl derivatives of $R_2AuL(X)$ complexes, including deuteromethyl substituted ones, with R = CH_3, CF_3, CD_3, Et, *n*-Pr; X = NO_3, OTf, O_2CCF_3, O_2CCH_3, Cl, Br, I, ClO_4, CN, SCN; L = PMe_3, PEt_3, PPh_3, $P(C_6H_{11})_3$, $AsPh_3$, $SbPh_3$, Py were obtained and studied [95]. Most of them start to decompose even at room temperature. Bidentate complexes exhibiting noticeably better stability compared to monodentate ones and melting above 170°C can be obtained in similar ways [61, 122].



Cis-[AuR$_2$XL] complexes can be synthesized via the reaction of [AuR$_3$L] with acids [92], metal halogenides [94] or halogens [55]. The reaction of redistribution can be noted as an important synthetic approach:

$$2[AuMe_3(PMe_2Ph)] + [AuBr_3(PMe_2Ph)] \longrightarrow 3\textit{cis}\text{-}[AuMe_2Br(PMe_2Ph)]$$

The method of oxidation of gold(I) compounds is used for the synthesis of Au(III) complexes with a pentafluorophenyl fragment:

$$[AuCl(PPh_3)] + (C_6F_5)_2TlBr \longrightarrow \textit{cis}\text{-}[Au(C_6F_5)_2Cl(PPh_3)] + TlBr$$

Such compounds can enter into an exchange reaction, e.g. with silver salts, giving products like [Au(C$_6$F$_5$)$_2$LPPh$_3$]. Fluorosubstituted complexes of dialkylgold(III) are well studied, and most compounds from this wide series decompose during melting [61].

It is possible to sum up that the O,N-coordinated compounds exhibit better stability in comparison with the corresponding O,O-coordinated derivatives. It is only possible to assume that gold compounds stabilized by nitrogen atoms exhibit high enough thermal stability, since studies dealing with the dialkylgold(III) complexes with N-coordination are sporadic as we can see from the literature analysis. As in the case of gold(I) compounds, trialkyl- and triarylphosphines are good stabilizing agents of gold(III) complexes, however, compounds suitable as MOCVD precursors were not found among their dialkylsubstituted derivatives.

2.2.3.4. Olefinic complexes of gold(III) (group IV)

The chemistry of olefinic complexes of gold has been described in several review articles [96, 123]. In most cases these compounds are not stable [94]. For instance, the unstable complex of dichlorogold(III) with 1,5-cyclooctadiene quickly decomposes upon heating. Moreover, it is insoluble in most organic solvents and unstable when exposed to light [66]. Upon its heating above 50°C in CCl$_4$ in the presence of triphenylphosphine, the gaseous 1,5-cyclooctadiene is formed and its amount gradually increases when temperature increases. Chalk *et al.* [66] have established that the complex has olefinic rather than allyl nature with one of chlorine atoms joined to the ring. Apart from that, dimeric complexes of Au(III) dichlorides with such ligand as butene-2, decene-5, cyclooctene, cyclodecene, norbornene, norbornadiene and bicyclopentadiene are known. All π-olefinic complexes of gold(III) are unstable and decompose even at low temperatures.

As a conclusion, the unstable olefinic complexes of dimethylgold(III) cannot be used as MOCVD precursors.

2.2.4. Monoalkyl- and monoarylsubstituted complexes

The reaction of arenes with gold trichloride in dry CCl_4 gives rise to the formation of arylgold(III) dichloride as a dimer [124]:

$$2Au_2Cl_6 + 2ArH \longrightarrow (ArAuCl_2)_2 + 2H[AuCl_4]$$

The process can be described as an electrophilic substitution of aromatic compounds. The reaction product forms as a brown suspension. The reaction itself can be terminated by the addition of ether in order to avoid further interaction with the arene. In the case of alkylbenzene, the *para*-derivative is usually formed, which is in a good agreement with the common principles of electrophilic substitution [94]. In the case where arene has substituents capable to coordinate gold, a simple monomer coordination compound forms:

$$2PhCN + [Au_2Cl_6] \longrightarrow 2[AuCl_3(PhCN)]$$

A number of various monoalkyl- and monoarylsubstituted complexes $[AuX_2RL]$ with X = Cl, Br, I; R = CF_3, C_6F_5, C_6Cl_5, C_6Br_5; L = PPh_3, PMe_2Ph, PEt_3, PMe_3, $AsPh_3$ and R = Ph, p-MeC_6H_4, p-ClC_6H_4; L = SPr_2, PPh_3, PMe_3, Py etc. were also synthesized and investigated [61].

In the last few years the emphasis was on gold complexes with N,N-dimethylbenzylamine possessing pharmacological properties [125-128] (Fig. 22). Abram *et al.* [126] did not describe their thermal properties, though it was mentioned that the complexes slowly decompose in solutions.

Fig. 22.

Preparation of several examples of gold(III) carborane complexes was also described [129]. It was emphasized that the presence of the Au–C bond in such compounds is doubtful. A series of arylgold(III) complexes with 2-benzoyl-, 2-phenoxy-, 2-(phenylsulfanyl)-, 2-anilinopyridine was studied by Fuchita *et al.* [130] and Nonoyama *et al.* [131]. There are also some data available in the literature on 2-phenylpyridine and 2-phenyl-4-(methylcarboxylato)quinoline derivatives [132].

Thus, monoarylsubstituted Au(III) complexes are the most widespread among the compounds of this class, however the aryl substituents results in the decreases of their volatility.

The presence of halogens in the molecules also limits their application as MOCVD precursors. Speaking of gold(III) compounds in general, the most interesting class with potential applications in MOCVD technology is dialkylsubstituted complexes of gold(III), in particular dimethylgold(III) chelates. They can sublime in vacuum without decomposition and exhibit thermal stability acceptable for MOCVD. Besides, most of them can be kept in air for a long time.

3. Thermal properties of gold complexes with organic ligands

3.1. Properties of gold complexes upon heating in solid phase

The methods of thermogravimetry and differential thermal analysis (TG/DTG) are usually used for the determination of temperature ranges in which complexes could vaporize with no change of component composition. The methods are also employed for the estimation of volatility and sublimation enthalpy based on Langmuir equation and for the determination of decomposition temperatures. Such data concerning thermal properties of gold complexes are sporadic due to difficulties encountered with their interpretation, which result from overlapping of the processes of vaporization and decomposition. Moreover, in most published works only TG data are found, which provide very limited understanding of the thermal behavior of these compounds.

3.1.1. Gold(I) complexes with organic ligands

The [R_3PAuCN] complexes (R is various alkyl and aryl substituents) were studied by a combined method of TG/DTA to investigate their decomposition in the temperature range 200–600°C with the formation of gold metal (Table 1) [133].

Table 1.

Griffiths *et al.* [85] have studied thermal stability of Au(HMDS)(NHC) and Au(HMDS)(PMe_3) by an air-free TGA method; the complexes start to evaporate at 110 and 80°C, and decompose at 190°C and 170°C, with residual masses of 26% and 6%, respectively (Fig. 23). The temperatures, at which the vapor pressure of Au(HMDS)(NHC) and Au(HMDS)(PMe_3) is 1 Torr, were estimated from the stepped isothermal TGA to be 115 and 80°C, respectively.

Fig. 23.

Mäkelä *et al.* processes [76] used a dymanic TGA to estimate the applicability of chloro(dimethylsulfide)gold(I) ($AuCl(SMe_2)$, chloro(tetrahydrothiophene)-gold(I) ($AuCl(SC_4H_8)$), methyl(triethylphosphine)gold(I) ($MeAu(PEt_3)$), (diethyldithiocarbamate)(triethylphosphine) gold(I) ($Au(S_2CNEt_2)(PEt_3)$, (2,2-dimethyl-6,6,7,7,8,8,8-heptafluorooctane-3,5-dionato)-(triethylphosphine)gold(I) ($Au(fod)(PEt_3)$), (bis(trimethylsilyl)amido)(triethyl-phosphine)gold(I) ($Au(N(SiMe_3)_2)PEt_3$), and chloro(triethylphosphine)gold(I) ($AuCl(PEt_3)$) as precursors for ALD of gold (Fig. 24). It has been shown that all compounds transfer to the gaseous phase in one step; most of them decompose upon heating and evaporates only partially (Fig. 24). $Au(N(SiMe_3)_2)(PEt_3)$ was chosen from the series of investigated complexes as the best liquid ALD precursor.

Fig. 24.

Grodzicki *et al.* [54] have demonstrated that the decomposition of perfluorinated gold(I) carboxylate complexes proceeds in two steps which can be divided or coincided. For most complexes, decarboxylation proceeds at the first step between 140 and 160°C in dependence on carboxylate. No correlation was observed between the temperature of the decarboxylation onset and the length of perfluorinated chain. At the same time, the lowest temperature (220◦C) of gold formation was found for $[Au(OOCC_7F_{15})(PMe_3)]$ and $[Au(OOCC_3F_7)(PEt_3)]$, while the highest (600◦C) was observed for $[Au(OOCC_6F_5CH_2)(PPh_3)]$. Taking into account the thermal stability of these complexes it has been concluded that they are applicable as precursors for gold deposition in a hot-wall CVD reactor. However, it is worth mentioning that their air and moisture instability restrict their application in CVD experiments.

Coyle *et al.* [84] have studied gold(I) *tert*-butyl-imino-2,2-dimethylpyrrolidinate by the TG method; the temperature of mass loss onset was 209 °C with a metal residue of 40%. According to the DSC analysis the compound showed sharp decomposition at 290 °C. The evaporation kinetic was evaluated by a stepped isothermal TG method between 130 and 190 °C. The temperature at which the vapor pressure of the compound is 1 Torr was estimated to be 238°C using the Langmuir equation. For investigation of the mechanism of compound decomposition by NMR, the complex solution in deuterobenzene was sealed in a heavy-walled NMR tube and heated in isothermal oven in the presence of light. It has been stated that the complex decomposes at 100°C with the formation of gold metal on the walls of NMR tube and protonated ligand as a single product which was observed by NMR.

3.1.2. Gold(III) complexes with organic ligands

Zharkova *et al.* [108-111] have revealed a regularity of the change of volatility and thermal stability of β-diketonate derivatives in dependence on terminal substitutes in the chelating ligand. It has been concluded that introduction of fluoro-containing ligands leads to an increase in the volatility, while it causes a decrease in the thermal stability of these complexes. However, Larson *et al.* [134] have noted that fluorosubstituted β-diketonates demonstrate good enough thermal stability and can therefor effectively be used in CVD processes, giving high quality gold films. Introduction of *t*-Bu substituents into the ligand causes a decrease in the volatility of dimethylgold(III) β-diketonate, while improving its thermal stability [108-111], which correlates with the data on capability of *t*-Bu groups to improve the thermal stability of another volatile chelates [135]. The DTA data (Table 2) also points to the improved stability of chelates containing two -CMe_3 groups [108-111]. Introduction of Ph group results in an increase of the compounds stability compared to dimethylgold(III) acetylacetonate, but the decomposition onset temperatures of Ph-containing complexes are lower than those of the complexes with *t*-Bu substituents (Table 2).

The nature of donor atoms in the chelate center was suggested to be the crucial factor in the change of thermal stability of dimethylgold(III) chelates rather than the type of substituents of (R and R’) [108-112]. The thermal stability of the complexes is found to decrease in the order (O, NH)>(S, NH)>(O, O)>(O, S) depending on the type of chelate center [108-112, 136]. This order of thermal stability correlates with the order of the increase in the metal-ligand force constants (K(AuN) > K(AuC) > K(AuO) > K(AuS)) obtained from the calculations of vibrational spectra of dimethylgold chelates [137]. Bessonov *et al.* [138, 139] have noticed that similar to β-diketonate derivatives, carboxylate complexes have a tendency to increase their volatility on introduction of trifluoromethyl substituents into the ligand.

Table 2.

In the series of complexes with salicylaldimine ligands [117], the use of “lighter” substituents at the nitrogen atom (e.g. Me in $Me_2Au(Sal{=}N–Me)$) results in the complex transition to the gaseous phase with the formation of less percentage of solid residue (mass loss ~80%). On the other hand, the introduction of cyclohexyl and phenyl substituents into salicylaldimine ligands of $Me_2Au(Sal{=}N–Cy)$ and $Me_2Au(Sal{=}N–Ph)$, respectively, leads to the complete decomposition of the complexes with the formation of a residue equal to the mass of gold in the compounds (46% for $Me_2Au(Sal{=}N–Cy)$ and 47% for $Me_2Au(Sal{=}N–Ph)$).

Bessonov *et al.* [140] have described the behavior of dimethylgold(III) quinolinates upon heating in helium atmosphere; the mass loss for $Me_2Au(OQ)$ and $Me_2Au(SQ)$ was 35% and 48%, respectively. The decomposition onset temperature of $Me_2Au(SQ)$ (150°C) was demonstrated by DTA to be lower compared to $Me_2Au(ox)$ (220°C). As a consequence, the replacement of oxygen donor atom by sulfur atoms leads to a decrease in the thermal stability of dimethylgold(III) quinolinates similar to dimethylgold(III) β-diketonates.

Turgambaeva *et al.* [141] have studied the thermal behavior of dimethylgold(III) diethyldithiocarbamate under heating in inert atmosphere and have shown that vaporization proceeded in one step (97.9% mass loss at T=240°C). Two liquid dimethylgold(III) complexes with substituted dithiophosphinate of the general formula $Me_2AuS_2PX_2$ (X=OMe and OEt) were shown to vaporize with partial decomposition, using TG analysis; the residual masses were 87% and 93% at 453K, respectively [142].

Mäkelä *et al.* [143] studied several gold(III) complexes of different classes, namely $AuCl_3$, $AuCl_2S_2CNEt_2$, $Me_2Au(MeNacac)$ (dimethyl(4-(methylimino)pent-2-en-2-olato)gold(III)), $Me_2Au(OAc)$ (dimethylgold(III)acetate), $Me_2AuS_2CNEt_2$, by TGA in nitrogen atmosphere. It was shown that all four compounds decompose at the conditions of TG experiment, except $Me_2AuS_2CNEt_2$, which shows a single step evaporation with a residual mass close to zero; the same result was published by Zharkova and Turgambaeva [118, 141]. In addition, $Me_2AuS_2CNEt_2$ is solid at normal conditions with a low melting point (40–44°C) and transforms to liquid at the conditions of ALD experiment at 99°C which is an additional advantage for its application as an ALD precursor.

3.2. Volatility of gold complexes with organic ligands

One of the important properties of MOCVD precursors is their volatility, *viz.* their capability to transfer to gaseous phase without decomposition. The quantitative characteristic of volatility is the partial vapor pressure at a certain temperature. The temperature dependence of vapor pressure is described by the equation $\lg P = A - B/T$, where $A = \Delta S_T^o/R$ and $B = \Delta H_T^o/R$ [144].

Published work on the direct measurements of vapor pressure dependence on temperature of gold(I, III) complexes with organic ligands are rather sporadic. For $Me_2AuS_2CNEt_2$ the saturated vapor pressure was found to be ~10^{-3}–10^{-1} Torr within the temperature range of 50–90°C [141]. The equation $\lg P\ (\mathrm{Torr}) = 11{,}7 \pm 0{,}3 - (4{,}617 \pm 95)/T$ and thermodynamic parameters $\Delta H_T^o = 88{,}3 \pm 1{,}8$ kJ/mol and $\Delta S_T^o = 168{,}7 \pm 5{,}3$ J/(mol·K) were obtained by means of the Knudsen effusion method with mass spectrometric recording of gas phase composition.

Griffiths *et al.* [145] have synthesized trimethylphosphinotrimethylgold(III) $AuMe_3PMe_3$ which is liquid at room temperature and estimated the enthalpy of sublimation by isothermal thermogravimetry. The compound has a vapor pressure that follows Langmuir equation $\ln(p) = 0.059T - 1.65$, where p is the pressure in Pascals, and T is the temperature in Celsius [146].

Using Knudsen effusion method Semyannikov *et al.* [147] have studied the temperature dependence of vapor pressure of some dimethylgold(III) β-dikenonates with aromatic and aliphatic terminal ligands (Table 3). In the series of investigated complexes, Me_2Au(acac) and Me_2Au(thd) have the highest volatility. N,O-coordination in Me_2Au(i-acac) causes a decrease in volatility compared to Me_2Au(acac) with O,O-coordination, however Me_2Au(acac) becomes more stable than Me_2Au(i-acac) [147].

Table 3.

The P(T) dependencies of other three dimethylgold(III) complexes (Fig. 25) with fluorinated β-diketonates were measured by the flow method (Table 4) [148, 149], however the thermal behavior of their vapor in the investigated temperature ranges was not described. These derivatives were used as precursors for MOCVD of gold films.

Fig. 25.

Table 4.

Larson *et al.* [134] have shown that the introduction of fluorine-bearing substituents into the ligand improves the volatility of dimethylgold(III) β-diketonates: the saturated vapor pressure of Me_2Au(acac) was measured at 24°C to be 9 mTorr; the vapor pressure values of fluorinated complexes Me_2Au(tfac) and Me_2Au(hfac) at the same temperature were 40 and 400 mTorr, respectively.

The fluorosubstituted $[Me_2Au(OOCCF_3)]_2$ complex was shown to possess the best volatility among dimethylgold(III) carboxylates (Table 5) [138, 139], confirming the tendency for increased volatility of the complexes with fluorine-bearing ligands [134]. At the same time the substitution of methyl group by *t*-Bu one in the carboxylate ligand results in volatility deterioration [147]. $[Me_2Au(OBz)]_2$ has quite low vapor pressure because of its high molecular weight [139]. It is worth mentioning that dimethylgold(III) carboxylates with the exception of benzoate possess quite high vapor pressure despite the fact that they occur as dimmers in vapor phase. The values of sublimation enthalpy of $[Me_2Au(OAc)]_2$, $[Me_2Au(Piv)]_2$ and

$[Me_2Au(OOCCF_3)]_2$ are very close to each other, whereas sublimation entropies are quite different (Table 5), suggesting that the lattice energies of these compounds are comparable and the entropy factor mainly contributes to the difference in their vapor pressure values.

Me_2Au(Sal=N–*i*–Pr) is the most volatile compound among N-substituted dimethylgold(III) salicylaldiminates (Fig. 26, Table 5) [117].

Table 5.

Despite the bulky substituent at the nitrogen atom, the vapor pressure of Me_2Au(Sal=N–*i*-Pr) is higher than that of Me_2Au(Sal=N–Me) at the same temperature because the replacement of Me group by *i*-Pr leads to the weakening of intramolecular interactions and, consequently, to an increase of the volatility (Fig. 26). Me_2Au(Sal=N–Ph) containing aromatic fragments is the less volatile complex in this class of compounds [117].

Among dimethylgold(III) quinolinates, the complex Me_2Au(OQ) ($P = 10^{-3}$ Torr at 87°C) has higher volatility than Me_2Au(SQ) ($P = 10^{-3}$ Torr at 114°C) (Fig. 26) [140], while their sublimation enthalpies are very close (Table 5). The higher value of sublimation entropy of Me_2Au(OQ) can be explained by the influence of oxygen and sulfur donor atoms on the molecular packing in Me_2Au(OQ) and Me_2Au(SQ) crystals.

P(T) dependence (Fig. 26) of a number of dimethylgold(III) complexes with N,O,S-donor ligands reveals that volatility can be tuned in a wide range of pressures and temperatures by variation of ligands of different nature [117, 138-140, 147-149].

Fig. 26.

Therefore, the main factors that affect the volatility of dimethylgold(III) complexes are owing to ligands having different electronic and steric effects and the entropy factor determining the degree of disordering of the system upon vaporization. Variation of ligands allows the vapor pressure to be changed over a wide range (10^{-5}-10^{-1} Torr).

3.3. Thermal decomposition of the vapors of gold complexes with organic ligands

The works devoted to the investigation of gold complexes transformation on heated surfaces are also sporadic. Semyannikov *et al.* [112, 136] were studied temperature dependencies of the composition of gaseous phase during thermolysis of dimethylgold(III) β-diketonates by high-temperature mass spectrometry in the “isolated molecule” approximation with the use of a CVD reactor combined with a mass spectrometer and equipped with a high-temperature molecular beam source. The method allowed the gaseous phase composition to be registered *in situ* and the measurements to be carried out over a wide range of temperatures in different atmospheres (vaccum, oxygen, hydrogen and some other gas-reactants). Due to the very low-pressure operating conditions in a hot wall reactor, any conversions of the compound vapor took place on the reactor's walls. The time between the moment a particle left the reactor and the moment it was ionized did not exceed a millisecond. Examination of mass spectrum changes at different temperatures allowed revealing the gaseous by-products formed during the thermal decomposition of the compound vapor. The suggested scheme of the thermolysis of dimethylgold(III) chelates is shown in Fig. 27 [112, 136]. The process starts when adsorption of the complex molecule onto the surface and the thermal activation accompanied by opening of the chelate cycle. The processes of intermolecular reorganization with the formation of free ligands, methyl-ligands and ligand radical will then take place.

Fig. 27.

The main stages of the above described processes can be both parallel and consecutive. The probability of one or another variant is determined by the nature of donor atom or the type of substituent in the ligand. Such gaseous products of thermolysis as methane and ethane form as a result of consecutive decoupling of alkyl substituents of gold(III) derivatives [112, 136]. According to the results described by Oglezneva *et al.* [150] $Me_2Au(acac)$ also decomposes in solution with the decoupling of the ligand and methyl groups, indicating the presence of ethane and free acetylacetone among the main decomposition products. The temperatures of decomposition onset and the main thermal decomposition products of dimethylgold(III) carboxylate vapors are summarized in Table 6 [117, 138, 139].

Table 6.

Temperature dependence of the intensities of ion peaks of main gaseous products of thermal decomposition in the mass spectra of $[Me_2Au(OAc)]_2$ are given in Fig. 28. The presence of the free ligand in the by-products can be explained by the dehydrogenation of the complex molecule as a result of the intramolecular or intermolecular rearrangements. The peaks corresponding to gold-containing ions are absent in the mass spectra because the compound decomposes completely above 120°C.

Fig. 28.

Fig. 29 shows the mechanism of molecules decomposition on the surface as suggested based on the analysis of thermal dependence of $[Me_2Au(OAc)]_2$ gas phase composition.

Fig. 29.

The temperature of decomposition onset of $[Me_2Au(Piv)]_2$ vapor decreases to 60±5°C. The main volatile products of its decomposition are ethane, carbon dioxide, pivalic acid and its tert-butyl ester. The mechanism of this decomposition is similar to that of $[Me_2Au(OAc)]_2$. A distinctive feature of the process is the presence of carbon acid ester in by-products, which is not observed in the case of $[Me_2Au(OAc)]_2$.

Thermal decomposition of Me_2Au(Sal=N–Me) starts at 120±5°C; the main volatile products are H–Sal=N–Me, MeSal=N–Me and EtSal=N–Me. Me_2Au(Sal=N–*i*-Pr) decomposes at a lower temperature of 110±5°C. A similar tendency of the decrease of thermal stability threshold of $[Me_2Au(Piv)]_2$ on introduction of more bulky substituents was observed in the case of dimethylgold carboxylates. The products of Me_2Au(Sal=N–*i*-Pr) thermolysis are similar to those of Me_2Au(Sal=N–Me): HSal=N–*i*-Pr), MeSal=N–*i*-Pr) and EtSal=N–*i*-Pr). An addition of oxygen has no impact on the decomposition onset temperatures and reaction pathways, but leads to the oxidation of gaseous products.

The mechanisms of thermal decomposition of the vapors of dimethylgold(III) complexes with salicylaldimine are the same (Fig. 30) and involve the stage of opening of the chelate cycle of the adsorbed molecule followed by migration of methyl groups from the gold atom to the oxygen atom of salicylaldimine ligand with the formation of methyl- and ethyl-derivatives of the initial salicylaldimine.

Fig. 30.

The presence of free N-substituted salicylaldimine in the system points to a possible thermolysis pathway with splitting out of dimethylgold. In contrast to the case of dimethylgold(III) carboxylates, where most thermolysis by-products are clearly volatile light compounds, only bulky organic molecules which do not undergo further destruction with the temperature growth are recorded in the mass spectra of dimethylgold(III) salicylaldiminates. This fact suggests different mechanisms of film growth in CVD processes of these two classes of dimethylgold(III) derivatives.

Parkhomenko *et al*. [119] have determined temperature ranges and main gaseous products of decomposition of three dithiophosphate complexes of dimethylgold(III), viz. $Me_2AuS_2P(OMe)_2$, $Me_2AuS_2P(OEt)_2$, and $Me_2AuS_2P(\textit{i}\text{-}Bu)_2$ (Table 7).

Table 7.

Thermolysis of $Me_2AuS_2P(OMe)_2$ and $Me_2AuS_2P(OEt)_2$ vapors proceeds with the formation of methylated or protonated ligands, that are typical for dimethylgold(III) complexes [142]. Two decomposition paths can take place depending on the temperature. The scheme of thermal decomposition of $Me_2AuS_2P(OMe)_2$ vapors on a heated surface is given in Fig. 31 as an example.

Fig. 31.

Thermal decomposition of $Me_2AuS_2P(\textit{i}\text{-}Bu)_2$ [119] can also proceed according to several different paths with the formation of protonated ligand as one of the gaseous products. It is worth mentioning that sulfur and phosphorous enter into the composition of volatile products of the decomposition and do not contaminate the growing coatings. Because the vapor phase composition changes depending on thermolysis temperature, the choice of regimes of MOCVD experiments can affect the composition and physico-chemical properties of gold coatings, as exemplified by XPS study of the composition of gold coatings deposited from $Me_2AuS_2P(OMe)_2$ and $Me_2AuS_2P(OEt)_2$ [142].

$Me_2AuS_2CNEt_2$ vapors were shown by mass spectrometry [141] to start decomposing at 210 ± 10^{o}C and their decomposition follows three main pathways. Two pathways lead to the formation of elemental gold, saturated C2-C4 alkanes and protonated ligand or methylated ligand. The third decomposition pathway results in elemental gold and gaseous products of C2-C3 alkylmercaptanes and $MeSCNEt_2$.

In summary, the analysis of the presented data shows that the type of the ligand, nature of substituents and reaction additives have a considerable impact on the mechanisms of decomposition of gold(I, III) complexes. On the first stage of thermolysis of all investigated compounds the opening of chelate cycle with the release of free, methylated or protonated ligands takes place. The stability threshold depends first of all on the type of terminal substituents in the ligand. Both bulky organic substituents and large quantity of carbon-containing groups in gaseous by-products of complex vapors thermolysis can lead to the contamination of deposited gold coatings when using these compounds as precursors. The knowledge of mechanisms of thermal decomposition of precursors and the effects of the reaction additives allows the researchers to control the processes of films growth and to govern their composition and properties.

4. Applications of volatile compound of gold in CVD/ALD processes

Gold metal is a highly effective corrosion-resistive material due to its high electrical and thermal conductivity. Thin films and nanomaterials of gold have found some wide range applications such as in optical devices [4, 6, 8], power sources [151], microelectronic devices [2-10] and so on. In the end of last century, Haruta *et al.* [152-154] have revealed that gold nanoparticles with diameters less than 10 nm, uniformly dispersed in metal oxides exhibit high catalytic activity in the reaction of CO oxidation at low temperature. Later it has been found that gold nanoparticles can be catalysts of many other processes used both in industry and for environmental protection; these include, complete and selective oxidation of hydrocarbons, oxidation of methanol to formaldehyde, oxidative decomposition of chloro- and fluorocarbon, water gas process and so on. Along with its catalytic activity, nanogold demonstrates unusual selectivity to hydrogenation of various substances (CO, CO_2, alkenes *etc.*) [31, 148, 153, 154]; the catalytic activity of the catalyst depends directly on the size and distribution of nanoparticles [155-157]. Au is also used in electrical connectors, contacts, relays, wires, plasmon resonance, photonics and microelectromechanical systems (MEMS); conformal continuous films are required for application in [143].

Deposition from gaseous phase is one of the methods, which allows controlling the parameters of fabricated nanomaterials [45]. Depending on the required characteristics of gold nanomaterial, the methods of CVD and ALD are used for deposition of gold both as nanoparticles [147, 154, 158, 159] and as thin films [4, 160, 161]. There are some differences between CVD and ALD processes. In the CVD process, the constant and simultaneous supply of the vapors of metal-containing precursors (or one precursor) takes place at medium or high deposition temperature in the region of a “kinetically limited regime”. At these conditions simultaneous heterogeneous reaction with the formation of different intermediate products can proceed. The rate of the films’ growth is determined by the pressure of the components in the reactor, deposition temperature, speed of carrier gas supply and is equal to tens of microns per hour. An excess of the gas-reactant relative to the concentration of metal precursor vapor determines the kinetics of the first-order reaction. The region of a “diffusion limited regime” at high temperatures is of little practical interest.

ALD on the other hand is a layer-by-layer gas phase deposition technique [143]. In ALD process, sequential non-overlapping pulse injections of at least two gaseous components separated by purging stages take place. The main characteristics of ALD process are relatively low deposition temperatures, self-limiting mechanism, presence of a temperature window, and low rate of layer deposition close to the thickness of one monolayer per one experimental cycle. In a number of cases, the thickness can be even less than that of monolayer per one experimental cycle, pointing to a strong influence of the substrate surface. A simplified mechanism represents a reaction on the substrate surface without formation of intermediate products. No linear dependence of deposition rate on the number of cycles is observed in the ALD process. As a rule, ALD is used for the deposition of conformal continuous metal layers in complex structures with high aspect ratios.

Precursors for CVD and ALD processes meet some common requirements; these are volatility and thermal stability of the precursor; however, the two processes differ in their surface chemistry. A CVD precursor is activated by a heated surface with the formation of films via decomposition or reaction with a gas-reactant. A precursor has limited application in CVD processes if its evaporation and decomposition temperatures coincide. An ALD precursor should have high thermal stability and reactivity. An ALD precursor is thermally activated via chemisorption to a surface forming a self-limiting monolayer, which exists in the “ALD window” and is stable during the subsequent stages of the cycle until it reacts with the secondary precursor. The film growth here is due to the reaction with the secondary precursor. The «ALD window» is observed between the temperatures of evaporation and decomposition of the precursor.

A number of gold(I) and gold(III) complexes have been used as CVD/ALD precursors for deposition of gold-containing films and nanoparticles (Fig. 32). Gold(III) complexes $Me_2Au(III)L$ (where L can be β-diketonates, carboxylates, thiocarbamates, salicylaldiminates, dialkyldithiophosphates, β-iminoketonates, β-thioketoiminates, 8-hydroxyquinolinates, 8-mercaptoquinolinates, dialkylphosphinates) were considered as potential precursors more often than those of gold(I), however there are some examples of successful application of gold(I) compounds for the formation of gold films nanomaterials [62, 93, 162]. The main classes of promising CVD precursors are shown in Fig. 32.

The commonly used CVD precursors are dimethylgold(III) β-diketonates and their derivatives [134, 163-167]. Some examples of gold precursors are given in Table 8.

Fig. 32.

Table 8.

$Me_2Au(acac)$ [147] was used for the formation of gold nanoparticles (<5 nm) with high dispersion on porous surfaces by the vapor infiltration technique. Au/α-Al_2O_3 systems exhibited high catalytic activity in CO oxidation reactions at 40°C [147]. Larson *et al.* [134] used $Me_2Au(acac)$, $Me_2Au(tfac)$ and $Me_2Au(hfac)$ as precursors for the deposition of high-quality gold films. A series of iminoketonate derivatives with N,O-coordination was also utilized in CVD processes [166]. $[Me_2AuOSiMe_3]_2$ is stable at normal conditions and was therefore considered as a promising precursor as reported in several studies [166, 167]. Its evaporation temperature was no more than 40°C, indicating high vapor pressure at quite low temperatures; the content of gold in the deposited films was >95–97%. Uniform gold films were also obtained using MeAu(CNMe) precursor which decomposes at 200°C [62, 137]. Puddephatt *et al.* [62] have studied the dependence of film composition on the type of volatile precursor and the results are summarized in Table 9.

Jansen *et al.* [169] have used $MeAuP(OMe)_2Me$ and $MeAuP(OMe)_2(t\text{-}Bu)$ as CVD precursors for the deposition of gold films and studied the kinetics of their decomposition during the deposition processes. The use of these precursors has enabled high growth rates to be realized at comparatively low temperatures.

Table 9.

UV- [170] or laser- [93, 170] assisted CVD processes used for the deposition of gold coatings allow to decrease the deposition temperature. For instance, in the case of Me_3AuPR_3 (R = Me, Et) and $MeAuPMe_3$ the deposition temperature was decreased to room temperature [170]. Moreover, such additional activation has resulted in a decrease of the amount of impurities in gold deposited films (98% Au) [170].

Baum *et al.* [93] have pointed out that the composition and properties of precursors will significantly influence the morphology and characteristics of the deposited gold films. Using CVD method, Bessonov and co-workes [138, 171] have carried out experiments to produce gold coatings from carboxylates and salicylaldiminates of gold(III). Continuous compact gold coatings were produced using $[Me_2Au(OAc)]_2$ and $[Me_2Au(Piv)]_2$ as precursors (Fig. 33, **1**).

Fig 33.

At the same time films deposited from $Me_2Au(Sa{=}N{-}Me)$ and $Me_2Au(Sal{=}N{-}i\text{-}Pr)$ consisted of separate nanocrystallites and did not form a continuous structure as was observed in the case of dimethylgold(III) carboxylate precursors (Fig. 33, **2-3**). This difference was explained by the formation of bulk gaseous carbon-containing products during the thermolysis of dimethylgold(III) salicylaldiminates as confirmed by mass spectrometry data (see Chapter 2, Fig. 30). Those decomposition products prevented the formation of gold film with compact structure during its growth. However this peculiarity of $Me_2Au(Sal{=}N–i\text{-}Pr)$ was used by Bessonov *et al.* [117, 171] to form gold films on Si(100) and carbon nanomaterials. Gold nanoparticles (5-15 nm) were formed by pulse-CVD at 200^oC (Fig. 34). It has been shown that the increase of deposition temperature leads to the increase in the amount of nanoparticles, but without a change in their size.

Fig. 34.

The influence of UV-radiation of excimer lamp placed under the substrate on the process of gold coating growth were studied by Parkhomenko and co-workers [172] using $Me_2Au(S_2CNEt)_2$, $Me_2Au(thd)$, $Me_2Au(SQ)$, $Me_2Au(OQ)$, $[Me_2Au(Piv)]_2$, $[Me_2Au(OAc)]_2$, $Me_2AuS_2P(i\text{-}Bu)_2$, $Me_2AuS_2P(O(i\text{-}Pr))_2$, $Me_2AuS_2P(OEt)_2$, and $Me_2AuS_2P(OMe)_2$ as volatile CVD precursors. It has been shown that the film morphology and structure are mainly determined by the precursor molecular structure; for instance, continuous gold films have been obtained from $[Me_2Au(OAc)]_2$ (image 1, Fig. 35), while $Me_2Au(OQ)$ have been used for the deposition of Au nanoparticles (image 3, Fig. 35).

Fig. 35.

It has been shown that the UV-activation has led to the increase in the rate of coating growth. Due to additional energy of electromagnetic radiation and possible formation of ozone ($3O_2 \rightarrow 2O_3$) during thermolysis the obtained films exhibited 3-5 fold increase in thickness. Besides, UV-activation caused the change of gold films growth mechanism, resulting in the change of the preferential crystallite orientation from (111) to (200).

Later Parkhomenko *et al.* [173] have deposited gold nanoparticles and thin films onto the matrix of photonic crystals (180-400 nm SiO_2 microspheres) using $Me_2Au(thd)$ and $[Me_2Au(OAc)]_2$ as precursors (Fig. 36). The subsequent etching of the samples in diluted hydrofluoric acid resulted in the formation of hollow gold nanoshells (Fig. 36, **3**).

Fig. 36.

Among gold(I) precursors, mainly perfluorinated carboxylates and *t*-Bu derivatives of short chain carboxylates are used in CVD processes. Since carboxylate ligands form weak bonds with gold(I), their thermal stability is usually improved by means of such ligands as tertiary phosphines [54], and the complexes with the common formula $[Au(OOCR)(PR'_3)]$ become applicable as CVD precursors [174]. It has been shown that the film quality depends on the deposition temperature and length of the perfluorinated chain (R). For instance, dense metallic layers were produced from $[Au(OOCC_3F_7)(PEt_3)]$ and $[Au(OOCC_7F_{15})(PMe_3)]$ at deposition temperatures between 260 and 290◦C (p = 4 mbar) on Si(111), glass, and glass fiber substrates [54].

Gold guanidinate has also been used to cover fiber optics for the creation of plasmonic devices [175, 176]. Gold(I) tert-butyl-imino-2,2-dimethylpyrrolidinate was used as a precursor for the deposition of gold films (96 nm) with the resistivity of 5.58 mΩ·cm in the tube furnace reactor at the evaporator temperature of 130°C [84]. Thin films deposited onto substrates held at 350°C were confirmed by P-XRD and XPS to be pure gold metal films consisted of densely packed particles less than 50 nm in diameter. Mandia *et al.* [10] have also used the same precursor for the deposition of thin gold films due to its advantages, which include thermal stability, absence of fluoro-containing ligands and Lewis bases. They have prepared gold layers with thickness of 30–65 nm on an intermediate Al_2O_3 layers with the thickness of 50-100 nm to investigate the combined effect of dielectric and metallic layers on the refractometric properties of optical fiber Bragg gratings.

Griffiths *et al.* [85] have used another type of gold(I) precursors, *viz.* Au(HMDS)(NHC) and $Au(HMDS)(PMe_3)$, in the processes of self-seeded growth of high aspect ratio gold plates and wires on Si(100) substrates in a hot-walled CVD reactor. Au plate grown between 370 and 460°C was shown to be governed by N-heterocyclic carbene (NHC) and phosphine ligands as transient surfactants forming as a result of thermal decomposition of two used precursors. Trimethylsilyl fragments of HMDS ligands of both precursors, in their turn, passivated the hydroxyl terminated substrate, leading to the island growth and directed decomposition of the precursor on the gold surface.

Pallister *et al.* [177] studied the mechanism of initial chemisorption of $AuMe_3PMe_3$ on high surface area silica (HSAS) by C-13, P-31, and Si-29 NMR, which led to the formation of a number of surface species on HSAS; these are, gold(III) trimethylphosphine, reduced gold phosphine, methylated phosphoxides, and graphitic carbon. The overall coverage of $AuMe_3PMe_3$ on HSAS was only about 10% at 100^{o}C. Those processes have influenced the growth rate and purity of metal films prepared from that type of precursors. Compound $AuMe_3PMe_3$ was also used in CVD to produce gold nanoparticles with plasmonic properties on amine-terminated surfaces for biosensing applications [38]. Basova *et al.* [27] have deposited Au nanoparticles using $Me_2Au(OAc)$ as a precursor to prepare organic-inorganic conductive hybrid materials based on liquid crystalline metal phthalocyanine AuNPs with enhanced electrical conductivity.

Work devoted to the application of ALD processes for the deposition of gold is not so numerous. Griffiths *et al.* [145] have studied plasma-assisted ALD process using $AuMe_3PMe_3$; they have revealed that oxygen plasma and water have given pure Au thin films on silicon and borosilicate substrates with the growth rate of 0.5 Å/cycle at 120°C. At the same time dark violet films containing gold metal as well as impurity oxygen and phosphorous arising from fragments of the phosphine ligand are formed if only oxygen plasma was used. Oxygen plasma was shown to burn the precursor with the formation of both gold and phosphorous oxides. To avoid the formation of phosphorous impurities and to produce high quality gold films, water was used as a ternary reactant, providing the hydrolysis of phosphorous impurities with the formation of volatile phosphorous acid. The authors have identified $AuMe_3PMe_3$ as a promising precursor which is liquid at room temperature, due to its good volatility, tolerance to water vapor and oxygen under standard conditions.

Using ALD with O_3 Mäkelä *et al.* [143] prepared homogeneous, continuous, polycrystalline and highly conductive (4-16 μΩ·cm) thin Au films of cubic phase with low content of impurities at 120-200°C on Si(100) and glass substrates using $Me_2Au(S_2CNEt_2)$ as a precursor (Fig. 37). Self-limiting ALD growth was observed at 180°C with the rate of 0.9 Å/cycle.

Fig. 37.

The same group of researchers [76] has synthesized seven potential Au(I) compounds and checked their applicability in ALD processes. Consequently pure uniform visually smooth Au thin films were obtained from liquid $Au(N(SiMe_3)_2)(PEt_3)$ and $BH_3(NHMe_2)$ on Si(100) and glass substrates. FESEM images have revealed thin particulate films (Fig. 38, **1**), with cubic structure and were non-conductive. Thick films deposited at 160°C with 3000 or 4000 cycles were continuous (Fig. 38, **2**) and conductive but not uniform.

Fig. 38.

In the last few years an interest in the application of bimetallic gold nanoparticles for modern technologies has advanced very rapidly. For instance, nanoporous AuPt thin films incorporated in graphene (AuPt@GR) exhibited excellent catalytic activity, sensitivity and selectivity due to its unique nanoporous structure and synergetic effect of AuPt nanoparticles and

GR. Such films were used as active layers of a binder-free electrochemical sensor toward epinephrine [35]. This AuPt@GR hybrid material was prepared via self-assembly of ultradispersed AuPt nanoparticles (~ 3 nm) inside graphene layers using CVD method.

Summary

In this review an outline and critical analysis is presented of literature concerning the chemistry of CVD/ALD of gold over the last 20 years together with a historical overview of synthetic chemistry of the main classes of gold complexes with organic ligands. The literature analysis has allowed us to establish a selection of criteria of volatile precursors and to demonstrate their possible application for the deposition of both gold thin films and nanoparticles.

A comprehensive analysis of the available literature has shown that gold(III) volatile complexes were studied in greater details than those of gold(I) compounds. Moreover gold(III) complexes were shown to be important for the wider variety of coordinating ligands. Ilyde and isocyanide derivatives of gold(I) and gold(III) as well as gold(III) complexes with N,O- and O,O-donor ligands are the most promising precursors for both MOCVD and ALD processes due to the combination of their good volatility and high thermal stability. In some cases however, N,S-coordinated complexes can also be used as MOCVD and ALD precursors. Depending on the type of chelate center in the order (O, S) < (O, O) < (S, NH) < (O, NH) an increase in thermal stability was established using dimethylgold β-diketonates as an example. It is worth stating that the combination of donor atoms has stronger effect on the thermal stability of gold(III) complexes than the variation of end substituents in their ligands. Dimethylgold β-diketonate complexes with N,O-donor ligands exhibit the highest thermal stability. Among N,O-, O,O- and N,S-coordinated dialkylgold compounds, dimethylsubstituted gold(III) complexes are the most attractive precursors for CVD applications due to their highest thermal stability. It is known that dimethyl derivatives of gold complexes with organic ligands are more stable in crystalline phase than their diethyl analogues, whereas di-*n*-propyl and di-*n*-butyl derivatives are liquids at normal conditions. Further analysis of the literature shows that the most promising precursors for ALD processes are the complexes of gold(I) since they exhibit high thermal stability when subjected to long-term heating.

As to the thermal behavior of gold compounds and decomposition of their vapors upon heating and under the influence of some other factors, there has been very scattered work devoted to the investigation of the mechanisms of gold compound vapor transformation nearby and on heated substrate surfaces during deposition. In most cases, the presented data are limited by the description of the composition of main volatile products of thermolysis and the temperature ranges of decomposition.

The possibility of deposition of nanoparticles or continuous uniform films is determined to a greater extent by the nature of the precursor, or more precisely, by the gaseous products of the thermal decomposition of precursor molecules which take place on the heated surface during the film growth. The presence of bulk organic fragments within such products leads to the possibility of contamination of the film by carbon products, which do not undergo further degradation at higher temperatures. In this case, and in contrast to volatile compounds with low carbon content, the decomposition products prevent the formation of a dense compact structure of the gold layer during its growth. This leads to the accumulation of carbon impurities and the growth of individual gold nanocrystallites, which do not form a continuous structure. In this case, CVD and ALD precursors differ in their surface chemistry: CVD precursors are activated by a heated surface to form a film by decomposition or reaction with a reactant gas, while ALD precursors are thermally activated by chemisorption to the surface forming a self-limiting monolayer that is stable during the next stages of the cycle until it reacts with the secondary precursor.

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Figure captions

Fig. 1. Structure of gold(I) β-diketonates.

Fig. 2. Pyridine (**1**), benzothiazole (**2**) and benzoimidazole derivatives of gold chloride and complexes of (triphenylphosphine)gold with 1,2,3- and 1,2,4-triazole.

Fig. 3. Scheme of preparing gold(I) tert-butyl-imino-2,2-dimethylpyrrolidinate.

Fig. 4. Compounds Au(HMDS)(NHC) (**1**) and Au(HMDS)(PMe_3) (**2**).

Fig. 5. The reactions of methyllithium with halogenated derivatives of dimer ylides.

Fig. 6. Diethylgold(III) bromide.

Fig. 7. Azide and cyanate of dimethylgold(III).

Fig. 8. Thio- and selenocyanate of dimethylgold(III).

Fig. 9. Cyanides of dimethylgold(III).

Fig. 10. Structure of dimethylgold(III) hydroxide.

Fig. 11. Complexes of dimethylgold(III) with O- and S-donor ligands.

Fig. 12. Structure of dimethylgold(III) carboxylates $[Me_2Au(OOCR)]_2$ with R = CF_3 (**1**), *t*-Bu (**2**), Ph (**3**).

Fig. 13. The transformation of β-diketonates stabilized by orto-nitrobenzene radicals

under the action of triphenylphosphine.

Fig. 14. Structure of Me_2Au(ox) (**1**) and Me_2Au(tox) (**2**).

Fig. 15. Gold(III) complexes with trimethylsiloxy group.

Fig. 16. Structures of Me_2Au(Sal=NMe) (**1**), Me_2Au(Sal=N(*i*-Pr)) (**2**), Me_2Au(Sal=NCy) (**3**), and Me_2Au(Sal=NPh) (**4**).

Fig. 17. Dimethylgold(III) compounds stabilized by S atom.

Fig. 18. Molecular structure of $[Me_2AuSCN]_2$.

Fig. 19. Molecular structure of $Me_2AuS_2P(i\text{-}Bu)_2$.

Fig. 20. Dimer (**1**) and monomer (**2**) thiocomplexes of dimethylgold(III).

Fig. 21. Complexes of diethylgold(III) with N,S-coordination.

Fig. 22. Gold complexes with N,N-dimethylbenzylamine.

Fig. 23. TGA experiments of Au(HMDS)(NHC) (green) and Au(HMDS)(PMe_3) (black) are shown as solid lines. Derivative curves are shown by dashed lines. Reprinted with permission from Ref. [85]. Copyright 2015 American Chemical Society.

Fig. 24. TGA curves of Au compounds. Reprinted from Ref. [76] with permission from American Vacuum Society, Copyright 2017.

Fig. 25. Dimethylgold(III) β-diketonates: Me_2Au(ttfac) (**1**) (ttfac - 1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedionate), Me_2Au(ftfac) (**2**) (ftfac - 1-(2-furanyl)-4,4,4-trifluoro-1,3-butanedionate), Me_2Au(btfac) (**3**) (btfac - 1-phenyl-4,4,4-trifluoro-1,3-butanedionate).

Fig. 26. *P*/*T* dependence for volatile complexes of dimethyigold(III) with organic ligands:

1 – $[Me_2Au(OAc)]_2$; **2** – $[Me_2Au(Piv)]_2$; **3** – $[Me_2Au(OOCCF_3)]_2$; **4** – $[Me_2Au(OBz)]_2$; **5** – Me_2Au(Sal=N–Me); **6** – Me_2Au(Sal=N–*i*-Pr); **7** – Me_2Au(Sal=N–Cy); **8** – Me_2Au(Sal=N–Ph); **9** – Me_2Au(OQ); **10** – Me_2Au(SQ); **11** – Me_2Au(bac); **12** – Me_2Au(ttfac); **13** – Me_2Au(btfac); **14** – Me_2Au(i-acac); **15** –Me_2Au(acac) [117, 138-140, 147-149].

Fig. 27. Scheme of the thermolysis of dimethylgold(III) chelate vapors [112, 136].

Fig. 28. Temperature dependence of the intensities of ion peaks of main gaseous products of thermal decomposition in the mass spectra of $[Me_2Au(OAc)]_2$: (a) – $[Au_2(OOCCH_3)]^+$, (b) – $[COCH_2]^+$, (c) – $[OOCCH_3]^+$, (d) – $[C_2H_6]^+$. Adapted by permission from Ref. [139] Springer Customer Service Centre GmbH, Nature Springer, Copyright 2008.

Fig. 29. Scheme of the chemical transformation of $[Me_2Au(OAc)]_2$ vapors on a heated surface in vacuum [138, 139].

Fig. 30. Scheme of the chemical transformation of the vapors of dimethylgold(III) complexes with salicylaldimine on a heated surface in vacuum [117].

Fig. 31. Mechanism of thermal decomposition of $Me_2AuS_2P(OMe)_2$.

Fig. 32. Volatile gold complexes for CVD processes [93, 162].

Fig 33. SEM images of gold coatings on Si(100) deposited using $[Me_2Au(OAc)]_2$ (**1**), Me_2Au(Sal=N–Me) (**2**) and Me_2Au(Sal=N–*i*-Pr) (**3**) as precursors. Adapted from Ref. [138] with permission from Elsevier, Copyright 2007.

Fig. 34. SEM (**1**), AFM (**2**) and TEM (**3**) images of gold nanoparticles deposited by pulse-CVD on the surface of nanocarbon [171].

Fig. 35. SEM images of gold films and nanoparticles deposited under similar conditions from different precursors: $[Me_2Au(OAc)]_2$ (**1**), Me_2Au(Piv) (**2**), Me_2Au(OQ) (**3**), Me_2Au(SQ) (**4**),

$Me_2Au(thd)$ (**5**), $Me_2Au(S_2CNEt_2)$ (**6**). Reprinted with permission from Ref. [172]. Copyright 2012 John Wiley and Sons.

Fig. 36. SEM images of gold nanoparticle (**1**) and thin films (**2**) deposited onto the matrix of photonic crystals as well as hollow gold nanoshells (**3**). Reprinted from Ref. [173] with permission from Elsevier, Copyright 2013.

Fig. 37. FESEM images of Au films deposited with 0.5 s (**1**) and 2 s (**2**)

$Me_2Au(S_2CNEt_2)$ pulses at 180°C. The O_3 pulse was 1 s. Adapted with permission from Ref. [143]. Copyright (2017) American Chemical Society.

Fig. 38. FESEM images of Au thin films (**1**) and thick films (**2**). Reprinted from Ref. [76] with permission from American Vacuum Society, Copyright 2017.